Reinforcement of Natural Rubber by “Expanded Clay” Adopting “Propping-Open Approach”

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M.Tech Rooj, Sandip

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Gutachter: Prof. Dr. rer. nat. habil. Gert Heinrich

Prof. Dr. rer.nat. Ulrich Giese

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Dedicated to My Dearest Friend and Beloved Wife
Sumela
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Eidesstattliche Erklärung
Hiermit versichere ich, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus fremden Quellen direkt oder indirekt übernommenen Gedanken sind als solche kenntlich gemacht.

Dresden, den 01.03.2013
Abstract

During the last years rubber nanocomposites obtained by incorporating anisotropic clay nanoparticles within a rubber matrix to tailor material properties have attracted steadily growing interest. However, one main complication preventing rubber-clay nanocomposites from many potential applications is the difficulty to achieve a high degree of exfoliation particularly in case of melt mixing or compounding (using mixing equipment like internal mixer, two roll mills which can be up-scaled in industry). Albeit commercially available organo-modified montmorillonite clays (OMt) are fairly compatible with the polar rubber like Acrylo-nitrile butadiene rubber (NBR), carboxylated nitrile rubber (XNBR), chloroprene rubber (CR) etc., its dispersion in non-polar rubbers like natural rubber (NR), is rather unsatisfactory.

Incorporation of only 5 phr of OMt in NR by mechanical mixing leads to very poor dispersions with larger aggregates. Large agglomerates of OMt were observed with bare eyes throughout the matrix. Even in the TEM micrographs, highly agglomerated structures of clay particle were observed. A high degree of exfoliation of such clay is achieved in NR utilizing the so called ‘Propping-open approach’ where stepwise expansion of interlayer spacing of Mt took place. A series of long chain fatty acids (C16-C22) are intercalated into the interlayer space of OMt and a gradual expansion of the interlayer space were observed as the chain length of the fatty acid increased. Wide angle X-ray diffraction (WAXD), Fourier transform infrared spectroscopy (FTIR) and contact angle measurement indicated successful intercalation of the fatty acids into the interlayer space of the clay minerals.

Since the fatty acid containing 22 carbon atoms has the largest interlayer distance among the modified samples studied, it has been selected for further study to understand the reinforcing behavior in NR matrix. An unusual mechanical percolation behavior of EOMt nanoparticles was observed in a NR matrix. The value of the mechanical percolation threshold ($\varphi_p$) and the fractal nature of nanoparticle clusters were determined through an analysis of the experimental data based on a theory put forward by Huber and Vilgis. This phenomenon was discussed in terms of fractal dimensions of the nanoparticle cluster. The impact of filler dispersion and rubber-filler interactions on the viscoelastic behavior of NR nanocomposites was systematically investigated. Significant non-linear viscoelastic behavior (Payne effect) was observed at very low EOMt content. Kraus and Maier-Göritz models were utilized to interpret such non-linear viscoelastic
behavior. The nanocomposites showed enormous improvement in different physic-mechanical properties in the presence of EOMt.

Technical elastomers are generally filled with certain fillers (e.g. carbon black) in order to reinforce the rubber matrix for some typical applications like tires, conveyer belts etc. Such rubber goods are always exposed to cyclic stress and deformations attributed to their dynamic application. Under constant and repeated applied stress, cracks develop at a stress concentration point, which could lead to ultimate failure. Therefore, the crack initiation and propagation behavior in such rubber products is very fundamental and need proper attention. The role of EOMt nanoparticles on the microstructure and fracture mechanical behavior of CB filled NR composites was investigated. Using pure-shear test specimen tear fatigue analysis (TFA) tests under cyclic conditions were carried out to explicate the crack growth behavior of CB filled NR in the presence of EOMt. A significant reduction in crack growth rate was noticed in the presence of only 5 phr of EOMt. Furthermore, instrumented tensile-impact tests (IT-IT) were also performed for the characterization of the crack resistance of the materials under impact-like loading conditions.
Kurzfassung


### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Mt</td>
<td>Montmorillonite</td>
</tr>
<tr>
<td>OMT</td>
<td>Organo-montmorillonite</td>
</tr>
<tr>
<td>EOMT</td>
<td>Expanded organo-montmorillonite</td>
</tr>
<tr>
<td>WAXD</td>
<td>Wide angle X-ray diffraction</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>CB</td>
<td>Carbon black</td>
</tr>
<tr>
<td>SENT</td>
<td>Single edge notch tensile</td>
</tr>
<tr>
<td>TBBS</td>
<td>N-tert-Butyl-2-benzothiazolesulfenamide</td>
</tr>
<tr>
<td>FA</td>
<td>Fatty acids</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimeter</td>
</tr>
<tr>
<td>TFA</td>
<td>Tear fatigue analyzer</td>
</tr>
<tr>
<td>IN-TI</td>
<td>Instrumented notched-tensile-impact test</td>
</tr>
<tr>
<td>DENT</td>
<td>Double edge notched tension</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>QUAT</td>
<td>Quaternary ammonium compound</td>
</tr>
<tr>
<td>CRI</td>
<td>Cure Rate Index</td>
</tr>
<tr>
<td>TS</td>
<td>Tensile strength</td>
</tr>
<tr>
<td>EB</td>
<td>Elongation at break</td>
</tr>
<tr>
<td>CCA</td>
<td>Cluster-cluster aggregation</td>
</tr>
<tr>
<td>DLA</td>
<td>Diffusion-limited aggregation</td>
</tr>
<tr>
<td>WLF</td>
<td>Williams-Landel-Ferry</td>
</tr>
<tr>
<td>TTS</td>
<td>Time-temperature superposition</td>
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</tbody>
</table>
Symbols

\( \eta_m \)  
Polymer melt viscosity

\( T_t \)  
Tearing energy

\( da/dn \)  
Crack growth rate

\( V_r \)  
Volume fraction of the rubber in swollen gel

\( \nu_c \)  
apparent crosslinking density

\( \chi \)  
Flory-Huggins polymer solvent interaction parameter

\( M_c \)  
Molecular weight between crosslinks

\( J_d \)  
Crack toughness parameter

\( \alpha \)  
Degree of cure at a time, \( t \),

\( K \)  
Temperature-dependent rate constant

\( d\alpha/dt \)  
Rate of conversion

\( E_{a,v} \)  
Activation energy of vulcanization

\( \tan \delta \)  
Loss factor

\( T_g \)  
Glass transition temperature

\( B \)  
Phenomenological interaction parameter

\( \phi \)  
Volume fraction

\( E' \)  
Dynamic storage modulus (tensile mode)

\( E'' \)  
Dynamic loss modulus (tensile mode)

\( \sigma \)  
Applied stress

\( \lambda \)  
Extension ratio

\( C_1 \) and \( C_2 \)  
Mooney-Rivlin (MR) constants

\( \Delta C_p \)  
Change in heat capacity at constant pressure

\( X_{im} \)  
Fraction of immobilized polymer layer

\( E_c \)  
Young’s modulus of the nanocomposite
$E_m$  
Young’s modulus of pure matrix

$f$  
Aspect ratio

$E_0'$  
Storage modulus at small amplitude

$E_\infty'$  
Storage modulus at high amplitude

$E_0' - E_\infty'$  
Amplitude of Payne-effect

$\gamma_c$  
Critical strain

c  
Defines the position of the $E''$, maximum on the strain axis

e  
Excess modulus

$\varphi_p$  
Percolation threshold

$d_f$  
Mass fractal dimension

$D$  
Spectral dimension

$n$  
Huber-Vilgis exponent

$a_T$  
Horizontal shift factor

$f_0$  
Fractional free volume

$\alpha_f$  
Coefficient of thermal expansion

$E_{app}$  
Apparent activation energy

$Q$  
Amount of solvent per unit weight of the rubber

$\Phi_{PEL}$  
Fraction of micropellets

$d_{pel}$  
Average diameter of micropellets

$d_{fil}$  
Average diameter of filler inclusions

$l_{fil}$  
Length (the longest distance from edge to edge of segment) of filler inclusions

$c_{fil}$  
Compactness of filler inclusions

$a_{fil}$  
Aspect ratio (relation between length and diameter of inclusion) of filler inclusions
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1 General introduction

The emergence of research and development in the field of nanoscience and nanotechnology can be traced back over 40 years (1). However, during the past few decade nanosciences and nanotechnology contended through a wide range of disciplines e.g. starting from chemistry to biology, materials science to electrical engineering etc. Scientists and researcher are creating new tools and developing the expertise to transport the blessing of nanotechnology out of the research labs and into the market place. Nanoscience and nanotechnology are enabling to produce new and promising high performance materials and applications across all disciplines of science and technology (2).

The use of different polymeric materials as matrix for the preparation of composite materials increases rapidly compared to some conventional solid materials like metals and ceramics. This is attributed to their low cost, ease of production and flexibility. However, the low strength and modulus hinders its application compared to metals and ceramics. One common way by which the strength of such materials can be improved is to reinforce the polymer matrices with several rigid particles such as fibers, whiskers, platelets etc. This particle reinforced materials often termed as advanced polymer composites (3-6).

Nanocomposites are a new class of composites in which polymers are generally filled with some nano-sized filler. At least one dimension of such dispersed nanoparticles should be in the nanometer range. Since the invention of polymer-layered silicate nanocomposites by Toyota group (7-8), polymer-layered silicate nanocomposites have attracted a great interest in the field of polymer science and technology (9-17). Over the past few years rubber nanocomposites have been widely discussed by researchers considering the number of potential nano-fillers such as layered silica (18-21), carbon nanotubes (22-23), silicate nanotube (24-25) etc. Addition of a small amount of such layered clay minerals into such rubber matrices can lead to tremendous improvement in various physical properties. The main reason for these marked improvements originates from the large aspect ratio. The high aspect ratio leads to a large contact surface area and, thus, providing more physical interactions between the rubber chains and clay particles. There are few advantages of rubber nanocomposites over conventional rubber composites for instance, (i) lighter weight attributed to the low loading level of such nano particles (ii) improved
material properties and with new functionalities (iii) easy processability compared to conventional composites

1.1 Challenges

The areas of polymer based nanocomposites are the new trend in the field of polymer science and technology. They register surprisingly enhanced material properties and novel functionalities which cannot be seen in case of conventional fillers and composites. However, commercial applications of rubber nanocomposites are yet to gain real momentum, since there are a few unresolved issues that need to be resolved in order to the successful conversion of these novel materials into commercial artifacts. The biggest problem in the preparation of polymer-clay nanocomposites is the difficulty of dispersion at higher loadings (typically above 5-7 phr where phr stands for parts per hundred grams of rubber), because beyond such critical loading most of the properties incline due to agglomeration of the nanoparticles. Thus, only a well-informed and judicious choice of nanoparticles and its incorporation technique can produce materials suitable for the most rigorous and advanced applications. Additionally, a strong interfacial bonding is required in order to obtain an efficient load transfer across the polymer-filler interface.

Nevertheless, since the layered silicates typically exist as aggregates due to strong attractive van der Waals forces, improvements in various physical properties do not attain theoretical expectations. Achieving a nanocomposite with a highly exfoliated structure in which each individual layer has been separated from its initial stack and dispersed uniformly throughout the polymer matrix is the key to reach the full potential of the nanoclay to enhance various physical properties of a polymeric matrix.

1.2 Aim and objectives of this work

One main complication preventing polymer-clay mineral nanocomposites from many potential applications is the difficulty to achieve a high degree of exfoliation particularly in case of melt mixing or compounding (using mixing equipment like internal mixer, two roll mills which can be up-scaled in industry). Most of the earlier efforts have been paid in changing the surface character of clay minerals. Albeit the modified clay minerals are fairly compatible with the polar rubber like carboxylated nitrile rubber (XNBR), chloroprene rubber (CR) etc., its dispersion in nonpolar rubbers like natural rubber (NR), styrene-butadiene rubber (SBR),
ethylen propylene diene monomer rubber (EPDM), butadiene rubber (BR) etc. is rather unsatisfactory. Fig. 1.1a and 1.1b displays the state of dispersion of organo-montmorillonite (OMt) in non-polar NR matrix. Big agglomerates of OMt can be observed with bare eyes throughout the matrix which is given in the photomicrograph. Even in the TEM micrographs, highly agglomerated structures of clay particle are observed.

![Photomicrographs of NR-OMt nanocomposites](image1a.png) ![TEM micrographs of NR-OMt nanocomposites](image1b.png)

Fig. 1.1. (a) Photomicrographs of NR-OMt nanocomposites (b) TEM micrographs of NR-OMt nanocomposites

Figure 1.2 represents a scheme of exfoliation of OMt in polymer matrix during the course of melt blending. The exfoliation of OMt takes place when the attraction (designated as $f_1$) between the OMt layers generally well known as the van der Waals force of attraction, is minimized.

![Scheme of exfoliation of OMt in polymer](image2.png)

Fig. 1.2. Scheme of exfoliation of OMt in polymer
There are another two important factors namely as the interaction (designated as $f_2$) between polymer and OMt and the melt viscosity (labeled $\eta_m$) of polymer matrix. The former is related to the chemical structures of polymers and the modifiers, and the modifier content in the OMt subsequently has no importance in our study since we are here dealing with non-polar rubber matrix.

Therefore, the prime aim of the present work is to develop a novel way to disperse such clay minerals in the non-polar rubber matrices by minimizing the van der Waals forces between the OMt layers. It is believed that in case of short interlayer spacing the van der Waals forces are predominating factor. Therefore, it is very essential to reduce the high electrostatic force ($f_1$) between the clay layers in preparing polymer nanocomposites. Many large molecules are not directly intercalated into the interlayer space but can be introduced by “Propping-open approach”. A schematic illustration is given in the Fig. 1.3. This method was first introduced by Brindley and Ray in 1964 (26). Brindley and Ray were able to enhance the interlayer spacing of Ca$^{2+}$-Mt to a considerable extent by stepwise swelling with ethanol, hexanol and followed by octadecanol. Although, this method is well known in the field of clay science but never utilized in the field of polymer nanocomposites. Therefore, to utilize such nano-structured clay materials efficiently in rubber matrix, this novel “Propping-open approach” has been adopted in the present study. The choice of NR in the present investigation attributed to their excellent mechanical and physical characteristics.

![Fig. 1.3. Schematic of ‘Propping-open procedure’](image-url)
1.3 Structure of the thesis

This dissertation addresses both fundamentals of nanocomposite technology and its application to rubber. The investigation started with a thorough and systematic literature review of the present state-of-the-art of work involving clay and clay-based rubber nanocomposites. An overview of different ways of clay modification and rubber/clay-based nanocomposite preparation is given at the very beginning in the Chapter 2. Furthermore, various characteristic features of clay-based rubber nanocomposites in terms of particle dispersion, properties, etc. are described in details.

The various materials used in the present study and their basic features are described in Chapter 3. The experimental methods and analytical tools used for the characterization of the OMt and expanded organo-montmorillonite (designated as EOMt) and the nanocomposites are also presented in the chapter 3.

Chapter 4 describes the results and discussion of this work. In this section, the first subchapter deals with modification and characterization of clay minerals. The actual experimental work started with the pre-intercalation of Mt and OMt with different fatty acids, which are reported in first subchapter. The main purpose of this section was to study the intercalation behavior of OMt in the presence of various alkyl chain containing fatty acids. Both the OMt and EOMt clay materials have been characterized in details using various analytical techniques. Second subchapter is devoted for the preparation and characterization of highly exfoliated nanocomposites utilizing the novel propping-open procedure. In this subchapter, the effect of different fatty acid chain length on the exfoliation of EOMt and corresponding reinforcement behavior in NR matrix has been studied. The nanostructure of the both EOMt and NR-EOMt nanocomposites were characterized by wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM) which indicated different extents of the clay dispersion depending on the fatty acid chain length. A detailed rheometric study along with curing kinetics of different NR-EOMt nanocomposites was studied and interestingly low activation energies of the vulcanization process were observed specially in the case of NR/EOMt nanocomposites. The incorporation of expanded organo-montmorillonite (EOMt) clay nanoparticles dramatically affects the composite properties whereas dynamic mechanical analysis (DMA) indicates
significant reduction of tan δ peak height and the tensile strength approximately doubles from 14 MPa to 30 MPa with only 5 phr EOMt. Afterwards, the different loading of the highest interlayer spacing C22EOMt has been scrutinized in the same NR matrix and reported in the third subchapter. Fatty acid with longer alkyl chain length showed best set of properties, mainly in terms of interlayer separation, dispersion and improvement in physical properties. Therefore, it was chosen further for the preparation of NR-C22EOMt nanocomposites using melt compounding technique. Primarily, WAXD and TEM were used to investigate morphological features and the nature of dispersion in non-polar NR matrix. Different phenomenological models such as Kraus and Maier-Göritz were utilized to understand the non-linear viscoelastic behavior of NR-C22EOMt nanocomposites. The Huber-Vilgis model has been used to find the percolation behavior of EOMt and compared with the percolation behavior of OMt. In a fourth subchapter, the role of such expanded montmorillonite (EOMt) on the synergy of carbon black (CB) filled natural rubber nanocomposites will be explored with the special emphasis on the fracture mechanical behavior of the final NR-CB composites. Initially, the effect of OMt was observed in the final properties of NR-CB composites.

Finally, the summary of the whole work and future outlooks regarding the use of this EOMt are presented in Chapter 5.
2 Literature review

2.1 Clays and Layered silicates

2.1.1 Montmorillonite (Mt)

Among all clays, montmorillonite (Mt) is the most commonly used layered silicate in nanocomposite preparation due to its high cation exchange capacities, large surface area, good surface reactivity and surface adsorptive properties (9-17, 27). Mt belongs to the 2:1 family of phyllosilicate clay minerals, where each crystal layer is composed of a silica tetrahedral layer sandwiched between two octahedral sheets of aluminum and magnesium hydroxides (28). In Mt, the isomorphous substitution of $\text{Al}^{3+}$ by $\text{Mg}^{2+}$, $\text{Fe}^{2+}$, etc. in the octahedral sheets results in a net negative charge in the sandwiched layers (Fig. 2.1). As a result, cations ($\text{Na}^+$, $\text{K}^+$, etc.) and water molecules are intercalated in the interlayer region of Mt. The layer thickness is around 1 nm and the lateral dimensions of these layers may vary from 300 Å to several microns and even larger depending on the particular silicate.

![Crystalline structure of Montmorillonite (Mt) clay](image)

**Fig. 2.1. Crystalline structure of Montmorillonite (Mt) clay** (27)

2.1.2 Organoclay (OMt)

Addition of a small amount of nanofiller (for instance Mt) into the polymer matrix can improve various physical properties. But it is not an easy task. When polar nano-fillers are mixed
together with non-polar polymer matrix one can certainly come up with a physical mixture of them. The physical mixture of a polymer and Mt may not form a nanocomposite. This situation is comparable to polymer blends, and in most cases separation into discrete phases takes place. In the case of immiscible polymer blends, which typically correspond to the more conventionally filled polymers, the poor physical interaction between the organic and the inorganic components leads to inferior mechanical and thermal properties. In contrast, strong interactions between the polymer and the Mt in polymer nanocomposites lead to the organic and inorganic phases being dispersed at the nanometer level. As a result, nanocomposites exhibit unique properties.

In general, pristine Mt contains hydrated Na\textsuperscript{+} or K\textsuperscript{+} ions. Therefore, they are only miscible and compatible with polar polymers. In order to make it compatible with hydrophobic polymers, the interlayer cations are exchanged with quaternary alkylammonium cations through ion-exchange reaction. Ion-exchange reactions can be done with several cationic surfactants including primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium cations (28).

### 2.2 Composites structures

Three main types of composites can be achieved by the incorporation of layered clay minerals into the polymer matrix depending on the nature of the components used (for instance, layered silicate, cation exchange capacity and polymer) and the method of preparation (11). When the polymer is unable to intercalate the interlayer space of clay minerals, a phase separated composite (Fig. 2.2a) is obtained. The properties of such composites are equivalent to the conventional micro-composites. Beyond this classical family of composites, two types of nanocomposites can be observed. Intercalated structure (Fig. 2.2b) in which a single (and sometimes more than one) extended polymer chain is intercalated into the interlayer space of silicate layers ensuing in a well ordered multilayer morphology built up with alternating polymeric and inorganic layers. When the silicate layers are completely intercalated by polymer chains and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained (Fig. 2.2c).
2.3 An overview of natural rubber/clay nanocomposites

Rubber-clay nanocomposites have been of particular importance in several research groups during the past few years attributed to their unique properties (29-31). According to the survey of Freedonia Group which was published in the year of 2010, the total consumption of rubber will increase to 31 million metric tons by 2015 (32). However, to accomplish the excellent mechanical properties in accordance with the end use application, rubbers have to be reinforced with some conventional filler such as carbon black and silica (33-36). In principal, 40-60% conventional fillers are required to get the satisfactory level of reinforcement according to their final application. There are certain problems associated with these filled rubbers for instance mixing at such a high loading and final weight of the product. Therefore, the concept of nanotechnology is highly relevant for rubber compounds since their application needs filler reinforcement. Nanofillers are not easy to mix in the non-polar rubber matrix owing to its inherent incompatibility with the rubber matrix. It has been proved that the dispersion state of
such nanofillers and rubber filler interactions play a vital role in order to achieve the ultimate desirable properties.

2.3.1 Natural rubber (NR)-organoclay nanocomposites

2.3.1.1 Method of preparation

At present there are four principal methods for producing natural rubber-clay nanocomposites: (1) melt mixing or compounding (2) in situ polymerization (3) latex blending (4) solution intercalation. Among the aforesaid methods, melt intercalation and in situ polymerization are considered as commercially attractive approaches for preparing so called “rubber-clay nanocomposites”. The latex blending route is also promising for some rubbers available in aqueous dispersions (e.g., natural rubber (NR) because in this case pristine layered silicates can be used (37-42). But the problem comes when considering many synthetic rubbers because latex of those synthetic rubbers is not available commercially. There are also few reports on the preparation of rubber-clay nanocomposites and can be found based on solution intercalation procedure (43, 44). Melt intercalation, in particular, is especially of practical interest, since it offers significant advantages. The advantages of forming nanocomposites by melt processing are rather appealing, rendering this technique a promising new approach that would greatly expand the commercial opportunities for nanocomposites technology. If technically possible, melt compounding would be significantly more economical and simpler than in situ polymerization. It minimizes capital costs because of its compatibility with existing processes. That is, melt processing allows nanocomposites to be formulated directly using ordinary compounding devices such as extruders or mixers. Therefore, it swings nanocomposite production downstream, giving end-use manufacturers many possibilities with respect to final product specifications (e.g. selection of polymer grade, choice of organoclay, level of reinforcement, etc.). At the same time, melt processing is environment friendly since no solvents are required; and it enhances the specificity for the intercalation of polymer, by eliminating the competing host-solvent and polymer-solvent interactions. The melt-compounding method used for the preparation of rubber-clay nanocomposites is similar to that used for conventional polymer-clay nanocomposites. The organically modified clay is the suitable precursor for this process, which are mixed with molten polymer in the typical rubber processing equipment. Due to the several advantages, most of the rubber-clay nanocomposites were prepared utilizing melt
blending technique. The first effort was paid by Varghese et al. (45) who prepared NR-Mt nanocomposites using melt blending technique in a two roll mixing mill. Arroyo et al. (46) have also reported the preparation of NR-clay nanocomposites adopting melt blending method. Carretero-Gonzalez et al. have reported the preparation of NR-clay nanocomposites using melt mixing technique in a two roll mixing mill (47). Very recently many literatures can be found reporting the preparation of NR-clay composites following melt blending technique (48, 49).

2.3.1.2 Physical properties

The first effective effort for the preparation of rubber-clay nanocomposites was paid by Vu et al. (43) which have attracted tremendous interest among the scientific community. They have prepared nanocomposites based on synthetic natural rubber (NR) and epoxidized natural rubber (ENR) with the help of both melt mixing and solution intercalation technique. The clay was either a Na⁺-Mt or OMT to make the galleries more hydrophobic and thus more compatible with the non-polar rubbers. The chemical modifications were carried out using an ion exchange reaction with alkyl ammonium cations. The organically modified clays used in this work were bis-(2-hydroxyethyl) methyl tallow ammonium montmorillonite (C1), dimethyl dihydrogenated tallow ammonium montmorillonite (C2), and dimethyl hydrogenated tallow (2-ethylhexyl) ammonium montmorillonite (C3). X-ray diffraction results indicated intercalation of NR and ENR into the silicate interlayers, followed by exfoliation of the silicate layers into the elastomer matrices. But unfortunately, they did not show any morphological evidence to visualize the dispersion of clay minerals in rubber matrices by SEM or TEM. They have also reported that NR vulcanizates with organically modified clay exhibits better tensile properties compared to the silica filled vulcanizates attributed to the better polymer-filler interactions and weaker filler-filler interactions in the case of the modified clays. It has been observed that with 10 phr loading the C2 compound had better tensile properties than those of C1.

The effect of dynamic strain amplitude on the storage modulus revealed that storage modulus of the compound ENR50 (50 mol% epoxy groups) with Na⁺-Mt was higher in comparison to that of the compound with Hi-Sil (Silica), possibly due to a greater hydrodynamic reinforcement as a result of melt intercalation of the rubber in the Na⁺-Mt (clay) galleries. Further, with an identical Na⁺-Mt loading, storage modulus of ENR50 was greater than that of
ENR25 (25 mol% epoxidation) and this can be attributed to the stronger rubber-filler interactions in the more polar ENR50. The storage modulus increased with increasing filler loading. However, the storage modulus of NR and the cited networking effects were much smaller than were those for the polar epoxidized rubber compounds. Composites based on NR and organoclay were produced and reported by Varghese et al. (45) adopting melt compounding technique. Clay surfaces were modified using primary amine (Mt-ODA) and quaternary amine (Mt-TMDA). The organoclay content was 10 phr.

![Graph and images](image-url)

**Fig. 2.3. (a) XRD and (b) TEM of different NR-clay nanocomposites (45)**

The partial intercalation of macromolecular NR chain into the interlayer space of Mt was evidenced by XRD and TEM and given in the Fig. 2.3.

![Image](image-url)

**Fig. 2.4. Morphological analysis of NR-Organoclay nanocomposites (50)**
The interlayer spacing of NR/Mt-ODA was higher than that of NR/Mt-TMDA. The property improvements caused by the fillers were ranked as follows: organophilic clays > pristine synthetic layered silicate (sodium fluorohectorite) > pristine natural clay (purified sodium bentonite) > precipitated non-layered silica (used as a reference).

In a study of Modhusoodanan et al. (50), nanocomposites based on NR and organoclay was produced by melt-mixing technology. The dispersion of these silicates was studied by XRD and TEM (Fig. 2.4). Highest interlayer distance of 3 nm was observed in the case of organoclay filled NR nanocomposites. The addition of organoclay in to the NR decreased both cure time and scorch time of the compounds, while much change is not observed compared to NR gum compound in the case of bentonite and English Indian Clay (EIC). High Mooney viscosity values revealed that intercalation occurred during mixing of the silicate into the rubber. Mechanical properties such as tensile strength, modulus, hardness, abrasion resistance, tear strength, etc. of natural rubber improved in the presence of organo clays, even at low loading. The improvements in the mechanical properties of the organo silicates are due to the exfoliation of the silicates, which causes several fold increase in surface area.

Very recently, the influence of nanoclay on the morphological and microstructural changes of NR network has been reported by Carretero-Gonzalez et al. (47). The molecular structure of the polymer network and its morphological changes during deformation were characterized by using broadband dielectric spectroscopy and in situ synchrotron wide angle X-ray diffraction, respectively. It was found that the presence of nanoclay introduces a dual crystallization mechanism due to the alignment of nanoparticles during stretching. The improved properties in NR-nanoclay nanocomposites can be attributed to both microstructural and morphological changes induced by nanoclay as well as to the nanoclay mobility in the NR matrix during crystallization.

The effectiveness of organoclay in NR was observed and reported by Carli et al. (51). They evaluated the technical feasibility of natural rubber nanocomposites with Cloisite 15A, a commercial organoclay to substitute conventional silica filler. TEM analysis indicated that the organoclay was homogeneously dispersed in the rubber matrix. A shift of the characteristic peaks to lower angles was observed in XRD attributed to the intercalation of the organoclay by
macromolecular rubber chains. Based on the mechanical properties of the compounds they concluded that 50 phr of silica can be replaced by 4 phr of organoclay with a reduction of the filler content by 12.5 times, without adversely affecting the tensile properties of the final material even after aging.

2.3.2 Natural rubber (NR)-Organoclay nanocomposites: with compatibilizers

Many exertions have been paid towards the preparation of rubber-clay nanocomposites based on non-polar NR. However, the dispersion of such nanoclay in nonpolar NR matrices was rather unsatisfactory. In this section, we would like to outline some preparation and characterization of NR-clay nanocomposites in the presence of certain compatibilizers added into the system externally. Teh et al. (52) prepared NR/organoclay nanocomposites by melt compounding method. ENR25 and ENR50 were used as compatibilizers. Pristine Mt was modified with octadecyltrimethylamine and abbreviated as Mt-ODTMA. The amount of organoclay was only 2 phr while the amount of ENR was varied. NR/Mt-ODTMA showed mostly intercalated structure of the organoclay given in the Fig. 2.5.

![Fig. 2.5. (a) XRD of the Mt-ODTMA, ENR 25 and ENR 50 compatibilized and uncompatibilized NR/OMt nanocomposites (b) TEM image of ENR-50 compatibilized NR/OMt nanocomposites (52)](image)

The best dispersion of organoclay in NR nanocomposites was achieved in presence of ENR50. This was attributed to the incorporation of ENR50 in NR which facilitates the penetration of both molecules in the interlayer space of Mt. The organoclay filled NR
vulcanizates showed the lowest torque values in rheometric experiment compared to carbon black (CB) and silica filled compound. However, the improvements of tensile strength, elongation at break and tear properties in organoclay filled NR compound were considerably higher compared to CB and silica filled compound. Arroyo et al. (46) have prepared NR nanocomposites with the help of melt blending technology. The nanocomposites were prepared by blending NR with ENR25 and ENR50. Clay was modified with two different modifier namely as dimethyl dihydrogenated tallow (Mt-2M2HT) and methyl tallow bis-2-hydroxyl quaternary ammonium (Mt-MT2EtOH). Exfoliated structure of NR/organoclay nanocomposite was observed in the presence of ENR attributed to its polarity which further favors the intercalation of long rubber chains in the interlayer space of clay. Unmodified clay slightly changed the cure characteristics of NR as observed in the rheometric study and they attributed this fact due to the poor compatibility between the unmodified clay and hydrophobic polymer. Nevertheless, the optimum cure time was reduced steeply in the presence of the organoclay. Similar observation was also noticed in the case of CB but extent of decrement was smaller compared to the organoclay. NR filled with 10 phr of organoclay exhibited higher torque compared to the NR with 40 phr CB attributed to the higher cross-link density which was further confirmed by swelling and differential scanning calorimetry (DSC) experiments. The mechanical behavior of NR with 10 phr organoclay was comparable with the compound with 40 phr CB.

Nanocomposites based on (70/30) blends of NR, styrene-butadiene rubber (SBR), and organoclay have been prepared successfully via melt-mixing process by Tavakoli et al. (53). Maleated EPDM (EPDM-g-MAH) and ENR50 were employed as compatibilizer. EPDM-g-MAH showed more potential in enhancing dispersion of the clay nanolayers and their interaction with rubber phases. More potential for separating and dispersing the clay nanoplatelets with better interface enhancement was exhibited in the presence of EPDM-g-MAH as compatibilizer. Both XRD and TEM examinations verified that the two rubber phases of the rubber blend compatibilized by both EPDM-g-MAH and ENR50 could be intercalated into the galleries of organoclay and high extent of clay intercalation/exfoliation could be obtained in these nanocomposites. They have also studied the effectiveness of maleic anhydride grafted ethylene propylene diene rubber (EPDM-g-MAH) as an interfacial compatibilizer in enhancing the extent of interaction between NR matrix and organoclay nanolayers (54).
characterizations revealed better interfacial compatibilization by EPDM-g-MAH compared to ENR50, which is attributed to the lower polarity of the EPDM-g-MAH and hence more affinity for the NR matrix to be diffused onto the galleries of organoclay. The above observation was confirmed with the help of TEM analysis and higher elasticity exhibited by the unvulcanized NR/organoclay/EPDM-g-MAH nanocomposites in melt rheological measurements. Few literatures can be found describing the effect of external compatibilizers in NR based rubber blend-clay nanocomposites prepared by solution mixing technology (55-56).

![Fig. 2. 6. WAXD patterns of 5 phr organoclay filled NBR, cured by sulfur in the presence of 1, 2 and 4 phr stearic acid in (a), (b) and (c), respectively (57)](image)

Incorporation of organoclay in NR by mechanical mixing leads to very poor dispersions with larger aggregates as discussed earlier. The dispersion of organoclay in NR was rather unsatisfactory and could be observed in the respective TEM image, except they were prepared in the presence of some external compatibilizers. In view of the above-mentioned shortcomings of organoclay in the case of non-polar NR, the main task of this work is aimed at further modification of such organoclay to get highly intercalated structure which helps in the
intercalation of long rubber chains into the interlayer space of clay. To do so organoclay was further treated with different long chain fatty acids and the corresponding results are discussed in Chapter 4.

Very recently, it has been reported by Das et al. (57) that an additional amount of stearic acid has a beneficial effect on the intercalation-exfoliation process of MMT in different rubber. They revealed that stearic acid has a profound effect on the intercalation/exfoliation process of the OMt in the NBR matrix when a sulfur-curing package is chosen for the vulcanization of NBR (as shown in the Fig. 2.6). Stearic acid is a small molecule and it can easily move to the gallery gap in between two clay layers, as a result it promotes the dispersion of the clay. A considerable effect of additional amount of stearic acid on “Payne effect” was also reported by Das et al. (57). With increasing stearic acid content the absolute value of high amplitude modulus (designated as $G_0$) was also increased. They claimed that stearic acid supports the exfoliation/intercalation process of the OMt to dissociate into very fine nanometer sized particles. Although there was similar change in viscoelastic behavior observed in case of both sulfur and peroxide cured NBR-clay composites.

![Diagram](image)

**Fig. 2.7. Area of the 001 reflection versus the area difference (gum-filled) of the tan $\delta$-temperature peaks** (58)

The effect of stearic acid on the properties of different rubbers/Mt composites was studied very recently in our group by Das et al. (58). A good correlation was observed from Fig. 2.7
between the area of the (001) basal reflections and the area of the tan δ-temperature curve from DMA study. A small basal reflection was related to a large difference (filled sample-gum rubber) tan δ peak area in good agreement with the improved physical properties in the presence of such clay particles. Better improvement in different physical properties was reported for the non-polar rubbers like NR, EPDM, BR compared to polar rubbers like NBR, CR and XNBR.

2.3.3 Natural rubber with hybrid filler system based on Carbon black and clay

Two or more different filler types are utilized in the case of multi component compounding, which produces very famous hybrid structures where effects of the different materials or components are combined (59-62). Recent investigations on composites having multi component filler systems focused mainly on thermoplastics and thermosets polymer and not so familiar with rubbery materials. In most of the applications, CB and silica have been used together as a hybrid filler system to optimize the advantages and disadvantages of the individual filler system (63). When CB is compounded with rubbers many of the properties like tensile strength, tear strength, modulus hardness and abrasion resistance are increased. For this reason, CB has been extensively exploited in numerous rubber engineering products. In general, CB-reinforced rubber has a higher modulus than silica-reinforced rubber composites. In tire treads, silica provides a lower rolling resistance at equal wear resistance and wet grip than CB. Like silica, nowadays clay has been utilized in rubber compounding along with carbon black to overcome certain negative aspects of CB such as tire tread wear etc.

In the presented thesis, nanocomposites were prepared based on NR considering expanded organo-montmorillonite (EOMt) and OMt as nanofiller in the presence of a suitable amount of CB. This part of the thesis is mainly focused on the ability of nanostructured clay to create a filler network and to become building block of a hybrid filler network, in the presence of CB. Till now the preparation and characterization of rubber nanocomposites with clay/CB hybrid filler system were presented and reported in the scientific literatures considering systems based on different rubber matrices such as BIMS brominated poly(isobutylene-co-paramethylstyrene) rubber (64), styrene-butadiene rubber (SBR) (65-66), both synthetic (67) and natural rubber (68, 69), used as the only rubber or in blend with SBR (70). Other rubbers were examined, such as chlorobutyl rubber (CIIR) (71), epoxidized natural rubber (ENR) (72, 73) and ethylene-
propylene-diene rubber (EPDM) (74). These works show, in particular, a remarkable enhancement of material dynamic and static mechanical properties obtained by combining the two fillers, which were also commented to give rise to a synergistic effect. Most of the earlier efforts have been paid to establish a structure-property relationship of the hybrid filler (clay and CB together) filled rubber composites. A detail state of the art will be presented here in this section based on natural rubber filled with hybrid filler since we are dealing with only natural rubber as a primary polymer matrix. A detailed structure-property relationship will be considered to realize the fact of fracture mechanical behavior in such complex system.

2.3.3.1 Morphology and Physical properties

The combined effect of clay and CB in NR matrix was reported by Qing-xiu et al. using emulsion polymerization technique (75). They characterized the nano-morphology in terms of XRD and TEM. A phase separated structure was observed in the XRD and it was further supported from TEM analysis. In a study of Liu et al. NR nanocomposites based on CB and two poly(ethylene glycol) (PEG)-modified clay were fabricated (76). Intercalated and exfoliated structure was dominated in the case of organoclay and ORD-filled rubber and was further confirmed by WAXD and DSC. Synergy of CB and nanoclay was also reported by Bhattacharya et al. (69). NR/clay and NR/carbon nanofiber (CNF) nanocomposites were consolidated with different loadings and grade of CB to obtain ternary nanocomposites. Transmission electron micrographs of the nanocomposites displayed that CB formed “nano-blocks” of reinforcement-close association of nanoclay and CB. A pronounced interaction between clay and CB was reported by Chattopadhyay et al. in ENR matrix (72). On the basis of TEM micrographs authors hypothesized the formation of “nano-units”, speculating synergy between the two fillers and proposing a “reinforced intercalated structure”, with polymer chains intercalated in the interlayer space and CB adsorbed on the clay surface.

Most of the earlier efforts have been paid to understand the synergistic effect of both OMT and CB on the mechanical and dynamic mechanical behavior of the resulting rubber composites. However, the fracture mechanical behavior has not been fully explored in the literature. The hybrid CB/nanoclay-filled NR nanocomposites were prepared and reported in the presence of two PEG-modified organoclay by melt mixing (76). Tensile tests and dynamic mechanical analysis
showed that the two phase fillers have significant synergistic reinforcing effect on NR, which was believed to be originated from the filler network. The mechanical properties of NR composites were investigated with emphasis on the fatigue and cut resistance in another work of Liu et al. (77). The hybrid fillers of carbon black and nanoclay were found to provide superior performance to rubber vulcanizates over carbon black at the same filler loading. The fatigue crack growth test showed that the hybrid-filled specimens exhibited better crack resistance black-filled samples at higher tearing energy region.

2.4 Application of Fracture mechanical analysis in rubbers

Technical elastomers are generally filled with certain fillers (e.g. CB) in order to reinforce the rubber matrix for some typical applications like tires, conveyer belts etc. Such rubber goods are always exposed to cyclic stress and deformations attributed to their dynamic application. Under constant and repeated applied stress, cracks develop at a stress concentration point, which could lead to ultimate failure. Therefore, the crack initiation and propagation behavior in such rubber products is very fundamental and need proper attention. Elastomer materials are used in a wide application range and subjected to different loading from which failure of the material results and subsequently fracture mechanical analysis has high importance in the prevailing thesis. The application of fracture mechanics methods for the assessment of the material is obvious since this failure is caused by initiation and propagation of cracks. In the following a detail of the basic theory of fracture mechanical analysis which deals with crack initiation and propagation, is discussed in this literature review section purposely. Some literature review based on few old important books and literatures about this topic is also essential in order to understand this behavior in this complex system. This survey furthermore offers new interpretations of existing studies and theories, and identifies areas where additional research is needed.

2.4.1 Tearing energy

The tearing energy \( T_t \) is an important parameter in fracture mechanical investigations. It can be defined as the energy released per unit area of crack surface growth.

\[
T_t = -\left( \frac{\partial w}{\partial A} \right)_t = -1/t \left( \frac{\partial w}{\partial \epsilon} \right)_t 
\]  

(1)
where $T_t$ = tearing energy, $W$ = stored elastic energy in specimen, $A$ = area of fracture surface of the crack, $c$ = crack length, $t$ = thickness of the sample, and $l$ = sample length.

It was first introduced by Griffith (78) for glassy materials and Rivlin & Thomas (79) formulated the tearing energy $T_t$ for rubber material in single edge notch tensile (SENT) specimen as well as in pure-shear test specimens. The pure-shear test specimen which was used for this analysis, initially defined by Rivlin & Thomas (79), is schematically visualized in the Fig. 2.8. It has been characterized by providing the crack length $a$, develop from the initial crack length $a_0$, is sufficiently long compared to the length of test specimen $L_0$. According to Rivlin and Thomas (79) the test specimen can be divided into different regions. Region $A_1$ is unstrained and region $C-D$ is in pure-shear state.

Furthermore, there is an area of complicated strain around the crack tip in region $D$, and a region of edge effect shown as $A$. If the maximum cyclic deformation remains constant and the crack length is increased by $da$, the region of complicated strain $D$ moves along by $da$, but the pattern of strain, and hence the energy stored, remains unaltered. For a pure-shear test specimen geometry the tearing energy $T_t$ is considered by Rivlin & Thomas (79) to be independent of the crack length:

$$T_t = wL_0 \quad (2)$$

**Fig. 2.8. Schematic of pure shear test specimen**

The value of $w$ can be found from the strain in the pure-shear region and knowledge of the pure shear stress versus strain relationship.
2.4.2 Fracture mechanical treatment of failure

Gent, Lindley and Thomas (80) determined experimentally the crack growth rate \( da/dn \) in dependence on the \( T_i \) for rubber materials. Figure 2.9 shows the typical relationship for a rubber material on a double logarithmic plot. Lake & Lindley (81) divided this plot into four regions which characterize different tear behavior. The crack growth rate \( da/dn \) depends on the tearing energy \( T_i \) in each of the four regions in a characteristic manner.

![Double logarithmic plot of crack growth rate da/dn vs. tearing energy (T_i) for rubber material](image)

**Fig. 2. 9. Double logarithmic plot of crack growth rate da/dn vs. tearing energy (\( T_i \)) for rubber material (81)**

As long as the value of \( T_i \) is lower than \( T_0 \), crack growth proceeds at a constant rate \( r \) and the crack growth is independent of the dynamical loading, but affected by the environmental attack.

\[
\frac{da}{dn} = r \quad \text{when } T_i \leq T_0 \quad (3)
\]

In the region 2 between \( T_0 \) and \( T_1 \) one finds a transition between a nucleation and propagation of crack growth:

\[
\frac{da}{dn} = A(T_i - T_0) + r \quad \text{when } T_0 \leq T_i \leq T_1 \quad (4)
\]
After this transient state the crack propagates in a region between $T_1$ and $T_C$ of stable crack growth which is denoted as region 3. The relationship between fatigue crack growth rate $da/dn$ and tearing energy describe Paris & Erdogan (82) with the power-law:

$$\frac{da}{dn} = B \Delta T_i^m \quad \text{when } T_1 \leq T_i \leq T_C$$

(5)

where $B$ and $m$ are material constants.

In the last region 4 the tearing energy $T_C$ proceeds to the instable state of crack growth and the crack growth rate will become essentially infinite.

$$\frac{da}{dn} = \infty \quad \text{when } T_i \approx T_C$$

(6)

The region 3 was utilized as the region that corresponds most closely to crack growth rates found in the engineering fatigue range. In this work an experimental an analysis of pure-shear test specimen was performed according to this region to compare the stable describe the crack growth in different rubbers.

2.5 The magic triangle in tire technology

In this section a brief overview of tire technology is given purposely since of the main application of this work could be realized in tire application. For a long period wheels have been utilized to diminution hefty frictional forces that oppose the movement of heavy objects. Vehicle tires are the most prominent and fascinating rubber articles in terms of volume and importance. More than half of the natural and synthetic rubbers produced worldwide are consumed in the tire industry. Soon after the development of rubber vulcanization by great scientist Charles Goodyear in 1839, the early effort has been made by a Scottish engineer, Robert William Thomson in the year of 1845, who invented and patented the world’s first pneumatic tires. Such tires were consisting of rubber tubes filled with air and protected by canvas cover with leather treads. Unfortunately, such tires were less resistant towards irregularities of road surfaces. Finally, in 1888, John Boyd Dunlop developed and revived practical pneumatic inflatable bicycle tires and patented for the same. Such pneumatic tires consisted of an inner-tube surrounded by a cover made up of numerous layers of woven canvas fabric, held together by rubber bonding. In year of 1895, André Michelin was the first person to use pneumatic tires on an automobile, nevertheless,
not successfully. Subsequently, tires have gone through a sluggish period of development with just an occasional discrete revolution such as the beginning of the radial ply tire in 1948 or the early attempts at run-flat technology in the mid-1970s.

The tire industry requires continuous development for truck tires in the following areas for increased durability, better fuel economy and improved safety. Figure 2.10 displays these three basic performances considered in modern tire production. These three most important properties: traction, abrasion resistance and rolling resistance form the so called: “Magic Triangle” of tire properties. These requirements can only be met by new fillers that can impart higher abrasion resistance, lower hysteresis at high temperature and improved wet skid resistance. Carbon black imparting higher abrasion resistance to the compound generally gives higher hysteresis at high temperature as measured by loss factor, tanδ, hence higher rolling resistance. This problem has been worked out by replacing certain quantities of carbon black with silica in the tire tread compound which enables to produce tires that provide wet skid properties, better winter performance and lower rolling resistance, all at the same time. During the last few years silica has been used with solution styrene butadiene rubber (SSBR) in passenger car tires in order to improve rolling resistance and wet traction (83). Silica displays a very low polymer-filler interaction and a strong tendency to form agglomerate (without coupling agent) compared to carbon black, with similar surface area and structure, thus forming a developed filler network in the compound. This results in inferior compound processability, lower failure properties such as ultimate strength and abrasion resistance, and unacceptable dynamic mechanical properties. However, surface modification with coupling agents such as bifunctional silane bis(3-triethoxysilylpropyl-) tetrasulfane (TESPT) lowers the filler-filler interaction by covering the polar surface with organo-grafts, and enhances the polymer filler interaction through creation of chemical linkages between the filler surface and polymer chains. The dynamic properties, as well as the static properties are improved, allowing applications of silica in passenger-tread compounds. However, it has been reported that the application of silica to truck tire compounds has not been efficacious attributed to its inherent incompatibility with NR matrix even in the presence of suitable silane coupling agents. It has been observed that (83) the abrasion property of silica filled NR is very poor. Although there are several reasons responsible for such behavior but the inferior interaction between NR matrix and silica particles probably the main issue. The
poor abrasion property even cannot be improved in the presence of coupling agent. Therefore, it could be realize from the above discussions that the optimum fillers for NR-based truck tread compounds are those which provide high polymer-filler and lower filler-filler interactions. The former ensures higher abrasion resistance, and the latter is necessary for lower hysteresis, therefore lower rolling resistance.

Fig. 2. 10. Magic triangle in tire technology
3 Experimental: Materials, Compounding and Characterization

3.1 Materials

3.1.1 Rubber

The main polymer used for the preparation of rubber-clay nanocomposites was natural rubber (NR). NR used in this study, was Standard Malaysian Rubber (SMR 10). Different specifications of this rubber are mentioned in the Table 3.1 below. Chemical structure of NR is also given in the Fig. 3.1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dirt retained on 44µ aperture (max,%wt)</td>
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</tr>
<tr>
<td>Ash content (max,%wt)</td>
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</tr>
<tr>
<td>Nitrogen (max,%wt)</td>
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<td>Volatile matter (max,%wt)</td>
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<tr>
<td>Wallace rapid plasticity (P°) (min)</td>
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</tr>
<tr>
<td>Plasticity retention index (PRI) (min, %)</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 3.1. Different specification of SMR 10

![Chemical structure of cis-polyisoprene, the main constituent of NR](image)

3.1.2 Different fillers

3.1.2.1 Clay nanoparticles

The organo-montmorillonite (OMt) was supplied by Süd-Chemie AG (now Rockwood Additives) Moosburg, Germany. Distearyl dimethylammonium chloride was used as an organic modifier. The specific gravity of this OMt was 1.8 g cm\(^{-3}\) with an average particle size of 25 µm.
3.1.2.2 Carbon black

Carbon black (Corax N 330) was obtained from ORION Engineered Carbons GmbH, Köln, Germany. Different parameters of this particular carbon black are summarized in the Table 3.2.

**Table 3.2. Statistical thickness surface area (STSA) and structure (oil adsorption number OAN) of this carbon black obtained from datasheet**

<table>
<thead>
<tr>
<th>Carbon black</th>
<th>STSA (m²/g)</th>
<th>OAN (ml/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corax N330</td>
<td>76</td>
<td>102</td>
</tr>
</tbody>
</table>

3.1.3 Other curing ingredients

The stearic acid was purchased from ACROS Organics, Geel, Belgium with 97% purity. The vulcanizing accelerator was N-tert-Butyl-2-benzothiazolesulfenamide (TBBS), kindly provided by Rhein Chemie, Rheinau, Mannheim, Germany. Sulphur (S) and zinc oxide (ZnO) used in this study were of industrial grade.

3.1.4 Fatty acids as intercalating agent

The fatty acids with different alkyl chain lengths (C16 to C22) were procured from ACROS Organics, Geel, Belgium (98% pure palmitic acid, 97% pure stearic acid, 99% pure eicosanoic acid and 98% pure docosanoic acid). Different chemical structures of these fatty acids are represented in the Table 3.3.

**Table 3.3. Different Fatty acids used for the intercalation**

<table>
<thead>
<tr>
<th>Chemical structures</th>
<th>No of carbon atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>COOH</td>
<td>16</td>
</tr>
<tr>
<td>COOH</td>
<td>18</td>
</tr>
<tr>
<td>COOH</td>
<td>20</td>
</tr>
<tr>
<td>COOH</td>
<td>22</td>
</tr>
</tbody>
</table>
3.2 Processing of rubber-clay nanocomposites

3.2.1 Intercalation of different long chain fatty acids

Pre-intercalation of OMt was done by a series of long alkyl chain fatty acids. Fatty acids and OMt were taken in a porcelain mortar at ratio of 1:1 by mass and well mixed by a pestle. The mixture was kept in an oven at 110 °C for 15 min. The mass was then cooled at room temperature and again it was grinded. This step was done several times for obtaining a homogeneous mass. The resulting product is called “expanded organo-montmorillonite” (EOMt). Intercalation of fatty acids in the interlayer space of clay was also done in an internal mixture (Fig. 3.2) (Haake, Rheomix, Thermo Electron GmbH, Karlsruhe). For this purpose a mixture of OMt and fatty acids (1:1 by mass) was taken and mixed at a fixed rotor speed of 50 r.p.m and temperature of 100 °C. These mixtures were mixed for 20 minutes. The mass was then cooled at room temperature and subsequently grinded. The resulting product is abbreviated as expanded organo-montmorillonite (EOMt).

![Fig. 3.2. Haake Internal mixer](image-url)
3.2.2 Compounding

3.2.2.1 Preparation of different NR-clay nanocomposites

Mixing of NR with different clay was performed in an open two-roll mixing mill (Fig. 3.3) (Polymix 110L, Servitec GmbH, Wustermark, Germany) at 90 °C. The typical formulation and the recipe of the rubber compounds are shown in respective Table (3.4 and 3.5). The mixing was done at 90 °C to ensure complete melting of fatty acids. The rubber was first masticated and mixed with zinc oxide (ZnO). EOMt was then incorporated. This step was continued for 5 min with a very small nip gap of ~0.15 mm between the rolls to facilitate the intercalation process. Finally clay containing rubber compound was mixed with accelerator and sulphur. For control batches the mixing sequence was the following: first ZnO, followed by stearic acid, clay, accelerator and finally sulphur.

Table 3.4. Typical formulation for NR-Clay nanocomposites

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>NR gum</th>
<th>NR-OMt</th>
<th>NR-C16-EOMt</th>
<th>NR-C18-EOMt</th>
<th>NR-C20-EOMt</th>
<th>NR-C22-EOMt</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR gum</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>ZnO</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>OMe</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C16-EOMt</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C18-EOMt</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C20-EOMt</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>C22-EOMt</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>TBBS</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>

* Weights in parts per hundred rubber (phr)
3.2.2.2 Preparation of hybrid filler (CB and clay) filled NR composites

The basic formulation of NR compounds expressed as parts per hundred of rubber (phr) is shown in Table 3.6. Mixing was accomplished in two steps. In the first step CB was mixed with rubber matrix in the internal mixer (Haake rheomix, Fig. 3.4) together with ZnO and stearic acid. Total time of mixing in the internal mixer was fixed to 10 minutes. Second step mixing was carried out in an open two roll mill at 90 °C. This temperature was selected to ensure the melting of fatty acids during the course of mixing. Clays and curatives are added in this step. Total mixing time was 10 minutes in the roll mill. The stocks were cured under pressure at 150 °C to 2
mm plates using the optimum cure time ($t_{90}$) previously determined from a vulcameter (Scarabaeus, Langgöns, Germany).

Table 3. Compound formulations of CB filled NR-clay nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>NR</th>
<th>ZnO</th>
<th>Stearic acid</th>
<th>CB</th>
<th>Oil</th>
<th>OMt</th>
<th>EOMt</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR-CB30</td>
<td>100</td>
<td>3</td>
<td>2</td>
<td>30</td>
<td>3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NR-C30-FA</td>
<td>100</td>
<td>3</td>
<td>5</td>
<td>30</td>
<td>3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NR-C30-OMt</td>
<td>100</td>
<td>3</td>
<td>2</td>
<td>30</td>
<td>3</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>NR-C30-EOMt</td>
<td>100</td>
<td>3</td>
<td>-</td>
<td>30</td>
<td>3</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>NR-CB50</td>
<td>100</td>
<td>3</td>
<td>2</td>
<td>50</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Amount of S and TBBS is fixed to 1.4 phr in all cases

Fig. 3.4. Haake rheomix
3.2.3 Moulding

The thin sheet obtained after mixing was marked with the milling direction and cut in the required dimension and stacked each other to the desired volume for moulding. A picture of compression moulding machine is shown in Fig. 3.5. The test specimens were molded in standard moulds by compression molding on an electrically heated hydraulic press. The rubber samples were vulcanized up to their respective optimum cure time at 150 °C. Moldings were cooled quickly in water at the end of the curing cycle and stored in a cool and dark place for 24 hours and were used for subsequent physical tests.

3.3 Characterizations

3.3.1 Curing study

Curing studies were performed using Scarabaeus SIS-V50 (Fig 3.6), a rubber processing analyzer (Scarabaeus, Langgöns, Germany) in the isothermal time sweep mode for the samples at different temperature (140, 150, 160 °C) for 60 minutes. For the preparation of the vulcanized
sample 150 °C was selected for the measurement of the curing time $t_{90}$, scorch time $t_2$ and others, data were used for the curing kinetics study.

3.3.2 X-ray diffraction (XRD)

A Seifert XRD 3003 Θ/Θ (GE Inspection Technologies/Seifert-FPM, Freiberg, Germany) (Fig. 3.7) with CuKα radiation was used in transmission mode.
Experimental: Materials, Compounding and Characterization

The diffraction angle was varied between 0.5° and 50° with an increment of 0.05°. The measurement time for the intensity at each angle was 15 s. The d-spacing of the layered particles was then calculated from Bragg’s equation \( n\lambda = 2d \sin\theta \), where \( \lambda \) is the wavelength of the X-ray, \( d \) is the interlayer distance and \( \theta \) is the angle of incident X-ray radiation. The shift in the first order diffraction peak (<001>) was calculated from the XRD spectra, which can be attributed to intercalation of polymer chains in clay galleries.

3.3.3 Fourier Transform Infrared (FTIR) spectra

The Fourier-transform infrared (FTIR) spectra of the composites were obtained using the BRUKER VERTEX 80 V spectrometer (Fig. 3.8) over the wave number range of 4000-400 cm\(^{-1}\) in an attenuated total reflection (ATR) mode.

![Vertex 80v FTIR spectrometer from Bruker](image)

**Fig. 3.8.** Vertex 80v FTIR spectrometer from Bruker

![Schematic representation of the Wilhelmy technique of dynamic contact angle measurement on a particle covered plate. During immersion of the plate the advancing \( \theta_a \), during withdrawal the receding contact angle \( \theta_r \) is measured](image)

**Fig. 3.9.** Schematic representation of the Wilhelmy technique of dynamic contact angle measurement on a particle covered plate. During immersion of the plate the advancing \( \theta_a \), during withdrawal the receding contact angle \( \theta_r \) is measured
3.3.4 Contact angle measurement

The wetting behaviour of the modified filler particles was measured at a fixed particle layer by means of a modified Wilhelmy method (Fig. 3.9) using a dynamic contact angle meter and tensiometer DCAT21 (DataPhysics, Filderstadt, Germany). The contact angles for water (Millipore, Milli-Q) were obtained from the mean value of advancing and receding angle.

3.3.5 Tensile testing

Tensile tests of cured samples were carried out using Zwick 1456 (model 1456, Z010, Ulm, Germany) with crosshead speed 200 mm/min (Fig. 3.10).

![Mechanical testing machine](image)

**Fig. 3.10. Mechanical testing machine**

3.3.6 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis was performed on strips with 10 mm width using a dynamic mechanical thermal spectrometer (Gabo Qualimeter, Ahlden, Germany, model Eplexor-2000N) in the tension mode. The isochronal frequency used was 10 Hz and the heating rate was 2 °C/min with a dynamic load at 0.5% strain and static load at 1% strain. Amplitude sweep measurements were performed on the same Eplexor 2000 N (Gabo Qualimeter, Ahlden, Germany) in the tension mode at room temperature, at a constant frequency of 10 Hz, static load
at 60% strain and dynamic load, 0.01-30%. Frequency master curves were made by using the time temperature superposition principle (TTS), after measuring a combined temperature frequency sweep at temperatures from 20°C to 100°C and frequencies from 0.5Hz to 50Hz. For creating the master curves the instrument software (Eplexor version 8.374g from Gabo, Ahlden, Germany) was used. Figure 3.11 shows the set-up of DMA machine.

![Figure 3.11. Dynamic mechanical analyzer (Eplexor-2000N)](image)

3.3.7 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was done using a TA TGA, Q 500 instrument (USA) with a heating rate of 10 °C/min under nitrogen atmosphere and the sample was swept by oxygen flow at 700 °C. A picture of this TGA machine is shown in Fig. 3.12.
3.3.8 Transmission Electron Microscopy (TEM)

The state of dispersion of the clay particles in the nanocomposites was investigated using transmission electron microscopy (TEM) with the microscope JEM 2010 model. The ultra-thin sections of the samples were prepared by ultramicrotomy (Leica Ultracut UCT) at -120 °C with a thickness of a section 100 nm. Figure 3.13 reveals the TEM instruments.
3.3.9 Swelling experiment: measurement of crosslink density

In order to analyze the network structure of the NR-clay nanocomposites, a swelling experiment was performed according to ASTM D 6814-02. Previously weighed samples were allowed to swell in toluene at 25°C for 48 h, the equilibrium swelling time (which was determined from a plot of mass uptake against time). The test pieces were then taken out, weighed and dried to a constant weight in a vacuum oven at 50 °C for 12 h. The volume fraction of the rubber in the swollen gel (\(V_r\)) was determined on the basis of simple additive rule of volumes as follows (Eq. 1):

\[
V_r = \frac{(D - FH)}{\rho_r (D - FH) + A_o \rho_r / \rho_s}
\]

(1)

where, H = weight of the test specimen, D = deswollen weight of the test specimen, F = weight fraction of the insoluble components, A_o = weight of the absorbed solvent, \(\rho_r\) = density of the rubber, \(\rho_s\) = density of the solvent

The apparent crosslinking density (\(v_c\)) was calculated according to the Flory-Rehner equation (84) as follows:

\[
-\left[\ln (1-V_r) + V_r + \chi x V_r^2\right] = \frac{\rho_r}{M_c} x V_s \left(V_r^{1/3} - \frac{V_c}{2}\right)
\]

(2)

\[
v_c = \frac{1}{2M_c}
\]

(3)

where \(V_r\) is the volume fraction of the polymer in the swollen specimen according to Eq. 1, \(\chi\) is the Flory-Huggins polymer solvent interaction parameter, \(M_c\) is the molecular weight between crosslinks and \(V_s\) is the molar volume of the solvent. For NR-toluene system, the value of \(\chi\) is 0.393 (85).
3.3.10 Differential Scanning Calorimeter (DSC)

Differential scanning calorimeter (DSC) measurements were carried out using a DSC Q1000 (TA instruments, New Castle, USA). The scans were taken in the temperature range from -80 to 200 °C with a programmed heating rate of 10 K/min under N2 atmosphere (Fig. 3.14).

![DSC from TA instruments](image)

**Fig. 3.14. DSC from TA instruments**

3.3.11 Description of Tear fatigue analyzer (TFA)

The fatigue tests were performed with a tear and fatigue analyzer (TFA) by Coesfeld GmbH, Dortmund, Germany and the following testing conditions were set: frequency 10 Hz, loading amplitudes 7, 10, 13, 16, 20 and 25% of the initial length \( L_0 \), pre-stress 1 N and the tests were performed in laboratory atmosphere (28 °C). One double notched pure-shear test specimen was analyzed for each loading amplitude. Figure 3.15 shows a schematic diagram of tear fatigue analyzer (TFA) which is used for investigating the fatigue crack growth of rubber materials by simultaneous SENT and pure-shear mode testing. It is possible to measure three pure-shear samples and simultaneously or separately four tensile test specimens. Each bottom clamp attachment of test specimens is fixed to the traverse. The traverse is connected to the piston, dynamically powered by a hydropulser. The hydropulser is driven by a frequency sweep generator through different loading modes (sine-, triangle-, pulse loading), within the frequency range 0.1-20 Hz. Each upper clamp attachment of test specimens is fixed to the load cell and its corresponding test specimen clamp attachment is connected to a separate computer-controlled stepping motor to ensure constant pre-stress during the whole time of testing. The crack growth of each rubber test specimen is monitored through an image process system with high-speed closed circuit camera (CCD) monochrome camera mounted on the linear motion axis system.
The camera moves along the X-axis from test specimen to test specimen and takes a picture of involved test specimen. The picture is then transferred to a frame grabber and stored. After the picture has been digitalized the software localizes the crack position and determines the crack length.

3.3.12 Instrumented Notched-Tensile-Impact Test (IN-TI): Fracture toughness

With the application of fracture mechanics it is supposed that materials fail as a result of initiation and propagation of cracks. Conditions of it are investigated by the result of quantitative connections between external loading of a notched specimen and size and kind of the resulting crack. Using such a relation, statements about the crack toughness becomes possible. For the purpose of derivation of failure criteria, various fracture mechanics concepts have been developed can be found in the literature (86, 87). The $J$-integral as fracture criterion has highest importance owing to its energetic interpretation of the fracture process. For elastomers, the tearing energy $T$ as toughness parameter was introduced by Rivlin and Thomas (79).

---

**Fig. 3.15.** Schematic and functional diagram of the test machine: A-tensile test specimen; B-pure-shear test specimen; C-traverse; D-hydropulser; E-isolated chamber; F-frequency generator; G-control unit 1; H control unit 2; I-load cells; J-CCD monochrome camera; K-PC1; L-PC2.
Owing to their definition, $J$ and $T$ are formally identical, and thus both parameters can be considered as equivalent. Starting from the valid standard for conventional tensile-impact tests DIN EN ISO 8256 “Plastics—Determination of Tensile-impact Strength,” some instructions for performance of instrumented tensile-impact tests have been adopted. In this way, a procedure for performance and evaluation of instrumented tensile-impact tests was developed. With the present knowledge and in accordance to the standard, the specimen shown in Fig. 3.16, called double edge notched tension (DENT) specimen, was selected additionally to TFA for fracture mechanics investigations with the instrumented tensile-impact test. The length $L$ is 64 mm, width $W$ is 10 mm and initial crack length $a$ should be 2 mm. Because the notch radius must be very small, the notches were made by a razor blade.

The test was carried out with the instrumented pendulum device RESIL IMPACTOR Junior (CEAST, Italy) and is represented in the Fig. 3.17 (86, 87). A pendulum hammer with a maximum working capacity of 7.5 J and a test speed of 3.7 m/s were used. An initial gauge length of 30 mm was realized. The tests were carried out at room temperature. For each of the vulcanizates investigated, at minimum 10 specimens were prepared and tested.

![Fig. 3.16. Schematic representation of double-edge notched test specimen for instrumented notch tensile impact tests](image)

Fig. 3. 16. Schematic representation of double-edge notched test specimen for instrumented notch tensile impact tests

Based on these diagrams, the analysis and calculation of the crack toughness parameter critical $J$-integral values $J_d$ according to the following equations were done. Test set-up and principle is shown in Fig. 3.18.

$$J_d = \frac{\eta A_2}{B(W-a)}$$  \hspace{1cm} (4)

with the geometry function $\eta$ according to (88)

$$\eta = -0.06 + 5.99\left(\frac{a}{w}\right) - 7.42\left(\frac{a}{w}\right)^2 + 3.29\left(\frac{a}{w}\right)^3$$  \hspace{1cm} (5)
For the tests DENT specimens with the following dimension length $L = 64$ mm, width $W = 10$ mm and thickness $B = 2$ mm were used. The ratio between the initial notch depth $a$ and the width $W$ was ca. 0.13.

Fig. 3. 17. Ceast pendulum device resil impactor junior for performance of instrumented notch tensile impact tests

Fig. 3. 18. Test set-up of the instrumented tensile-impact test and analysis of a load-extension diagram of an elastomeric material

3.3.13 Atomic force microscopy (AFM)

Micro-morphology of composites at representative scale was examined by atomic force microscopy (Fig. 3.19). The surfaces of fresh cuts of the materials prepared with cryo-ultramicrotome Leica UC7 at -90°C were studied. For each specimen, several high quality AFM-images of the size: 20x20 µm or higher and resolution in xy-plane 1280×1280 dots were scanned
for further analysis. The experiments were carried out on Dimension Icon (Veeco) AFM in tapping mode. Regular probes with nominal radii 8 nm were used. Custom algorithms developed in Matlab were employed for image processing and further analysis.

Fig. 3. 19. Atomic force microscopy
4 Results and discussion

4.1 Clay Modification: Characterizations of expanded organo-montmorillonite (EOMt)

4.1.1 Wide angle X-ray diffraction of different EOMt

The WAXD patterns of different EOMt are represented along with pure OMt in Fig. 4.1 and their position is shown in the Table 4.1. The characteristic (001) reflection for the OMt appears at $2\theta = 2.2^\circ$ corresponds to basal spacing, $d = 2.98$ nm. It can be observed from Fig. 4.1 that the $d$-basal spacing of the EOMt is shifted to the lower reflection angles compared to OMt. The interlayer distances are 3.6, 3.95, 4.1, and 4.2 nm for C16-EOMt, C18-EOMt, C20-EOMt, and C22-EOMt respectively measured from the reflection of $d\ (001)$ plane. The highest extent of intercalation corresponding to largest interlayer distance of 4.2 nm in C22-EOMt (compared to 3.6 nm for C16-EOMt) is obtained with C22 fatty acid. This indicates that the fatty acid with longer alkyl chain is beneficial to expand the interlayer space of Mt. Similar observation was reported by Lagaly et al. (89) for organoclays modified with alkyl ammonium compounds of different alkyl chain length (C6-C18).

![Fig. 4.1. WAXD patterns of EOMt at room temperature](image)

The shifting of all the diffraction maxima to lower $2\theta$ is proportional to the size of alkyl chain of the fatty acids and indicates a linear relationship between basal spacing and the number
of carbon atom in the fatty acid alkyl chain which is depicted in Fig. 4.2. A rather good linear correlation \((R^2=0.94)\) is observed between basal layer distance and the number of carbon atom \((n_C)\) of the fatty acid. It is also interesting to note that the slope of the linear fit (0.10 nm) is very close to the expected value of the C-C bond length of fatty acids (0.15 nm). The small deviation might be attributed to their tilted structure in the interlayer space of clay minerals.

![Fig. 4.2. Basal spacing as a function of the alkyl chain length of different fatty acids](image)

Table 4.1. Assignment of various WAXD reflections obtained for OMe and EOMe

<table>
<thead>
<tr>
<th>Materials</th>
<th>Reflections in (00l) series</th>
<th>2θ (deg)</th>
<th>d (nm)</th>
<th>2θ (deg)</th>
<th>d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMe</td>
<td>(001)</td>
<td>2.68</td>
<td>3.0</td>
<td>7.0</td>
<td>1.25</td>
</tr>
<tr>
<td>C16-EOMe</td>
<td>(002)</td>
<td>2.61</td>
<td>3.6</td>
<td>6.6</td>
<td>1.30</td>
</tr>
<tr>
<td>C18-EOMe</td>
<td>(001)</td>
<td>2.44</td>
<td>3.9</td>
<td>6.5</td>
<td>1.33</td>
</tr>
<tr>
<td>C20-EOMe</td>
<td>(002)</td>
<td>2.45</td>
<td>4.1</td>
<td>6.7</td>
<td>1.41</td>
</tr>
<tr>
<td>C22-EOMe</td>
<td>(001)</td>
<td>2.41</td>
<td>4.2</td>
<td>6.5</td>
<td>1.45</td>
</tr>
</tbody>
</table>

It is also found that there is always one sharp peak appear with all EOMe at lower angle associated with the basal reflection of the clay layers. This is attributed to the crystallites of the corresponding fatty acids in the di-mer form (90). The size of the crystallites increased with the
increase of the chain length of the corresponding fatty acids. However, the other sharp reflections in the higher diffraction angle are rather difficult to understand the complex morphology of the EOMt. The quaternary ammonium compound (QUAT) previously present in the silicate nanogalleries of OMt, propping open the silicate layers further and pave the way for long chain fatty acids during melting. Furthermore, the presence of the long alkyl chains in the interlayer galleries reduces the hydrophilic character of these domains and draws the host fatty acid alkyl chains inside the clay galleries owing to the van der Waals force of attraction. It has been reported by Lagaly et al. (91) that in dried alkylammonium vermiculites the alkyl chains in paraffin-type arrangement are tilted to the silicate layer. Figure 4.3 depicts the hypothetical model of clay layer expansion in presence of fatty acids.

4.1.2 FTIR spectra of different EOMt

For a completely disordered structure, such as liquid alkanes, the characteristic frequencies are 2924 cm\(^{-1}\) for CH\(_2\) symmetric stretching and 2856 cm\(^{-1}\) for CH\(_2\) asymmetric stretching and for a well-ordered layers, such as crystalline paraffins, the characteristic frequencies are 2915-18 cm\(^{-1}\) for CH\(_2\) symmetric stretching and 2846-50 cm\(^{-1}\) for CH\(_2\) asymmetric stretching (92). It can be seen from the Fig. 4.4 that the CH\(_2\) stretching band for the OMt is arising at 2924 cm\(^{-1}\), which indicates the organic modifiers previously present in the silicate interlayer space are in liquid like disordered arrangement.

Fig. 4. 3. Hypothetical representation of clay minerals layer expansion in presence of C22 fatty acid
After intercalation of such OMt with different long alkyl chain fatty acids, the CH₂ stretching band is shifted to lower wave number. This gives an indication of disturbance of the conformation of the surfactants already present inside the layer structures. It is also reported in the literature that the frequencies of the CH₂ stretching absorption bands of amine chains are extremely sensitive to the conformational changes of the chains (93, 94) and only when the chains are highly ordered (all-trans conformation), the narrow absorption bands appear around 2916 cm⁻¹ in the IR spectrum. On the other hand the CH₂ asymmetric stretching band for the OMt is appearing at 2850 cm⁻¹ which again inform us about the disorder state of surfactants in the silicate nanolayers. The above phenomenon is also well corroborated from WAXD results.

It can be observed from Fig. 4.4a that a broad peak appears at 3430 cm⁻¹ is attributed to the hydroxyl stretching vibrations (free and interlayer water molecules) in O Mt (95). Alternatively, the major band 1705 cm⁻¹ shown in the figure can be assigned to the stretching vibrations of C=O groups present in the C18 fatty acid. FTIR spectrum of docosanoic acid is given here as representative in the present discussion for clarity. It can also be observed from figure that a new peak is appeared at 1730 cm⁻¹ attributed to the strong interaction between C=O group and interlayer cations via water bridge shown in Fig. 4.4b (95). This indicates that fatty acid molecules intercalate the interlayer space of O Mt and again supports the results obtained from WAXD patterns.

![FTIR spectra of EOMt and WAXD diagram](image-url)
4.1.3 Contact angle measurement

As it was expected, all EOMt clay minerals show a lower wettability compared to OMt indicated an increase of their hydrophobic character which is shown in Fig 4.5. It was clearly observed from FTIR studies that there is strong interaction between clay minerals and fatty acid. Therefore, the contact angle which is measure of hydrophobicity of highly inorganic clay minerals is increased after the intercalation of different long chain fatty acid.

![Contact angle graph](image)

*Fig. 4.5. Contact angle of different EOMt with respect to water*

4.1.4 Thermogravimetric analysis (TGA)

The thermal decomposition expressed in terms of weight loss as a function of temperature of both OMt and EOMt were represented in Fig. 4.6. It is interesting to note that the degradation temperature of the entire fatty acids was decreased in the presence of clay minerals. It is mentioned in the literature that clay minerals accelerate the rate of degradation of fatty acids (96). The most interesting observation was to note that the degradation started more early as the chain length was shorter.

4.1.5 C22 fatty acid intercalated OMt (C22EOMt)

Since C22EOMt has the largest interlayer distance among all the modified samples studied, this EOMt was chosen further and extensively investigated to get more insight into it.
The characterization of C22EOMt in the previous section though provides several important information on its structure, a further analysis using FTIR and XRD at various temperatures can be useful to comprehend the changes in structure of Mt and C22EOMt with increasing temperature. Effect of intercalation time is also recorded on the particular expanded clay.

4.1.6 Temperature dependent WAXD

Figure 4.7 depicts the WAXD patterns of a physical mixture of OMt and C22 fatty acid (C22FA) (1:1 by mass) at different temperatures. The maximum temperature has been chosen 100 °C to ensure complete melting of C22 fatty acid. It can be observed from the Fig. 4.7 that the (002) basal reflection peak is gradually shifted to lower diffraction angle as the temperature gradually increased suggests that intercalation of docosanoic acid in the silicate layers. Simultaneously, due to melting of C22FA (80 °C) the sharp reflection at 21° arising from the stearic acid is gradually vanishing. A similar observation was also reported elsewhere (97).

![Fig. 4.6. TGA thermograms weight loss as function of temperature](image)

4.1.7 Temperature dependent FTIR spectra

For better understating of the new peak coming at 1730 cm\(^{-1}\), a temperature dependent FTIR spectrum was carried out. Figure 4.8 illustrates the temperature dependence of the shape of the 3430 cm\(^{-1}\) and 1630 cm\(^{-1}\) band mentioned in the Fig. 4.8.
Fig. 4. 7. WAXD patterns of OMt-C22FA mixture (1:1 by mass) heated to various temperatures. The spectra are displaced vertically for clarity, with different scan temperatures from top to bottom.

Fig. 4. 8. Heating cycle from 30 °C to 110 °C
The above mentioned bands correspond to O-H stretching vibration of adsorbed water molecules present in the interlayer space of C22EOMt. It was found that the O-H stretching peak remarkably became weaker upon heating and disappears completely above 100 °C. This is an indication of the evolution of the interlayer water during the thermal treatment. Figure 4.8 also showed that the evolution of water was associated with the shifting the corresponding band of the COOH vibrations. However, upon cooling to room temperature in air, the O-H stretching peak was appeared again. This signified that desorption and adsorption processes of water in Mt were reversible. These observations further suggest that even with pretty high surfactant loading, it is still not possible to transform the Mt into an entirely “hydrophobic” material. It was also observed from Fig. 4.9 that a sharp peak appeared at 1730 cm\(^{-1}\) during cooling. It can be attributed to the strong interaction between C=O group and metal ions via water bridge. The extent and strength of the bond depend on the nature of the exchangeable cation present in the interlayer space and on the thermal treatment. On heating more organic molecules coordinated directly to the metal ions. After hydration a band due to bonding through a water bridge was appeared.

![Fig. 4.9. Cooling cycle from 100 °C to 30 °C](image-url)
4.1.7.1 Effect of mixing time

It was also important to determine the appropriate processing time for the preparation EOMt by an internal mixture. For this purpose, a mixture of docosanoic acid (C22) and OMt (1:1 by mass) was taken. These mixtures were mixed for 10, 20 and 30 minutes respectively. Fig. 4.10 shows that the basal spacing was not significantly influenced by the mixing time. After 20 minutes of mixing a constant interlayer space was achieved.

Fig. 4. 10. Effect of mixing time on the intercalation behavior of C22 FA
4.2 NR-EOMt nanocomposites: role of different fatty acid chain length on dispersion

4.2.1 Wide angle X-ray diffraction (WAXD) study

The WAXD patterns of different nanocomposites are depicted in the Fig. 4.11a in the range of $2\theta = 1-12^\circ$. It can be seen from the Fig. 4.11a that the measured $d$(001) basal spacing of OMt is 2.98 nm, while in NR/OMt nanocomposites the basal spacing is 4.3 nm. However, in one hand the total dispersion as well as distribution of the OMt is found to be very poor as the big agglomerated particles of the OMt could be found in the rubber compound by simple visual examination and also in electron microscopy (Fig. 4.11b and 4.11c).

![WAXD patterns of various NR-EOMt nanocomposites](image1)

![Optical image of the cross-section of a compounded natural rubber filled with 5 phr OMt](image2)

![TEM image of NR-OMt](image3)
On the other hand, a significant increase in the $d(001)$ basal spacing is observed in the case NR/EOMt nanocomposites. It is also very clear from the Fig. 4.11a that as the length of fatty acid alkyl chain is increased, the $d(001)$ basal spacing is increased simultaneously. The WAXD pattern of NR-C22-EOMt displays a low angle broad halo. The broadening of the $d(001)$ peak in a low $2\theta$ region indicates the extensive layer separation associated to the clay lamellae intercalation and exfoliation. The reason is attributed to the long alkyl chains (C22) creating more interlayer space where the intercalation of macromolecular rubber chains are becoming easier.

4.2.2 Transmission electron microscopy (TEM)

TEM allows the morphological state of the nanocomposites to be delineated more completely. It can be observed from the Fig. 4.12 and Fig. 4.13 that the dark entities are the clay mineral layers which are embedded in the rubber matrix. Incorporation of OMt in NR by mechanical mixing leads to very poor dispersions with larger aggregates as discussed earlier. Fig. 4.12 and Fig. 4.13 show the dispersion of C22-EOMt clay layers. A very few aggregates are observed at low magnification found though the concentration of the clay was 5 phr. Co-existence of totally delaminated and intercalated sheets of the clay minerals observed at larger magnification. That means, there are regions where the regular hierarchy structure is still maintained with a layer of polymer between the sheets, and also some area with completely dispersed exfoliated sheets. Eventually, the overall dispersion can be described as a very good degree of exfoliated morphology of the nanocomposites as evidenced by TEM micrographs. There appears to be some evidence supporting to the formation of an exfoliated morphology at larger scale with NR-C22EOMt nanocomposites. High degree of orientational order of the intercalated sheets in particular direction is observed.

The TEM images obtained from different NR-EOMt nanocomposites are finally compared in Fig. 4.12 and it is found that the number of dark phase indicating the presence of clay sheets, are larger in the case of C22 fatty acid as compared to others. This essentially conveys the higher dispersibility of the C22-EOMt which has been nicely dissociated and distributed in NR matrix since in the all case the concentration of the Mt was more or less same. The thickness and the length of the tactoids were evaluated for each natural rubber nanocomposite and the evaluated values are shown in Table 4.2. The number of sheets present in the each tactoid was also calculated from the following Eq.
where \( t_{(tac)} \) is the tactoid thickness, \( d \) the space gap between two sheets (without intercalation), \( n \) is the number of sheets and \( t \) the thickness of one sheet. For the montmorillonite used in this study, \( t \) was 0.92 nm and \( d \) was 1.32 nm as determined elsewhere (98).

As far as the size distributions of the tactoids are concerned (represented in histograms in Fig. 4.14) for NR-C22-EOMt, the tactoid length thickness ranges from 25-300 nm, the thickness ranges from 3-10 nm, and the average number of sheets present in the tactoids is nearly \( \sim 4-5 \).
The number of the sheets per tactoid is remaining almost same with the decrease of the fatty acid chain length up to C18. However, we were not able to analyze the TEM image of C16-EOMt since most of the EOMt particle was either highly agglomerated or poorly dispersed in the NR matrix. It could be envisaged that the fatty acid with small chain length is not as effective compared to fatty acids with higher chain length in the delamination process of the clay.

NR-C22-EOMt has smaller tactoid size among all the nanocomposites reported in this study. These single layers and thin tactoids disperse uniformly and randomly in the matrix, indicating that our new approach is very effective in promoting both exfoliation and dispersion of clay nanoparticles. Nevertheless, the process reported in the present study is rather simple and straightforward.

Table 4.2. Analyzed data from TEM images

<table>
<thead>
<tr>
<th>Samples</th>
<th>Average particle length (nm)</th>
<th>Average tactoid thickness (nm)</th>
<th>Average no. sheets per tactoid</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR-C22-EOMt</td>
<td>70</td>
<td>5.5</td>
<td>~ 4-5</td>
</tr>
<tr>
<td>NR-C20-EOMt</td>
<td>98</td>
<td>6.2</td>
<td>~ 5-6</td>
</tr>
<tr>
<td>NR-C18-EOMt</td>
<td>120</td>
<td>8.2</td>
<td>~ 6-7</td>
</tr>
</tbody>
</table>
4.2.3 Cure study and kinetics

A detailed cure study has been done to explore and understand the curing activity. The extent of cross linking or degree of curing ($\alpha$) can be calculated from the torque using the rheometer. Here, in the present study we have reported the curing kinetics of different NR compounds using a moving die rheometer, Scarabeus (SIS-V50).

The degree of cure at a time, $t$, is expressed as $\alpha$ and can be defined as follows,

$$\alpha = \frac{M_i - M_o}{M_H - M_o}$$  \hspace{1cm} (2)
where \( M_0, M_t, \) and \( M_H \) are the torque values at the time zero, at a given time of curing, and at the end of the curing process, respectively. The isothermal vulcanization kinetics of the rubber compounds is usually characterized by two general model equations. The first one is known as \( n^{\text{th}} \)-order and the second one is known as an autocatalytic model equations. The \( n^{\text{th}} \)-order kinetics model, which is the simplest model to represent the overall curing process, can be expressed by the Eq. 3,

\[
\frac{d\alpha}{dt} = K(T)(1 - \alpha)^n
\]

where \( n \) is the reaction order and \( K \) denotes the temperature-dependent rate constant.

The \( n^{\text{th}} \)-order kinetic equation expects that the maximum reaction rate occurs at the very initial stage of reaction. On the other hand, the autocatalytic equation reveals that the maximum reaction rate will be at any point of time except \( t = 0 \) (99). Therefore, the autocatalytic model equation (100) is utilized in the present study for curing kinetics of NR compounds which is shown in Eq. 4,

\[
\frac{d\alpha}{dt} = K(T)\alpha^m(1 - \alpha)^n
\]

where \( K(T) \) is the rate constant dependent on temperature, \( m \) and \( n \) are orders of the reaction which also depend on temperature of the reaction. The function \( K(T) \) is described by the Arrhenius expression, given in the Eq. 5,

\[
K = Ae^{-E_a/RT}
\]

or, \( \ln K = \ln A - E_a/RT \)

where \( E_a \) is activation energy.

The effect of 5 phr OMt and EOMt on the rheometric profile obtained at 150 °C is demonstrated in Fig. 4.15a. It can be observed from the Fig. 4.15a that with the addition of 5 phr OMt has altered both minimum and maximum torque significantly. Maximum torque is generally considered as a measure of the modulus which is increased may be attributed to the clay-rubber interactions including intercalation and exfoliation of clay particles. Interestingly, the torque
Results and discussion

Enhancement is even pronounced in the case of nanocomposites with EOMt. This is an indirect intimation for improved intercalation-exfoliation behavior and good interfacial adhesion between NR and EOMt. The scorch time and cure time is reduced in presence of both OMt and EOMt. The effect of EOMt on the cure kinetics can be calculated in terms of Cure Rate Index (CRI). CRI is a parameter which is proportional to the average slope of the cure curve \((100/t_{90}-t_2)\) in the curing step region. Higher the value of CRI faster is the curing process. This phenomenon is attributed to the QUAT present in the interlayer space which is reacting with the other vulcanization ingredients (for instance sulphur, accelerator, ZnO etc.) during vulcanization. Similar observation was also reported in literature (99, 101). An additional explanation for fast curing might be due to the facilitation of cure reaction by intercalated silicate galleries as confirmed from the WAXD pattern.

![Graphs showing curing behavior](image)

**Fig. 4.15.** Rheometric curing curves of a) different NR compounds at 150 °C and b) the curing curves of NR-C22-EOMt at different temperature

The vulcanization behavior of the unfilled and clay filled NR compound was studied at three different temperatures 140, 150, 160 °C utilizing ODR. The influence of temperature on the curing behavior of NR-C22-EOMt is demonstrated in Fig. 4.15b. It is obvious that with the increase of temperature the value of \(t_2\) and \(t_{90}\) decrease, while the cure rate increases which is attributed to the availability of more thermal energy for the cure reaction.

Figure 4.16a exhibits the plot of rate of conversion \((d\alpha/dt)\) versus the degree of conversion \((\alpha)\) for NR-C22-EOMt at three different temperatures. The cure rate versus
Results and discussion

Conversion curves at three different temperatures indicate an increase in cure rate with rising temperature. It can be observed that the shape of the conversion curve is dependent on temperature.

Table 4.3. Different kinetic parameters and activation energy of the NR nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_c$ (°C)</th>
<th>$K$</th>
<th>$m$</th>
<th>$n$</th>
<th>$E_{a,v}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR gum</td>
<td>140</td>
<td>0.22</td>
<td>0.23</td>
<td>3.29</td>
<td></td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.48</td>
<td>0.29</td>
<td>2.76</td>
<td>110.3</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>0.90</td>
<td>0.42</td>
<td>1.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>0.38</td>
<td>0.32</td>
<td>4.26</td>
<td></td>
</tr>
<tr>
<td>NR-OMt</td>
<td>150</td>
<td>0.89</td>
<td>0.35</td>
<td>3.39</td>
<td>90.9</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>1.20</td>
<td>0.44</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>0.75</td>
<td>0.32</td>
<td>4.12</td>
<td></td>
</tr>
<tr>
<td>NR-C16-EOMt</td>
<td>150</td>
<td>1.01</td>
<td>0.43</td>
<td>3.76</td>
<td>82.6</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>2.02</td>
<td>0.56</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>0.85</td>
<td>0.34</td>
<td>4.16</td>
<td></td>
</tr>
<tr>
<td>NR-C18-EOMt</td>
<td>150</td>
<td>1.1</td>
<td>0.41</td>
<td>2.49</td>
<td>76.9</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>2.10</td>
<td>0.66</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>0.9</td>
<td>0.41</td>
<td>4.21</td>
<td></td>
</tr>
<tr>
<td>NR-C20-EOMt</td>
<td>150</td>
<td>1.16</td>
<td>0.59</td>
<td>2.45</td>
<td>72.5</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>2.14</td>
<td>0.67</td>
<td>1.29</td>
<td></td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>1.05</td>
<td>0.38</td>
<td>4.42</td>
<td></td>
</tr>
<tr>
<td>NR-C22-EOMt</td>
<td>150</td>
<td>1.21</td>
<td>0.49</td>
<td>3.34</td>
<td>69.9</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>2.29</td>
<td>0.77</td>
<td>1.48</td>
<td></td>
</tr>
</tbody>
</table>
As the temperature is increased, the peak height of the conversion rate curve is also increased with a shift in peak position toward higher $\alpha$ values. The maximum conversion is obtained at $\alpha = 0.4$ at all the measured temperatures. The aforementioned observation certainly indicates the dependence of temperature on the rate of conversion during the process of vulcanization. The above fact might be attributed to the effect of higher viscosity at lower temperature which prevents the formation of crosslink between the adjacent polymer chains.

Different kinetic parameters of the vulcanization reaction of NR, NR-OMt, NR-C16-EOMt, NR-C18-EOMt, NR-C20-EOMt and NR-C22-EOMt nanocomposites were determined and furnished in Table 4.3. The values of $K$, $m$, and $n$ at the different temperatures are calculated through linear multiple regression analysis from the experimental data (see Fig. 4.16b). To get more insight into the kinetics of vulcanization reactions of NR in the presence of EOMt, an Arrhenius type plot of $\ln K$ versus $1/T$ is drawn for the calculation of the activation energy of vulcanization ($E_{a,v}$), which can be considered as the ease of crosslinking process. The slope ($E_{a,v}/R$) of the straight line arising from the plot of $\ln K$ versus $1/T$ depicted in Fig. 4.17, gives the resulting values of activation energy where $E_{a,v}$ is the activation energy generated during the vulcanization process and $R$ is the universal gas constant. The activation energy ($E_{a,v}$) of NR gum compound is decreased with the incorporation of OMt from 110.3 to a value of 90.9 kJ/mol attributed to the synergistic effect of QUAT and the accelerator used in the recipe. This effect is even more pronounced in the case of EOMt filled nanocomposites. It can be seen from the above
Results and discussion

Table that the NR-C22-EOMt shows the lowest value of activation energy amongst all other composites which confirms the catalytic effect of the EOMt on the curing process of NR. Consequently, EOMt improves the processing conditions and vulcanization process compared to OMt. The abovementioned fact can be attributed to the QUAT compound which is coming out from the silicate layer of the OMt during intercalation of long alkyl chain fatty acids. Similar effect is observed in cure behavior by increasing the torque value and reducing the cure time indicating advantage of EOMt for the preparation of NR-clay nanocomposite.

![Arrhenius plot of ln K versus 1/T for the calculation of E_{a,v}](image)

4.2.4 Dynamic mechanical analysis (DMA)

The dynamic mechanical properties of unfilled NR and its composites with OMt and EOMt were studied over a wide temperature range from −80 to +80 °C and are depicted in Fig. 4.18 (a-d). The storage modulus of gum NR and its composites with 5 phr Mt loading as a function of temperature displays in the Fig. 4.18a. It can be observed that the OMt gives rise to a perceptible enhancement in modulus, but a remarkable improvement in storage modulus in the case of nanocomposites with EOMt is observed compared to gum vulcanize. NR-C22-EOMt is depicted higher value among the other EOMt nanocomposites. Such enhancement is attributed to the strong rubber-filler interaction arising from well exfoliation of EOMt clay minerals.
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throughout the rubber matrix. The large variation of shape and size of tan δ peaks for different nanocomposites clearly suggests different interaction between rubber and silicate particles. It can be observed from the Fig. 4.18c that the tan δ peak height of the neat rubber is reduced with the addition of 5 phr OMt. This effect is even pronounced when the same amount of EOMt is incorporated, particularly for the compound NR-C22-EOMt. The above fact can be explained in terms of strong rubber-filler interactions attributed to the exposed huge surface area of the fillers due to highly delaminated structures of the EOMt (102). In addition, the $T_g$ of NR gum slightly shifts towards higher temperatures in presence of EMMTs but OMt has no effect on it. The $T_g$ of NR gum shifted from -47 °C to -44 °C in the case of NR-C22-EOMt. The above fact suggests that there exist a strong rubber-clay interaction arising from well dispersion of EOMt throughout the matrix.

Fig. 4. 18. a) Storage modulus as a function of temperature b) Loss modulus as a function of Temperature c) tan δ as a function of temperature, and d) tan δ as a function of temperature (highlighted from Fig. 4.18c)
The relationship of the loss tangent value between the filled polymer and the unfilled polymer matrix can be calculated using the following Eq. (103, 104):

\[
\tan \delta = \frac{\tan \delta_m}{1 + 1.5B\varphi}
\]

(7)

where \( B \) is known as a phenomenological interaction parameter which determines the interfacial interaction between the polymer matrix and filler surface. Larger the value of \( B \) more will be the interaction between polymer and filler surface, \( \varphi \) is the volume fraction of filler; \( \tan \delta \) and \( \tan \delta_m \) symbolize the loss tangent value of the filled and unfilled polymer matrix respectively.

It can be observed from the Fig. 4.18c that the peak value of \( \tan \delta \) of the NR-OMt is almost the comparable to that of the unfilled NR gum compound. Therefore, the interaction parameter \( (B= 2.72) \) is very low, which implies a very weak physical interfacial interaction between the NR and OMt. It is interesting to note that in the presence of EOMt the \( \tan \delta \) peak height is decreased very significantly and, therefore, higher values of \( B \) can be found (Table 4.4). The lowest value of \( \tan \delta \) peak height is observed in the case of NR-C22-EOMt which gives the highest value of the interaction parameter suggesting a strong interfacial interaction between rubber and EOMt. This behavior is arising due to the well dispersion of the clay particle throughout the matrix which is already observed from TEM image.

![Fig. 4. 19. Dependence of storage modulus (E’) on the dynamic strain (γ)](image-url)
The strain sweep analysis of the NR vulcanizates filled with OMT and EOMt were also performed to investigate the formation of a “filler-filler” network. The values of $E'$ remains unaltered with strain for an unfilled rubber system and depends significantly for a filled system. In the present case it is observed from Fig. 4.19 that the gum NR as well as OMT filled NR did not response in showing strain dependencies. However, the NR filled with all EOMt showed the strain dependence of $E'$ to some extent though the concentration of the clay was same for all compounds. This simply implies that the clay mineral in the expanded form is finely dissociated into a large number of submicron particles which might have interacted at the edges by the virtue of hydrogen bonding (105). Considering different nanocomposites with EOMt, it was observed that NR-C22-EOMt occupied the highest value of $E'$ among the other EOMt. This strongly suggests that the clay expanded with more number of carbon chain fatty acid, dissociated to more number of tactoids due to larger opening of interlayer space between the inorganic sheets (106, 107).

### Table 4.4. Different dynamic mechanical parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volume fraction ($\phi$)</th>
<th>$\tan \delta$ peak height</th>
<th>$B$ (interaction parameter)</th>
<th>$E'$ @ 25°C (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR gum</td>
<td>-</td>
<td>2.65</td>
<td>-</td>
<td>1.55</td>
</tr>
<tr>
<td>NR-OMt</td>
<td>0.02</td>
<td>2.45</td>
<td>2.72</td>
<td>2.00</td>
</tr>
<tr>
<td>NR-C16-EOMt</td>
<td>0.02</td>
<td>1.97</td>
<td>11.33</td>
<td>3.25</td>
</tr>
<tr>
<td>NR-C18-EOMt</td>
<td>0.02</td>
<td>1.95</td>
<td>11.96</td>
<td>3.30</td>
</tr>
<tr>
<td>NR-C20-EOMt</td>
<td>0.02</td>
<td>1.90</td>
<td>13.15</td>
<td>3.53</td>
</tr>
<tr>
<td>NR-C22-EOMt</td>
<td>0.02</td>
<td>1.74</td>
<td>17.43</td>
<td>4.62</td>
</tr>
</tbody>
</table>

#### 4.2.5 Mechanical properties

The morphology of nanocomposites has a direct consequence on the mechanical properties. The stress–strain curves of the different nanocomposites in uniaxial extension are
shown in Fig. 4.20 and the results obtained from this curves are represented in Table 4.5. It can be observed from Fig. 4.20a that the tensile strength and modulus at 200% elongation of NR-EOMt nanocomposites are much higher compared to unfilled NR gum compound. With the inclusion of only 5 phr of C18-EOMt, these values increase by 107% and 76% respectively. This indicates that the EOMt behaves as reinforcing fillers for NR. In comparison, at the equivalent amount of (5 phr) clay loading, NR/EOMt nanocomposites exhibit higher tensile strength compared to NR-OMt composite. The above mentioned fact suggest that the EOMt is more compatible with NR matrix than OMt leading to better dispersion of EOMt throughout the matrix and, therefore, to a better interaction between matrix and filler.

The stress-strain relationship was analyzed from the stress-strain behavior illustrated by a phenomenological expression suggested by Mooney (108) and Rivlin and Saunders (109):

$$\frac{\sigma}{\lambda - \lambda^{-2}} = 2(C_1 + C_2 \lambda^{-1})$$

where $\sigma$ is the applied stress, $\lambda$ is the extension ratio, and $C_1$, $C_2$ are the Mooney-Rivlin (MR) constants. However, it does not explain the steep increase at large elongation.

![Fig. 4.20. (a) Stress-strain behavior (b) Mooney-Rivlin plot of different NR nanocomposites](image)

It is believed in many publications that the upturn or steep increase in the stress-strain plot of rubbers is frequently attributed to the limiting polymer chain extensibility and also to the strain-induced crystallization (110, 111). Hence, both crystallizable and non-crystallizable rubbers can exhibits a steep increase of elastic force due to the limitation of polymer chain
extensibility if the rupture is avoided. Furukawa et al. (110) proposed a modified Mooney-Rivlin equation, based on the assumption of uniform stress rather than uniform strain. The effect of limited chain extensibility was also considered in the modified equation in deriving the stress strain relationship. According to the Eq.

\[ \sigma = 2(C_1 + C_2/\lambda)F(\lambda) \]  

(9)

where, \(\sigma\) is the applied stress, \(C_1\) and \(C_2\) are the Mooney-Rivlin constants which are independent of the extension ratio \(\lambda\), and the function of \(F(\lambda)\) can be denoted as

\[ F(\lambda) = \lambda - \frac{1}{\lambda^2} + \frac{\lambda^2}{3\lambda_m^2} + \cdots \]  

(10)

\(\lambda_m\) being the maximum extension ratio, i.e, \(\lambda\) at break point

Table 4. 5. Static mechanical properties of various NR-clay nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>TS (MPa)</th>
<th>SD (%)</th>
<th>EB (MPa)</th>
<th>M200 (MPa)</th>
<th>Crosslinking (mol/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR gum</td>
<td>14</td>
<td>2.8</td>
<td>1295</td>
<td>56</td>
<td>1.04</td>
</tr>
<tr>
<td>NR-OMt</td>
<td>20</td>
<td>1.74</td>
<td>1010</td>
<td>35</td>
<td>1.78</td>
</tr>
<tr>
<td>NR-C16-EOMt</td>
<td>28</td>
<td>0.70</td>
<td>1334</td>
<td>18</td>
<td>1.65</td>
</tr>
<tr>
<td>NR-C18-EOMt</td>
<td>28</td>
<td>1.66</td>
<td>1305</td>
<td>47</td>
<td>1.74</td>
</tr>
<tr>
<td>NR-C20-EOMt</td>
<td>30</td>
<td>0.97</td>
<td>1271</td>
<td>22</td>
<td>1.85</td>
</tr>
<tr>
<td>NR-C22-EOMt</td>
<td>30</td>
<td>1.17</td>
<td>1324</td>
<td>19</td>
<td>1.84</td>
</tr>
</tbody>
</table>

*TS = tensile strength; M200 = modulus at 200% elongation; EB = elongation at break; SD = standard deviation

It is worth to be noted that at \(\lambda<<\lambda_m\), the function \(F(\lambda)\) approaches to \(\lambda^{-1}/\lambda^2\), and the Eq. 10 becomes original MR equation. According to the modified MR equation, a plot of \(\sigma/F(\lambda)\), generally known as reduced stress, as a function of inverse extension ratio, \(\lambda^{-1}\), should yield a
linear curve, from which the values of $C_1$ (intercept) and $C_2$ (slope) can be obtained from the stress-strain curves. According to Furukawa et al. (62) Eq. 9 can also be represented as for larger deformations,

$$\sigma_m = \frac{\sigma}{\lambda - \frac{1}{\lambda^2}} \approx 2(C_1 + \frac{C_2}{\lambda})(1 + \frac{1}{3}\frac{\lambda^2}{\lambda_m^2})$$  \hspace{1cm} (11)

which possess a maximum at a condition of

$$\frac{d\sigma_m}{d\lambda} = 0$$  \hspace{1cm} (12)

or,

$$\frac{4}{3}\frac{C_1}{\lambda_m^2}\lambda^3 = 2C_2 - \frac{2C_2}{3}\left(\frac{\lambda}{\lambda_m}\right)^2$$  \hspace{1cm} (13)

As $\lambda \ll \lambda_m$, the second term in the right side is neglected and the upturn $1/\lambda_{up}$ is given by the below Eq.

$$\lambda_{up}^3 = \frac{3}{2} \cdot \frac{C_2}{C_1} \lambda_m^2$$  \hspace{1cm} (14)

<table>
<thead>
<tr>
<th>Samples</th>
<th>C1</th>
<th>C2</th>
<th>$1/\lambda_{up}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR gum</td>
<td>0.20</td>
<td>0.310</td>
<td>0.189</td>
</tr>
<tr>
<td>NR-OMt</td>
<td>0.51</td>
<td>0.236</td>
<td>0.216</td>
</tr>
<tr>
<td>NR-C16-EOMt</td>
<td>0.45</td>
<td>0.23</td>
<td>0.218</td>
</tr>
<tr>
<td>NR-C18-EOMt</td>
<td>0.50</td>
<td>0.232</td>
<td>0.226</td>
</tr>
<tr>
<td>NR-C20-EOMt</td>
<td>0.52</td>
<td>0.235</td>
<td>0.223</td>
</tr>
<tr>
<td>NR-C22-EOMt</td>
<td>0.49</td>
<td>0.234</td>
<td>0.224</td>
</tr>
</tbody>
</table>
The values of $C_1$, $C_2$ and the quantitative value of upturn of the NR-clay nanocomposites are summarized in Table 4.6. A large and abrupt upturn can be observed from Fig. 4.20b at low $\lambda^{-1}$ for NR gum compound, mostly attributed to strain-induced crystallization, which is an important factor in the enhancement of the tensile properties of NR. It is interesting to note that this upturn is more prominent when only 5 phr O Mt is incorporated into the NR matrix. Such a phenomenon is very familiar in case of NR-clay nanocomposites and is reported in literature (112). But interestingly, this upturn is even more pronounced in presence of equivalent amount of EOMt which further furnish huge improvement in tensile strength.
4.3 NR-EOMt nanocomposites: Understanding the fundamental reinforcing mechanism

Since the fatty acid containing 22 carbon atoms has the largest interlayer distance among the modified samples studied, it has been selected for further study to understand the reinforcing behavior in NR matrix. In general nano-sized particles offer the same level of reinforcement as carbon black and silica but at relatively lower loading (113-115). The mechanical properties of conventional rubber composites depend mostly on the degree of the dispersion of fillers (116), the structure of the fillers (117), rubber-filler and filler-filler interactions (118-119). Using the ‘cluster-cluster aggregation’ model (CCA), Klüppel et al. (120) showed that the storage modulus of the filler network is directly related with $\phi^{3.5}$ ($\phi$ stands for filler volume fraction) where the exponent “3.5” reflects the characteristic structure of the fractal heterogeneity of the filler. Therefore, the reinforcement effect is mostly attributed to the development of a percolating network of the filler particles. However, many studies have shown that the addition of fillers within a polymer matrix can lead to the formation of a modified polymer layer at the vicinity of the filler surface, the so-called interphase or bound rubber (121-122). The presence of such an additional phase could affect the overall mechanical properties of the rubber composites. Immobilization of EPDM chains on the surface of carbon black and network structure in the rubber matrix of filled EPDM rubbers were studied and reported by Litvinov et al. using low-field proton NMR experiments (121). The thickness of the immobilized EPDM-carbon black interfacial layer was estimated to be $\gtrsim 0.6$ nm (121). Merabia et al. developed a microscopic model and pointed out that strong reinforcement is obtained when glassy layers between fillers overlap (122-123). Sternstein et al. (124) have established experimentally that the principal underlying mechanism for reinforcement and nonlinear viscoelastic behavior is attributed to filler-matrix interactions, for example trapped entanglements, rather than filler agglomeration. In this sub chapter C22 fatty acid intercalated clay is denoted as EOMt. A detail of clay preparation and characterization is given in the first sub chapter.

4.3.1 Rheometric study

The different rheographs of unfilled and filled NR compound at 150°C are represented in Fig. 4.21. The various curing parameters are also summarised in Table 4.7. It could be observed from Table 4.7 that cure time ($t_{90}$), scorch time ($t_2$) decreased gradually with the addition of EOMt. This behaviour indicates an accelerated curing process in the presence of EOMt compared
to unfilled gum compound. It has been reported (125) that amine used for the modification of clay minerals and sulphur containing compounds were participated in the formation of Zn-complex, which accelerated the rubber curing process. For all NR nanocomposites, the lower minimum torque (M_L) values signify lower viscosity and, therefore, an improvement of material processability.

![Rheographs of different NR compounds at 150 °C](image)

**Fig. 4.21.** Rheographs of different NR compounds at 150 °C

**Table 4.7. Cure characteristics of the EOMt filled NR at 150 °C**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Maximum Torque (M_H) (dNm)</th>
<th>Delta torque (dNm)</th>
<th>Cure time (t_90) (min)</th>
<th>Cure rate index (CRI) (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gum</td>
<td>6.19</td>
<td>5.86</td>
<td>17.8</td>
<td>7.2</td>
</tr>
<tr>
<td>EOMt-2</td>
<td>6.43</td>
<td>6.07</td>
<td>9.2</td>
<td>13.3</td>
</tr>
<tr>
<td>EOMt-4</td>
<td>6.48</td>
<td>5.84</td>
<td>8.7</td>
<td>15.0</td>
</tr>
<tr>
<td>EOMt-6</td>
<td>6.29</td>
<td>5.72</td>
<td>8.6</td>
<td>17.4</td>
</tr>
<tr>
<td>EOMt-10</td>
<td>6.07</td>
<td>5.53</td>
<td>7.8</td>
<td>18.1</td>
</tr>
</tbody>
</table>
Interestingly the above mentioned behaviour is independent of clay mineral content. On the other side, the maximum torque ($M_H$) decreased with increasing amount of EOMt loading. Generally, the $M_H$ obtained during rheometric study depends on the degree of cross-linking. It is mentioned in many literatures (126,127,128) that clay minerals adsorbed curatives onto their surface and inhibited the curing process. Hence, the decline in torque values could be associated to the intercalation of rubber chains into the interlayer space, which further prevented the formation of cross-links. This lowering of $M_H$ is an indication of improved filler dispersion in the NR matrix. There was an insignificant effect of an additional amount of C22FA on the curing behaviour of NR compound.

4.3.2 Modulated differential scanning calorimetry (MDSC)

Figure 4.22 shows DSC thermograms of NR and nanocomposites with various amounts of filler loading. It is observed that the $T_g$ of pure NR gum compound is ~ -62°C. In the present study results are analyzed in terms of $T_g$ and a change in heat capacity ($\Delta C_p$) at $T_g$. In principle, $\Delta C_p$ is related to the fraction of polymer participating at the glass transition and is proportional to the number of internal degrees of freedom of molecular motion. It is shown from Table 4.8 that $T_g$ does not change with composition. However, $\Delta C_p$ at $T_g$, normalized to the fraction of amorphous polymer, systematically decreases with increasing filler content. As more and more EOMt is added into the nanocomposite system, a higher fraction of polymer chains are confined between the clay layers. This would further decrease the degree of freedom of the polymer chain segments, thus causing $\Delta C_p$ values to decrease with increasing EOMt content. Similar results have been obtained also with other polymer nanocomposites (129). Therefore, the values of $\Delta C_p$ depend on the amount of EOMt in the polymer matrix and can be thus be conveniently utilized to indicate the approximate inherent interfacial interaction between polymer and filler surface. The fraction of immobilized polymer can be calculated by Eq. 15 given below (129),

$$x_{im} = 1 - \frac{\Delta C_p}{\Delta C_p(1 - w)}$$

(15)

where $\Delta C_p$ is the heat capacity increment of the neat rubber and $w$ is the weight fraction of EOMt.
The values of $X_{im}$ thus obtained are depicted in Table 4.8. For the NR-EOMt nanocomposites, they range from 10 to 14% and they are increasing with increasing EOMt content. Therefore, the increased amount of adsorbed rubber chains on the filler surface is attributed to stronger rubber-filler interactions.

![Fig. 4.22. DSC thermograms of different NR/EOMt nanocomposites](image-url)
4.3.3 Morphological analysis of nanocomposites: WAXD and TEM

WAXD patterns of pure OMt, EOMt and nanocomposites with various EOMt contents are shown in Fig. 4.23. The mean interlayer spacing of the \(d(001)\) plane for the OMt obtained by WAXD measurements is \(\sim 2.98\) nm \((2\theta = 2.78^\circ)\). The interlayer distance of OMt is further expanded to 4.42 nm after successful intercalation with long alkyl chain C22 fatty acid. In the scattering pattern three sharp peaks appear at \(2\theta = 2.1^\circ, 5.4^\circ\) and \(9.4^\circ\) respectively. Those are in addition to three broad peaks of Mt. Those sharp peaks indicate the presence of crystalline C22 fatty acid. For sake of simplicity we consider only the small peak at \(2\theta = 2.0^\circ\) \((\sim 5.3\) nm) which corresponds to the \((001)\) plane of the intercalated silicate layers in the NR matrix. With increasing EOMt content, this peak becomes stronger and gradually shifts toward the smaller diffraction angle \(2\theta = 1.78^\circ\) at \((\sim 5.6\) nm). We hypothesize that after the addition of large amount of EOMt the intercalation of the rubber chains becomes more facile due to the plasticization effect of the fatty acid.

![Graph showing XRD patterns of different NR/EOMt nanocomposites](image)

**Fig. 4.23.** XRD patterns of different NR/EOMt nanocomposites

TEM investigation was carried out to examine directly the intercalation of rubber chains and the state of dispersion of the EOMt into the NR matrix. Fig. 4.24 below shows the TEM micrographs of NR nanocomposites with both OMt and EOMt. The dark lines and areas are EOMt layers and aggregates, and the light area shows the rubber matrix. The thickness of most EOMt particles is 7-8 nm and the length about 80-200 nm and these numbers are invariant to the
EOMt loading. However, large agglomerates of clay particles are observed in the case of OMt filled NR composites (Fig 1.1). Therefore, a dramatic improvement in the dispersion of clay nanoparticles is observed when EOMt is used. At lower magnification, the EOMt appears to be well dispersed in the rubber matrix. Upon increasing the magnification of these images, one can observe the presence of individual silicate layers throughout the rubber matrix and some stacks of EOMt particles are visible indicating a partially to highly exfoliated morphology of EOMt.

Fig. 4. Different TEM images of NR nanocomposites with 10 phr of EOMt loading with various scale length
Due to the greater interlayer spacing, the macromolecular rubber chains can penetrate between the silicate layers of the EOMt and subsequently separate them into tactoids. This happens during the process of melt mixing. Consequently, individual silicate layers can be torn apart from the stack due to high mechanical shear force. TEM images are in good agreement with results obtained from WAXD.

4.3.4 Mechanical properties and modeling of tensile modulus

The stress-strain diagrams for pure NR and NR/EOMt nanocomposites containing various amounts of EOMt are shown in Fig. 4.25. For all the nanocomposites and at low strain the modulus is low and gradually increases with strain. However, when the strain exceeds 500 % the tensile stress increases sharply. This effect is attributed to the well-known phenomenon of strain-induced crystallization in the NR. The nanocomposites show an improvement in tensile strength in the presence of EOMt. Table 4.9 shows that the tensile strength is increased by 114 % (from 12 MPa for unfilled natural rubber to 30 MPa for the nanocomposite) with only 4 phr of EOMt. Qualitatively this enhancement of tensile strength is comparable to that generally achieved by high loading with conventional fillers (for instance carbon black or silica), clearly demonstrating the advantage of the high surface area and anisotropic character of Mt particles. The tensile strength increases with EOMt content as presented in Table 4.9, however this increment is highest at 4 phr. Apparently, at this concentration, the filler is dispersed well and is distributed more homogeneously compared to nanocomposites with higher filler loading. It should be mentioned here that with the increase of EOMt, the amount of fatty acid also increases. The fatty acid, adsorbed on the surface of the clay layers, can also contribute to strain-induced crystallization effect thus resulting into higher tensile strength. Therefore, comparison of modulus at certain percentage of elongation would be more realistic to understand the reinforcement capability of the EOMt. Modulus at 200% elongation (M200) is increased continuously with increasing filler loading. M200 for the 2, 4, 6 and 10 phr filler loadings are respectively 1.44, 1.74, 1.90, and 2.02 MPa while that of the unfilled gum compound is 1.04 MPa. It is also interesting to note that the elongation at break (EB) of nanocomposites is increased with increasing EOMt loading and approaches the highest value at about 4 phr. The improvement in EB may be attributed partially to the plasticizing effect of the fatty acid that is located at the Mt-
rubber interface. The hardness of the NR-EOMt composites also increases significantly with increasing EOMt loading. We attribute this effect to the enhanced rubber-filler interactions.

A large and abrupt upturn can be observed from the Mooney-Rivlin plot given in the Fig. 4.25b particularly at low $\lambda^{-1}$ for NR gum compound, mostly attributed to strain-induced crystallization. It is also interesting to note that the addition of only 2 phr EOMt in the NR matrix causes a remarkable enhancement not only in the extent of upturn but also in the $C_1$ value. This means that EOMt particles facilitate the strain induced alignment of NR chains at low strain. It has been pointed out that the presence of nanoparticle not only accelerates the strain-induced crystallization, but also increases the extent of strain-induced crystallinity compared to the unfilled compound or the compounds containing conventional fillers, like carbon black and silica (130-131). The superior dispersion of EOMt particles in the NR matrix improves the polymer filler interaction to a large extent. Therefore, this strong interfacial interaction facilitates the orientation of rubber chains and initiates crystallization even at low strain.

**Fig. 4.25.** (a) Stress-Strain plot (b) Mooney-Rivlin plot of different rubber nanocomposites

To further understand the reinforcement mechanism of these EOMt filled NR matrix, tensile properties of various systems were analyzed in detail utilizing particulate composite reinforcement models (132). Many empirical or semi empirical equations have been proposed to predict the so-called “hydrodynamic amplification” of the equilibrium modulus of particulate-polymer composites. If the filler particles are sufficiently rigid, i.e. their elastic modulus is much
larger than that of the rubber \((E_{\text{filler}}/E_m >> 1)\), then the large majority of the elastic energy will be stored in the rubber and one obtains

\[
\frac{E_c}{E_m} = 1 + 2.5\varphi + \beta\varphi^2
\]

(16)

\(E_c\) and \(E_m\) are Young’s moduli of the nanocomposite and pure matrix, respectively, and \(\varphi\) is the volume fraction of filler particles dispersed in the rubber matrix. The values of \(E_m\) and \(E_c\) are obtained from stress-strain graphs. The parameter \(\beta\) (although different symbol for this model-factor can be found in the literature) in the second order term varies according to the different approaches. Guth and Gold (133) reported \(\beta = 14.1\) whereas Batchelor and Green (134) derived \(\beta = 5.2\) for the shear modulus of a filled elastic solid with a predicted error in the \(\varphi^2\) term of \(\pm0.3\varphi^2\). A similar value of \(\beta = 5.0\) was found by Chen and Acrivos (135).

<table>
<thead>
<tr>
<th>Sample</th>
<th>TS (MPa)</th>
<th>EB (%)</th>
<th>M200 (MPa)</th>
<th>Hardness (Shore A)</th>
<th>C₁</th>
<th>C₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gum</td>
<td>14±2.8</td>
<td>1295±56</td>
<td>1.04±0.01</td>
<td>39</td>
<td>0.28</td>
<td>0.26</td>
</tr>
<tr>
<td>EOMt-2</td>
<td>26±1.4</td>
<td>1396±27</td>
<td>1.44±0.03</td>
<td>46</td>
<td>0.35</td>
<td>0.39</td>
</tr>
<tr>
<td>EOMt-4</td>
<td>29±1.8</td>
<td>1370±30</td>
<td>1.74±0.03</td>
<td>51</td>
<td>0.40</td>
<td>0.61</td>
</tr>
<tr>
<td>EOMt-6</td>
<td>27±0.77</td>
<td>1345±16</td>
<td>1.90±0.05</td>
<td>54</td>
<td>0.40</td>
<td>0.70</td>
</tr>
<tr>
<td>EOMt-10</td>
<td>25±0.73</td>
<td>1330±7</td>
<td>2.02±0.03</td>
<td>58</td>
<td>0.41</td>
<td>0.86</td>
</tr>
<tr>
<td>OMt-10</td>
<td>22±0.67</td>
<td>1289±24</td>
<td>1.51±0.02</td>
<td>52</td>
<td>0.35</td>
<td>0.67</td>
</tr>
</tbody>
</table>

However, it was also found that for higher volume fraction of filler (e.g. 10 vol%), the reinforcing factor increases more rapidly compared to the values calculated by Eq. 7 (136). The reason could be attributed to the formation of a network structure by the spherical filler. To circumvent that issue, Guth developed the following equation. What he did is introduced a
Results and discussion

parameter $f$ which is known as shape factor (can be defined as the ratio of length to thickness) in order to explain stiffening caused by chain-like structure or non-spherical particles:

$$\frac{E_c}{E_m} = 1 + 0.67 f \varphi + 1.62 f^2 \varphi^2$$  \hspace{1cm} (17)

The Halpin-Tsai Eq. (137) also has served as a popular model since it can be accurately employed to quantify the reinforcement of filler in nanocomposites. The elastic modulus of the nanocomposites filled with fully aligned fibrous reinforcing particulates is given by Halpin-Tsai (142) as follows:

$$E_\delta = \frac{E_c}{E_m} = \frac{1 + 2 f \eta \varphi}{1 - \eta \varphi}$$  \hspace{1cm} (18)

where $f$ is the aspect ratio, $\eta = \frac{E_{\text{filler}}/E_m - 1}{E_{\text{filler}}/E_m - 2f}$ and $E_{\text{filler}}$ the Young’s modulus of the filler.

In the dilute, stiff fiber limit ($\varphi<<1$ and $E_{\text{filler}}/E_m >>1$) the above equation can be expressed as

$$E_\delta = 1 + 2 f \left( \frac{E_{\text{filler}}}{E_m} \right) \varphi$$  \hspace{1cm} (19)

According to Schaefer and Justice (138) the above Eq. 19 becomes independent of fiber elastic properties especially in the case of short fiber limit ($2f<< E_{\text{filler}}/E_m$). Therefore, Eq. 19 reduces to

$$E_\delta = 1 + 2 f \varphi$$  \hspace{1cm} (20)

If the fibers are not aligned, a parameter known as angular factor should be included in the above Eq. 20, giving

$$E_\delta = 1 + 2 f C_\alpha \varphi$$  \hspace{1cm} (21)
For clay particles the value of $C_a$ is nearly 0.5. Therefore, Eq. 21 is reduced to

$$E_b = 1 + f \phi$$  \hspace{1cm} (22)

In this study we rely on the above mentioned models to fit the mechanical properties of the NR-EOMt nanocomposites. The aspect ratio ($f$), which is a fitting parameter, was obtained according to best fit and was determined to be 32 and 47 respectively. In general the average aspect ratio of the individual Mt nanoparticle is in the range of 100 to 150 (139). Although this finding is in accord with previous investigations, where it was reported that the mean value aspect ratio of the organo Mt dispersed in the polymer matrix is less than 50 (139, 140). The aim of this section is to select a few of the most widely used models from the literature (139, 140) and compare their usefulness in predicting the modulus of NR reinforced with expanded clay minerals. The reinforcement factor ($E_c/E_m$) is plotted in the Fig. 4.26 as a function of volume fraction ($\phi$) of EOMt. It is interesting to note that the reinforcement factor is increased with the increase of the filler volume fraction. The Guth-Smallwood model deviates from the experimental results but the Halpin-Tsai model fits well within the volume fraction range.
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investigated. Although it is not discussed in detail here, one might assume that larger deviations of Guth-Smallwood from experimental data could be traced back to a violation of the above mentioned assumptions behind Eq. 16 and 17, i.e. a certain amount of energy could be stored in bendable clay particles. This is different from carbon black or silica particles and might be especially important in the case of EOMt particles.

4.3.5 Dynamic mechanical analysis (DMA) and percolation threshold

4.3.5.1 Temperature sweep

The dynamic-mechanical spectra giving storage modulus \((E')\) and tan \(\delta\) for the NR gum and for NR nanocomposites containing various amounts of EOMt are shown in Fig. 4.27. Different DMA properties are summarized in Table 4.10.

![Fig. 4.27.](image)

Fig. 4.27. (a) Storage modulus \((E')\) as function of \(T\) (b) Loss modulus \((E'')\) as function of \(T\) (c) tan \(\delta\) as function of \(T\) of different NR-clay nanocomposites
The storage modulus ($E'$) at a given temperature above $T_g$ increases monotonically with increasing amount of EOMt. This fact may be attributed to the mechanical reinforcement by EOMt particles with highly exfoliated and intercalated morphology. Above the glass transition temperature ($T_g$), when rubber becomes soft, the reinforcement effect of the EOMt particles becomes significant, due to the restricted movement of the rubber chains, and consequently the strong enhancement of elastic modulus becomes visible.

The area under the tan $\delta$ vs. temperature ($T$) curve is a measure of the energy dissipated during deformation, which provides information about the viscoelastic properties of the nanocomposites. There is a significant decrease in the area under the tan $\delta$ vs. $T$ curve for all nanocomposites when compared to pure NR gum compound. A broadening of the tan $\delta$ curves for the nanocomposite is also observed in Fig. 4.27c. This behavior may be explained by considering the restricted segmental motions of the chains due to strong rubber-filler interaction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volume fraction</th>
<th>tan $\delta$ peak height</th>
<th>$E_R$ (MPa)</th>
<th>$E_G$ (MPa)</th>
<th>Area under tan $\delta$ curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gum</td>
<td>-</td>
<td>2.66</td>
<td>1.51</td>
<td>3340</td>
<td>52</td>
</tr>
<tr>
<td>EOMt-2</td>
<td>0.01</td>
<td>2.25</td>
<td>2.43</td>
<td>4210</td>
<td>50</td>
</tr>
<tr>
<td>EOMt-4</td>
<td>0.02</td>
<td>2.11</td>
<td>3.18</td>
<td>4520</td>
<td>48</td>
</tr>
<tr>
<td>EOMt-6</td>
<td>0.03</td>
<td>1.79</td>
<td>4.42</td>
<td>4620</td>
<td>47</td>
</tr>
<tr>
<td>EOMt-10</td>
<td>0.05</td>
<td>1.55</td>
<td>6.30</td>
<td>5000</td>
<td>45</td>
</tr>
<tr>
<td>OMT-10</td>
<td>0.05</td>
<td>2.09</td>
<td>3.16</td>
<td>4340</td>
<td>50</td>
</tr>
</tbody>
</table>

4.3.5.2 Strain sweep: non-linear viscoelastic behavior

Strain sweep measurements were performed in order to further investigate the polymer-filler and filler-filler interactions. Results demonstrate the qualitative features usually attributed
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to the Payne effect. The effect of the dynamic strain amplitude on the $E'$ and $E''$ at different EOMt loading is documented in Fig. 4.28. The storage modulus is the highest at small amplitude (referred to as $E_0'$) and gradually decreases to a lower value (referred to as $E'_\infty$). The magnitude of the Payne effect ($E_0' - E'_\infty$) is increased with increasing EOMt content. At low EOMt loading for instance 2 phr, the observed variation in the amplitude of the Payne effect is feeble. However, as the EOMt concentration increases, significant and pronounced variation is observed. This is principally due to the breakdown of the filler-filler networks at higher strains. When comparing the magnitude of the Payne effect (for equivalent volume fractions) 10 phr OMT has extremely low value relative to that of 10 phr EOMt. It should be noted here that the network structure of the exfoliated particles was not clearly observed in the TEM images but an indication of the filler-filler network has been observed in the strain sweep experiments (see Table 4.11). Such a network (filler-filler) could well be developed with the same volume fraction of fillers when the fillers break down into a large number of particles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E'_0$ (MPa)</th>
<th>$E'_\infty$ (MPa)</th>
<th>$E'<em>0 - E'</em>\infty$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOMt-2</td>
<td>2.58</td>
<td>1.82</td>
<td>0.76</td>
</tr>
<tr>
<td>EOMt-4</td>
<td>3.67</td>
<td>1.86</td>
<td>1.81</td>
</tr>
<tr>
<td>EOMt-6</td>
<td>4.87</td>
<td>1.91</td>
<td>2.96</td>
</tr>
<tr>
<td>EOMt-10</td>
<td>7.01</td>
<td>2.00</td>
<td>5.01</td>
</tr>
<tr>
<td>OMT-10</td>
<td>3.6</td>
<td>2.00</td>
<td>1.60</td>
</tr>
</tbody>
</table>

Several models are available for the interpretation of strain-sweep measurements (141, 142). To parametrize the amplitude-sweep curves, we employed the phenomenological but quantitative Kraus model (143). This is based on the assumption of an agglomeration/deagglomeration mechanism of filler agglomerates:
\[
\frac{E'(\gamma) - E'_\infty}{E'_0 - E'_\infty} = \frac{1}{1 + \left(\frac{\gamma_0}{\gamma_c}\right)^{2m}}
\]  

(23)

where \(E'_\infty\) is equal to \(E'(\gamma)\) for very large strain, \(E'_0\) is equal to \(E'(\gamma)\) for very low strain, \(\gamma_c\) is a characteristic shear strain amplitude known as critical strain, \(E'_0 - E'_\infty\) is reduced to half of its zero-strain value, and the parameter \(m\) gives the shear strain sensitivity of the mechanism of filler-filler contact breakage and defines the shape of the \(E'(\gamma)\) curves.

The values of \(E''\) are also fitted according the Kraus model. In this case the expression of \(E''\) is given by the Eq. 24

\[
\frac{E''(\gamma) - E''_\infty}{E''_m - E''_\infty} = 2 \frac{\gamma_0^m}{1 + \left(\frac{\gamma_0}{\gamma_c}\right)^{2m}}
\]

(24)

Where, \(E''_m\) is the maximum loss modulus at \(\gamma_0 = \gamma_c\).

**Fig. 4. 28. Dependence of Amplitude sweep on a) \(E'\) and b) \(E''\) of different nanocomposites**

It is clear from Fig. 4.29b that the Kraus model cannot match the asymmetric shape of \(E''\) vs strain (\(\gamma\)) data. A further comparison between experimental and theoretical data obtained with Kraus model is proposed in Fig. 4.29a and 4.29b. Fitted values are given in Table 4.12.
Table 4.12. Parameter values of the Kraus model for $E'$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\gamma_c$</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOMt-4</td>
<td>3.27</td>
<td>0.35</td>
</tr>
<tr>
<td>EOMt-6</td>
<td>3.99</td>
<td>0.41</td>
</tr>
<tr>
<td>EOMt-10</td>
<td>3.18</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Fig. 4.29. a) $E'$ values fitted according to Kraus model b) $E''$ values fitted according to Kraus model c) $E'$ values fitted according to Maier-Göritz model (d) Dashed lines and solid lines represent the calculated $E''$ using the Maier-Göritz and modified Maier-Göritz model for EOMt-10(►) and EOMt-6(■)
The Kraus model does describe the variation of $E' = f(\gamma)$ for EOMt concentrations that are higher than 4-6 phr (corresponding to the percolation threshold concentration). We cannot fit the Kraus model below this EOMt concentration. This result is consistent with the assumptions of this model. However, differences can be observed between experimental and theoretical values of the loss modulus, $E''$ versus strain amplitude (Fig. 4.29b). Fitted values are shifted toward higher deformations when compared with experimental variations. There is published work that reports similar observations (141, 142). The reason behind this is still under debate.

In order to better understand the influence of the matrix-filler interaction on the viscoelastic properties of nanocomposites we employed the Maier-Göritz model. This model offers a molecular interpretation of the Payne effect based on the rubber-filler interactions (144). In general, the adsorption process occurs at the filler surface when the filler is mixed with rubber. The formation of the first rubber-filler inter-link on an interaction site present on the filler surface favors the formation of several other links on neighboring interaction sites. The first rubber chain is adsorbed firmly on to the filler surface and form so-called ‘stable bonds’. The chains arriving later at the filler surface have fewer chances to generate bonds with the filler. Therefore those chains are only able to form ‘unstable bonds’ with the filler surface. Those unstable bonds are very fragile and are prone to break, when mechanical stress is applied or if the temperature is raised. According to this model, the evolution of storage modulus with strain is given by the Eq. 25:

$$E'(\gamma) = E'_s + \frac{1}{1 + c\gamma}$$

(25)

$E'_s$ is the value of storage modulus at high deformations (referred to as $E'_{\infty}$) and $E'_s$ represents the amplitude of Payne effect: $E'_s = E'_0 - E'_s$, where, '$c'$ defines the position of the $E'$ curve on the strain axis. Generally, the expression of $E'(\gamma)$ is similar to that of the original Kraus model (143), which uses filler networking as the reason for the Payne effect. In the equation of Kraus (143) an additional slope exponent $m$ appears, i.e. $E'(\gamma) \sim (1+c\gamma)^{-2m}$.

However, many authors (141) have shown that this exponent is near 1/2, i.e. $2m = 1$ as indeed is assumed in the Maier-Göritz model (144).
The loss modulus $E''$ variation versus strain amplitude is given by the Eq. 26

$$E''(\gamma) = E''_{st} + E''_i \frac{c\gamma}{(1 + c\gamma)^2}$$ (26)

$E''_{st}$ is the $E''$ value when $\gamma$ has very low or very high values, $E''_i$ gives the variation amplitude of $E''$ and ‘$c$’ defines the position of the $E''$, maximum on the strain axis. A good agreement is observed between experimental and fitted values of $E'$. This holds regardless of the volume fraction of EOMt (Fig. 4.29c). It is also interesting to note that Maier-Göritz model is able to fit the non-linear viscoelastic behavior of low EOMt loaded sample (2 phr) reasonably well. EOMt favors the intercalation of large number of rubber chains in the clay nanogalleries attributed to the high interlayer spacing of EOMt which further enhances the rubber-filler interactions. Different fitted parameters are given in the Table 4.13.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E'_{st}$ (MPa)</th>
<th>$E'_i$ (MPa)</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOMt-2</td>
<td>2.16</td>
<td>0.44</td>
<td>0.02</td>
</tr>
<tr>
<td>EOMt-4</td>
<td>2.70</td>
<td>1.00</td>
<td>0.06</td>
</tr>
<tr>
<td>EOMt-6</td>
<td>3.23</td>
<td>1.72</td>
<td>0.10</td>
</tr>
<tr>
<td>EOMt-10</td>
<td>3.75</td>
<td>3.32</td>
<td>0.14</td>
</tr>
</tbody>
</table>

However, a small discrepancy is detected in the case of $E''$ when fitted against dynamic strain amplitude (Fig. 4.29d). Mele et al. (145) proposed a modified Maier-Göritz model (149) where they were able to fit the $E''$ value satisfactorily. A new variable designated as ‘$a$’ was introduced into the original Maier-Göritz model (149) to get the following expression which is known as modified Maier-Göritz model (149).

$$E''(\gamma) = E''_{st} + E''_i \frac{a c\gamma}{(1 + c\gamma)^2}$$ (27)

This variable ‘$a$’ can be considered as a sensibility probe for the variations of the dissipative part $E''$ as a function of $\gamma$. Neither the Maier-Göritz model nor the modified Maier-
Göritz model was utilized properly to fit the experimental values of $E''$ especially at low EOMt content (Fig. 4.29d). Fitting parameters are tabulated in the Table 4.14 and Table 4.15.

### Table 4.14. Parameter values of the Maier-Göritz model for $E''$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E''_{st}$ (MPa)</th>
<th>$E''_i$ (MPa)</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOMt-6</td>
<td>0.209</td>
<td>0.165</td>
<td>0.11</td>
</tr>
<tr>
<td>EOMt-10</td>
<td>0.386</td>
<td>0.289</td>
<td>0.16</td>
</tr>
</tbody>
</table>

### Table 4.15. Parameter values of the modified Maier-Göritz model for $E''$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E''_{st}$ (MPa)</th>
<th>$E''_i$ (MPa)</th>
<th>c</th>
<th>a</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOMt-6</td>
<td>0.202</td>
<td>0.104</td>
<td>0.18</td>
<td>1.8</td>
</tr>
<tr>
<td>EOMt-10</td>
<td>0.353</td>
<td>0.241</td>
<td>0.22</td>
<td>1.9</td>
</tr>
</tbody>
</table>

We examine the occurrence of mechanical percolation behavior in NR-EOMt nanocomposites by employing the Huber-Vilgis approach (146).

The excess modulus ($e$) will be defined as

$$ e = \frac{E' - E'_m}{E_m} \quad (28) $$

where, $E'$ is the dynamic storage modulus of the filled rubber at low amplitude and $E'_m$ is the dynamic storage modulus of the unfilled rubber matrix at low amplitude.

Briefly, the excess modulus of filled rubbers as function of filler loading can be expressed as

$$ e \sim \begin{cases} \phi^n, & \phi > \phi_p \\ \phi, & \phi < \phi_p \end{cases} $$
where the exponent $n = 1$ for filler volume fractions below the percolation threshold $\varphi_p$, in accordance with the Einstein-Smallwood equation for the hydrodynamic reinforcement of perfectly spherical filler particles and for very small volume fraction. Above the percolation limit a power law with $n > 1$ can be proposed for jammed systems (147, 148). The mechanical percolation threshold ($\varphi_p$) is obtained in a log-log plot when the experimental data are linearly interpolated according to the two different straight lines. It can be observed from Fig. 4.30 that the $\varphi_p$ of EOMt particles is decreased when compared to OMt. This is attributed to the formation of a highly network structure. Therefore, filler-filler networking can be formed even at very low loading of EOMt particles. This conclusion is further supported by the observations from strain sweep measurements.

In the case of carbon black filled rubbers Huber and Vilgis (146) derived the expression $n = 2/(3-d_f)$ where $d_f$ is the mass fractal dimension of the carbon black clusters (agglomerates), which are formed by aggregates as basic units. Furthermore, the Huber-Vilgis approach (150) gives a pre-factor $A = (R/b)^\alpha$ in $e = A^\ast\varphi^n$ where $R$ is the mean cluster size, $b$ being the mean diameter of the basic unit of carbon black agglomerates, i.e. the mean aggregate size. The exponent $\alpha = 2d_f/(D-d_f)$ depends additionally on the spectral dimension $D$ of the fractal clusters, i.e. from the measure of cluster connectivity (149). In the case of modeling of carbon black agglomerates by diffusion-limited aggregation (DLA) clusters (150, 151) with $d_f \sim 2.5$ and $D \sim 4/3$ one finds $\alpha = 5/4$ and the Huber-Vilgis exponent $n = 4$ which means a strong deviation from a linear $\varphi$-dependence at large volume fractions $\varphi > \varphi_p$. Although the Huber-Vilgis approach is unsuitable for precise quantitative discussion we do arrive to some interesting conclusions. In the limiting case of compact filler particles ($d_f = 3$), the overlap condition of the Huber-Vilgis (146) model would be hard to meet. With fractal dimensions ($d_f$) even slightly larger than 2.5 a drastic increase of the exponent would be observed; i.e $n > 4$. Obviously, anisotropic clay filler particles lead to the opposite behavior as seen in Fig. 4.30. In the case of OMt we find that $n = 1.6$. Naively applying the Huber-Vilgis approach, leads to a fractal dimension of $d_f \approx 1.75$. Such clusters are less compact than DLA. A suitable visualization for it would be the cluster-cluster model (CCA) (141) with $d_f \approx 1.78$ in 3 (Euclidean) dimensions. In CCA, one starts with a low concentration of particles diffusing on a lattice. When two particles meet, they form a cluster of two, which can also diffuse. When this cluster meets another two particle or another cluster, a
larger cluster is formed. In the case of EOMt in rubber matrix (Fig. 4.30b), we find further reduction of compactness of the filler clusters (which may be attributed to the shaded diffuse spatial regions observed in the TEM micrograph). The slope $n \sim 0.7$ for EOMt approaches a nearly vanishing fractal dimension $d_f \sim 0.1$ which indicates less or even vanishing compactness of filler clusters. Low values of $d_f$ suggest better particle dispersion with a more open fractal structure. Note, that even negative fractal dimension have been introduced to help understand self-similar fractal measures called multifractals (152).

We note that from the work of Pötschke et al. (153) correspondingly scaling exponents for the equilibrium shear modulus as function of volume fraction in polycarbonate nanocomposites filled with carbon nanotubes (CNTs) can be calculated: $G_e \sim \phi^m$ with $m = 0.3$ and $m = 2.0$. This relatively low value of the exponent is also an indication of low compactness of CNT filler clusters. This is a similar situation to our clay systems, and is in contrast to the high compact filler clusters in carbon black filled polymers. Moreover, the great discrepancy between the two exponents for CNTs is mainly due to the nanotube properties, like purity, aspect ratio, single or multiwall, and their state of dispersion in the matrix.

![Fig. 4.30. Percolation threshold predicted from Huber-Vilgis model](image)

We observe that the last discussion point above helps to better understand mechanical properties of rubber nanocomposites within the context of common structural scaling models. However, these discussions should not be overstressed and considered as the last word on the subject. The fractal dimension of filler clusters in rubbers is sensitive to the surface modifications
of filler particles as has shown for silica (see, for example, the comprehensive discussion in reference (154). This aspect has been excluded from our discussion here.

4.3.5.3 Frequency sweep and viscoelastic master curves

The master curve shows the dynamic mechanical behavior of the material over a very wide frequency range. The master curves for $E'$ and $E''$ of gum NR and various NR-EOMt blends with different clay loadings are shown in Fig. 4.31.

At high frequencies, the qualitative behavior of both $E'$ and $E''$ is basically constant. However, the low frequency dependence of the moduli gradually changes for nanocomposites with 6 and 10 phr EOMt. The above fact might be attributed to the solid-like behavior of the nanocomposites beyond a certain volume fraction of EOMt. Chung et al. (155) have also reported the same dependence of frequency in the case of NBR-layered silicate nanocomposites.

In general, a reference temperature ($T_0$) must be selected (in this case 20 °C) and the viscoelastic parameters at other temperatures are shifted to the corresponding values at that particular reference temperature. A horizontal shift factor, $a_T$, which is a function of temperature, enables to obtain the master curves. The shift factor plots of various NR nanocomposites are documented in Fig. 4.32a.

The Williams-Landel-Ferry (WLF) equation (156) which is given below is used to understand the time-temperature behavior of all NR-EOMt nanocomposites.

![Fig. 4. 31. Master curves generated by shifting (a) Storage and (b) Loss modulus curves according to the time-temperature superposition (TTS)]
Results and discussion

\[
\log a_T = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \tag{29}
\]

where \(C1\) and \(C2\) are the WLF constants, \(T_0\) is the reference temperature and \(T\) is measurement temperature. Values of \(C1\) and \(C2\) obtained after fitting with WLF equation for various NR-EOMt nanocomposites are tabulated in Table 4.16. The values of \(C1\) and \(C2\) are related to the state of a material, in relation to its fractional free volume \((f_0)\). Consequently, changes in \(f_0\) are an indication of changes at the molecular level. However, the idea of free volume is difficult to define in a precise manner. In an approximate way we represent the segments of a polymer chain by rigid segments and the free volume as the “holes” present between those segments as a result of packing arrangements. Information on the dynamic free volume characteristics of the samples was deduced from the following Eq.

\[
C_1 = \frac{P}{2.303 f_0} \tag{30}
\]

\[
C_2 = \frac{f_0}{\alpha_f} \tag{31}
\]

\(\alpha_f\) is the coefficient of thermal expansion of the fractional free volume and \(P\) is a numerical constant, generally considered equal to unity. It is interesting to note that the values of \(C1\) and \(C2\) are increased after the addition of EOMt compared to unfilled NR gum.

\[\text{Fig. 4.32. (a) } a_T\text{ values of NR and the NR nanocomposites as a function of } T.\text{ The line shown in the graph is the best fit WLF equation (Eq. 29) to the } a_T\text{ values for all nanocomposites (b) } Ea\text{ as a function of EOMt loading at 303K}\]
Results and discussion

The temperature dependence of the $a_T$ values, which is defined as the ratio of the relaxation time at a specified stress and the linear relaxation time at approximately zero stress level, is shown in Fig. 4.32a. There are many literature articles (157, 158) stating that the $a_T$ values are independent of the silicate loading. This suggests that the temperature dependent relaxation processes of nanocomposites observed in the dynamic mechanical measurements are unaltered even in the presence of the clay. However, the applicability of the principle of time-temperature superposition (TTS) for various NR-EOMt nanocomposites indicate that the $a_T$ values are mostly unchanged up to 6 phr of clay loading and beyond that there is distinct change is observed in $a_T$ values. This change may be attributed to the higher degree of exfoliation of EOMt particles throughout the rubber matrix.

Table 4.16. Viscoelastic Parameters of different NR-clay nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$f_0$</th>
<th>$a_T$ (K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gum</td>
<td>2.5</td>
<td>106</td>
<td>0.173</td>
<td>1.63 x 10$^{-3}$</td>
</tr>
<tr>
<td>EOMt-2</td>
<td>3.0</td>
<td>112</td>
<td>0.143</td>
<td>1.27 x 10$^{-3}$</td>
</tr>
<tr>
<td>EOMt-4</td>
<td>3.5</td>
<td>114</td>
<td>0.124</td>
<td>1.08 x 10$^{-3}$</td>
</tr>
<tr>
<td>EOMt-6</td>
<td>3.6</td>
<td>116</td>
<td>0.120</td>
<td>1.03 x 10$^{-3}$</td>
</tr>
<tr>
<td>EOMt-10</td>
<td>6.0</td>
<td>126</td>
<td>0.076</td>
<td>5.75 x 10$^{-4}$</td>
</tr>
<tr>
<td>OMt-10</td>
<td>3.6</td>
<td>118</td>
<td>0.118</td>
<td>1.00 x 10$^{-3}$</td>
</tr>
</tbody>
</table>

Apparent activation energies ($E_a$), which is quantitative measure of the molecular mobility, can also be determined by substituting the WLF equation into the frequency shift factor in the Arrhenius equation, as follows,

$$E_a = R \left( \frac{d \ln a_T}{d(1/T)} \right) = 2.303 R \left[ \frac{C_1 C_2 T^2}{(C_2 + T - T_0)^2} \right]$$

(32)
Figure 4.32b represents the EOMt loading dependent flow activation energy ($E_{app}$) of pure unfilled NR gum and different nanocomposites obtained from Eq. 32. The apparent activation energy ($E_{app}$) of unfilled gum NR is 25.5 kJ/mol, and the $E_{app}$ of the different NR nanocomposites increases with the EOMt loading which is shown Table 4.17. This behavior may be attributed to the improved dispersion and distribution of EOMt nano layers in the NR matrix. Witten et al. also reported that trussing or attachment of the polymer chains onto the silicate surface may act as an energetic barrier to molecular motion (159). The highest $E_{app}$ value is obtained at 10 phr of EOMt (compared to same loading of OMt).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>213K</td>
</tr>
<tr>
<td>EOMt-2</td>
<td>285</td>
</tr>
<tr>
<td>EOMt-4</td>
<td>299</td>
</tr>
<tr>
<td>EOMt-6</td>
<td>308</td>
</tr>
<tr>
<td>EOMt-10</td>
<td>310</td>
</tr>
<tr>
<td>OMt-10</td>
<td>255</td>
</tr>
</tbody>
</table>

4.3.6 Swelling study: rubber-filler interactions

The extent of interaction between rubber and EOMt is analyzed on the basis of an equilibrium swelling study. The volume fraction of rubber ($V_r$) in the swollen vulcanizates has a direct relationship with the crosslink density. In particular the higher the value of $V_r$ the higher will be the reinforcing ability of the filler. The Lorenz-Parks model (160) has been used for the investigation of the swelling of filler-reinforced vulcanizates which is given in Eq. 33.

$$\frac{Q_f}{Q_g} = a e^{-z} + b$$  (33)
Where \( Q \) is the amount of solvent per unit weight of the rubber, \( f \) and \( g \) refer to filled and gum blends, \( z \) is the weight fraction of filler in the polymer, \( a \) and \( b \) are two constants which depend on the filler activity. In its current form this model has a drawback because it addresses the swelling behavior of a filled sample without acknowledging that the presence of filler would enhance the crosslinking efficiency of the curing agent. Therefore, in the present study the Cunneen-Russell equation (161) has been utilized. It represents a variant of the originally derived Lorenz- Parks equation.

\[
\frac{V_{r0}}{V_{rf}} = a \cdot e^{-z} + b
\]  

(34)

where \( V_{r0} \) and \( V_{rf} \) are the volume fractions of the rubber in unfilled and filled vulcanizates, respectively, swollen in a solvent.

**Fig. 4.33.** (a) Cunneen-Russell plot (b) Kraus plot of different NR-clay nanocomposites

The ratio of \( V_{r0} \) to \( V_{rf} \) is a measure of rubber-filler interaction in filled systems. The values of \( a \) and \( b \) calculated from the plot (Fig. 4.33a). Higher values of \( a \) and lower values of \( b \) indicate strong rubber-filler interaction. It is interesting to note that both requirements are favorable in the case of NR-EOMt system compared to NR-OMt. Fig. 4.33b shows the plot of \( V_{r0}/V_{rf} \) against \( \varphi/(1-\varphi) \) according to Kraus equation (162) given below,

\[
\frac{V_{r0}}{V_{rf}} = 1 - \frac{m \varphi}{(1 - \varphi)}
\]  

(35)
where \( m = 3C(1 - V_{r0}^{0.3}) + V_{r0} - 1 \) \hspace{1cm} (36)

here, \( C \) is the characteristic constant for filler, which is independent of solvent. \( \phi \) is the volume fraction of filler in the vulcanizate, \( m \) represents the polymer-filler interaction parameter obtained from the slope of the plot of \( V_{r0}/V_{rf} \) against \( \phi/(1 - \phi) \).

The highest value of \( m \) observed for NR-EOMt nanocomposites is attributed to its higher reinforcing ability compared to the NR-OMt system. The interaction parameter for EOMt is found to be 4.85 as opposed to 2.24 for OMt.
4.4 Role of expanded clay on the properties of carbon black filled NR composites

Technical elastomers are generally filled with certain fillers (e.g. carbon black) in order to reinforce the rubber matrix for some typical applications like tires, conveyer belts etc. Such rubber goods are always exposed to cyclic stress and deformations attributed to their dynamic application. Under constant and repeated applied stress, cracks develop at a stress concentration point, which could lead to ultimate failure. Therefore, the crack initiation and propagation behavior in such rubber products is very fundamental and need proper attention. In principal the rubber matrix around the filler surface is suffering from higher strain as compared to the rest of the matrix when a filled rubber component is exposed to cyclic stress or deformations (163, 164). If a large or repeated force is applied, the interface between the filler and the rubber matrix can be damaged and micro-cracks will be formed.

4.4.1 Morphological analysis

The resulting morphology was characterized in terms of both WAXD and TEM. The WAXD patterns of different clays and clay filled NR composites are depicted in Fig. 4.34a in the range of $2\theta = 1-12^\circ$. As expected, NR-CB system does not show any peak due to the absence of clay in the system. It can be seen from the Fig. 4.34a that the measured $d(001)$ basal spacing of OMt is 2.98 nm, whereas in sample NR-CB30-OMt the basal spacing is 4.3 nm. There is a significant increase in the $d(001)$ basal spacing and a low angle broad halo is observed in the case sample NR-CB30-EOMt. The broadening of the $d(001)$ peak in the low 2$\theta$ region indicates the extensive layer separation associated to the clay lamellae intercalation and exfoliation. The reason is attributed to the long alkyl chains creating more interlayer space where the intercalations of macromolecular rubber chains are becoming easier.

In order to examine the morphological hierarchy developed in the clay/NR/CB ternary component system, TEM was utilized. A three-phase morphology is obvious in the TEM micrograph which is represented in Fig. 4.34b. The nanoclay appears as dark entities whereas the CB appears as dark gray circular blocks generally aggregated in clusters. It is interesting to observe that clay/CB forms so called “nano-blocks” attributed to the strong intermolecular interactions between clay and CB. These are displayed in Fig. 4.34b. Similar interactions between clay and CB were observed and reported in the literature (165). They explained this fact in terms of zeta-potential. It is also interesting to note that the EOMt platelets essentially deform to wrap
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partially around the rigid primary CB aggregates. Konishi et al., (166) have reported the same when they prepared a ternary blend based on nylon6/CB/clay.

![Image](image.png)

**Fig. 4. 34.** a) WAXD pattern of different NR composites and b) TEM images of NR-CB30-EOMt and (c) NR-CB30-OMt composites

4.4.2 Morphology: atomic force microscopy (AFM)

AFM-images of different materials for instance, NR-CB30, NR-CB30-FA and NR-CB30-EOMt are shown in Fig. 4.35. Numbers near small vertical bar (Fig. 4.35, top row) denote the range of measured value, dimensionality (here is nanometers) also shown.
The presence of fillers is reflected in the irregularities of relief of AFM-height images (Fig. 4.35, top row). The corresponding phase images (Fig. 4.35, bottom row) qualitatively show stiffness contrast of the surfaces. Bright zones attribute to the rigid inclusions and dark area ascribes soft polymer. Distribution of rigid phase is not uniform. In general, the carbon black particles are organized in aggregates/agglomerate forms in the rubber matrix as they are not fully separated as individual particle results such images. Zinc oxide particles also can be found (Fig. 4.35b) along with the filler particles as they appeared in more bright phase with more rigidity. The presence of clay is observed at higher magnification in Fig. 4.36.
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For quantitative description of filler morphology in the materials, the continuous relief (Fig. 4.35, top row) is replaced by the field of discrete structures representing the fragments of the filler network in the material (see Fig. 4.37). The algorithm of segmentation involves two steps (167). Step 1: Find any local maxima of the surface under study (vertices of future segments). Step 2: Examine the contour lines around the obtained maxima and determine the boundaries of segments. Hence, the continuous relief is divided into a separate field of segments (Fig. 4.37).

Preliminary analysis of the sizes and shapes of segments allowed us to define two types of inclusions in the polymer: 1) micropellets - for segments of size $\geq 300$ nm with compactness $\geq 0.85$; 2) filler inclusions (CB aggregates or clay tactoids) - for the rest of segments. Compactness, mentioned here, is defined as area-perimeter ratio with respect to the circle, for which the
corresponding value is equal to unity. For branchy or rod-like shapes this value is less than unity. Segments, defined as micropellets, are shown in Fig. 4.37 as round or round-like silhouettes.

After analyzing the above mentioned images the following parameters can be estimated (given in the Table 4.18); \(\Phi_{PEL}\): fraction of micropellets i.e. ratio between the area of segments detected as micropellets and the total area of detected segments, \(d_{pel}\): average diameter of micropellets, \(d_{fil}\): average diameter, \(l_{fil}\): length (the longest distance from edge to edge of segment), \(c_{fil}\): compactness and \(a_{fil}\): aspect ratio (relation between length and diameter of inclusion) of filler inclusions. The average diameter is meant the distance between two opposite points of the boundary of the segment plotted through its geometrical center, as one of the point moves along the boundary with angular step 45°.

### Table 4.18. Structural parameters of investigated materials

<table>
<thead>
<tr>
<th>Code</th>
<th>(\Phi_{pel}), %</th>
<th>(d_{pel}), nm</th>
<th>(d_{fil}), nm</th>
<th>(l_{fil}), nm</th>
<th>(c_{fil})</th>
<th>(a_{fil})</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR-CB30</td>
<td>13</td>
<td>630</td>
<td>68±0.5</td>
<td>98±0.6</td>
<td>0.90</td>
<td>1.49</td>
</tr>
<tr>
<td>NR-CB30-FA</td>
<td>51</td>
<td>1440</td>
<td>66±0.4</td>
<td>96±0.6</td>
<td>0.90</td>
<td>1.49</td>
</tr>
<tr>
<td>NR-CB30-OMt</td>
<td>28</td>
<td>1790</td>
<td>77±0.5</td>
<td>117±0.7</td>
<td>0.86</td>
<td>1.56</td>
</tr>
<tr>
<td>NR-CB30-EOMt</td>
<td>21</td>
<td>870</td>
<td>68±0.3</td>
<td>108±0.4</td>
<td>0.87</td>
<td>1.64</td>
</tr>
</tbody>
</table>

*after “±” standard deviation of mean is shown.

A high fraction of micropellets \((\Phi_{pel})\) is observed in sample designated as NR-CB30-FA, NR-CB30-EOMt and NR-CB30-OMt. Extra amount of fatty acid as well as the organic modifier (quaternary ammonium salt) of the present in the interlayer space of the clay decreased the maximum rheometric torque in the curing study (not shown here). The plasticity effect of fatty acid is decreased the frictional force between the filler-filler and rubber-filler which further results in dispersion of CB agglomerates into large number aggregates. Average size \(d_{fil}\) of filler inclusions is almost equal in all samples, except NR-CB30-OMt. This fact is attributed to the higher thickness of OMt clay particles. Other structural parameters like length, compactness and aspect ratio of filler inclusions are higher for CB-clay composites. The sample NR-CB30-EOMt
is yielded with higher aspect ratio \( (a_{fil}) \). However, the distinction between clay tactoids and CB aggregates cannot be done clearly based on AFM-images (Fig. 4.36). Most likely CB aggregates and clay are forming a kind of ‘nano-blocks’ comprised of delaminated clay nanoparticles and CB aggregates and an average value of the aspect ratio is obtained especially in the case of NR-CB30-EOMt composite. A similar observation is noted from TEM analysis. Such joined structures are very common in clay/CB system and reported in the literature (166).

In order to investigate the \textit{in situ} generated microstructure of the composites, AFM images were taken under strained condition. During stretching the material becomes thinner and the polymer can be peeled from the filler what makes the shape of the aggregates and clay more pronounced. Another benefit of such procedure is to understand the surface topography under the stretched conditions. For this case, thin rubber strip was fixed in self-made stretching device. A tiny diagonal notch was produced and the sample was slowly stretched (Fig. 4.38). Hence, the crack propagated deeper into the material. After giving sufficient time for the relaxation process static surface microstructure was investigated by AFM (Fig. 4.38b). Material in the vicinity of crack-tip supposed to be (almost) extremely tensioned, if one turns the screw (Fig. 4.38a) and elongates strip some more, the notch will propagate further.

![Stretching device with elongated sample (a) and AFM-probe over the open notch in rubber (b)](image-url)
In these experiments we have used special nanomechanical AFM regime (Peak Force QNM) which allows mapping, along with surface relief, adhesion force, deformation, elastic modulus and some other parameters of surface (Veeco). In this mode we have utilized calibrated probes with radii ~4 nm. Modulus was calculated using Derjaguin-Muller-Toropov (DMT) model (168) of adhesive interaction of rigid sphere with elastic material. DMT model is applied to tips with small curvature radius and high stiffness. This is a static (equilibrium) model, describing the final equilibrium geometry, but not the dynamic growth of the contact immediately after adhesion or coalescence has occurred. AFM-images of surface of sample NR-CB30 are shown in Fig. 4.39. Tension direction is vertical. Dark regions in Fig. 4.39b and 4.39c corresponds to the lower values of measured parameters.

**Fig. 4. 39. AFM-images of height (a), adhesion force (b) and elastic modulus (c) of stretched sample D**

Rigid aggregates have lowest adhesion (dark zone at Fig. 4.39b) and highest modulus (bright zones at Fig. 4.39c). It must be noted, that all experiments done with soft AFM-cantilevers (stiffness ~0.4 N/m) and everything with elastic modulus higher than ~100 MPa cannot be deformed and shown with maximal allowed modulus (here is 500 MPa, further this value can vary). One can observe a lot of vertical strand-like structures connecting carbon black aggregates. They are NR-fibrils in glassy and/or oriented state with significantly higher modulus and lower adhesion in comparison with surrounding matrix.

AFM-images of surface of sample NR-CB30-EOMt are shown in Fig. 4.40. Clay tactoids (especially clearly seen on adhesion map, Fig. 4.40b) are pointed with arrows; some CB aggregates are circled. It is clearly seen now, that some CB aggregates are joined with clay
tactoids. It should be noted that relatively large clay plates (avg. size ~600 nm) and small ones (~100 nm) are very clearly observed. This means that deformation of polymer and presence of rigid CB aggregates and clay tactoids dissociated into smaller particles. One of the dashed lines in Fig. 10b shows possible initiation of cracking (bottom line) second indicates complete breakage (top dashed line) of clay tactoids. This kind of breakage can also occur during dynamic service of the rubber product.

Fig. 4. 40. AFM-images of height (a), adhesion force (b) and elastic modulus (c) of stretched sample D

4.4.3 Mechanical properties

Different static mechanical properties of CB filled NR-clay composites are represented in Table 4.19. The 30 phr CB filled NR control composite shows stress values at 100% and 200% elongation (usually termed in rubber technology as modulus M 100 and M 200 which means moduli at 100 and 200% elongations) of 1.30 MPa and 2.81 MPa, respectively. On introduction of OMt into the CB filled NR composite, the nanoclay-filled sample (designated as NR-CB30-OMt) registers a M 100 of 2.14 MPa and a M 200 of 4.65 MPa. There is even an increment in M 100 and M 200 observed for the sample NR-CB30-EOMt in the presence of EOMt. The values are comparable to the composite with 50 phr of CB. These values correspond to around 27% increment in M 100 and 18% in M 200 over the OMt filled NR-CB composites. However, tensile strength is decreased in the presence of both types of nanoparticles which are attributed to the enhanced cross-linked density of the rubber matrix. In general, the mechanical properties of a rubber intensely depend on cross-linked density. In one hand, modulus and hardness increase gradually with increasing cross-linked density. On the other hand tensile strength pass through a
maximum as cross-linked density is increased. When a rubber is deformed externally, part of the applied energy stored elastically in the chains and is available as driving force for fracture. The remaining energy is dissipated through molecular motions into heat and in this way, is made inaccessible to break further chains. At high cross-links level, chain motions become restricted and the tight network is incapable of dissipating much energy. Significant increment in the hardness value is observed when additionally 5 phr of EOMt is added with 30 phr of CB in the NR matrix. It is concluded that such a significant increment in different physical properties could be ascribed to the highly exfoliated structures of the EOMt particles in the NR matrix which is already confirmed from TEM and AFM.

The stress-strain relationship was analyzed according to the modified Mooney (108) and Rivlin and Saunders (109) and represented in Fig. 4.41. The different values of $C_1$ are summarized in Table 4.19. In general $C_1$ gives information about the crosslink density of the filled rubber system. The idea was to calculate $C_1$ from modified M-R equation in order to get the idea of cross-link density of our system. A higher value of $C_1$ signifies the higher cross-link density of the system. A significant increment in $C_1$ value is observed in the case of EOMt filled NR composites compared to NR-CB30-OMt.

![Mooney-Rivlin plots of different NR composites](image-url)
Table 4.20. Mechanical properties of different NR composites

<table>
<thead>
<tr>
<th>Properties</th>
<th>NR-CB30</th>
<th>NR-CB30-FA</th>
<th>NR-CB30-OMt</th>
<th>NR-CB30-EOMt</th>
<th>NR-CB50</th>
</tr>
</thead>
<tbody>
<tr>
<td>M50 (MPa)</td>
<td>1.08±0.12</td>
<td>1.05±0.14</td>
<td>1.27±0.04</td>
<td>1.78±0.03</td>
<td>1.34±0.02</td>
</tr>
<tr>
<td>M100 (MPa)</td>
<td>1.66±0.23</td>
<td>1.69±0.25</td>
<td>2.13±0.46</td>
<td>2.69±0.26</td>
<td>2.16±0.05</td>
</tr>
<tr>
<td>M200 (MPa)</td>
<td>2.81±0.23</td>
<td>2.79±0.19</td>
<td>4.65±0.46</td>
<td>5.47±0.26</td>
<td>4.53±0.11</td>
</tr>
<tr>
<td>M300 (MPa)</td>
<td>4.34±0.11</td>
<td>4.27±0.12</td>
<td>8.6±0.46</td>
<td>10±0.31</td>
<td>8.2±0.17</td>
</tr>
<tr>
<td>EB (%)</td>
<td>1112±8</td>
<td>1111±12</td>
<td>990±20</td>
<td>983±25</td>
<td>978±25</td>
</tr>
<tr>
<td>TS (MPa)</td>
<td>30.2±1.2</td>
<td>30.6±1.4</td>
<td>27.6±0.95</td>
<td>25±2.0</td>
<td>27±3.1</td>
</tr>
<tr>
<td>Hardness</td>
<td>53±1</td>
<td>52±2</td>
<td>58±1</td>
<td>67±3</td>
<td>65±2</td>
</tr>
<tr>
<td>(Shore A)</td>
<td>C₁</td>
<td>0.62</td>
<td>0.70</td>
<td>0.78</td>
<td>0.90</td>
</tr>
</tbody>
</table>

After “±” standard deviation is shown.

4.4.4 Dynamic mechanical properties

The dynamic mechanical behavior across a wide range of temperature of the different NR composites is shown in Fig. 4.42 while the important dynamic mechanical parameters are summarized in Table 4.20. A phenomenal increase of ~121% of the storage modulus (E’) at 25 °C is recognized in the presence of EOMt compared to the OMt. Interestingly, this increment in E’ is even higher (20%) compared to NR composites with 50 phr of CB designated as NR-CB50. Tan δ values at 0 °C and 60 °C represent the wet skid and rolling resistance performance, respectively, of rubber compounds employed in tire tread applications (69). There are often compromises between tire rolling resistance and tire wet traction. On one hand, it is desirable to have a high tan δ at 0 °C to achieve necessary wet traction and grip in one hand. On the other hand, a low loss factor at 60 °C ensures lower rolling resistance. An optimum compound would have the lowest rolling resistance with the highest wet traction. It can be observed from Table 4.20 that only the sample NR-CB30-EOMt matches these criteria.

The NR composite with only 30 phr of CB depicts the tanδ of 1.55 at Tg which is further decreased in the presence of OMt. Such decrement in the tanδ value at Tg is more pronounced and significant in the presence of EOMt particles. This phenomenon could be understood in terms
of intensive rubber-filler interactions. Higher interlayer space in the EOMt allows the penetration of the macromolecular rubber chains into the interlayer space causes high degree of exfoliation of such clay minerals in the NR matrix. Subsequently, stronger rubber-filler interactions are established.

![Graphs](image)

Fig. 4.42. a) storage modulus as a function of temperature b) tan delta as a function of temperature c) loss modulus as a function of temperature

4.4.4.1 Payne effect and filler-filler networking

Strain-induced filler-filler network breakdowns by dynamic tension mode at constant frequency and temperature was carried out and the corresponding storage modulus (E’) versus dynamic strain (%) is established in Fig. 4.43. The amplitude of Payne effect for different NR-CB composites is tabulated in the Table 4.21. The storage modulus (E’), a measure of energy stored during dynamic deformation monotonically decreases with the strain amplitude for all the NR-
Results and discussion

CB composites. Generally, the absolute value of $E'$ at low strain regime indicates the degree of filler-filler networking. It is observed that the NR composites with 30 phr CB and 5 phr EOMt acquires higher $E'$ value implying that the degree of filler-filler networking is stronger compared to NR composites with 50 phr CB. The stronger filler-filler interaction with fewer amounts of fillers indicates the possibility of the existence of a new kind of filler-filler interaction within the silicate particles. Exfoliated layered clay minerals possess free hydroxyl groups at the edges and these hydroxyl groups are interacting with each other to form a new kind of silicate-silicate network in the rubber matrix (105).

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E'$ at 25 °C</th>
<th>$\tan \delta_{\text{max}}$</th>
<th>$\tan \delta@0 , ^\circ \text{C}$</th>
<th>$\tan \delta@60 , ^\circ \text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>at 10 Hz</td>
<td>at 10 Hz</td>
</tr>
<tr>
<td>NR-CB30</td>
<td>4.96</td>
<td>1.55</td>
<td>0.12</td>
<td>0.058</td>
</tr>
<tr>
<td>NR-CB30-FA</td>
<td>6.19</td>
<td>1.40</td>
<td>0.14</td>
<td>0.077</td>
</tr>
<tr>
<td>NR-CB30-OMt</td>
<td>8.42</td>
<td>1.35</td>
<td>0.14</td>
<td>0.099</td>
</tr>
<tr>
<td>NR-CB30-EOMt</td>
<td>18.65</td>
<td>1.01</td>
<td>0.19</td>
<td>0.150</td>
</tr>
<tr>
<td>NR-CB50</td>
<td>15.64</td>
<td>1.01</td>
<td>0.20</td>
<td>0.155</td>
</tr>
</tbody>
</table>

However, the percentage of the edges surface area (only 2-3 % with respect to total surface area of a clay platelet) is very low compared to the total surface area of the exfoliated clay particles the participation in the formation of hydrogen bonding between two hydroxyl groups of two different silicate particles could be imagined. In this way exfoliated silicate layers could able to form a silicate-silicate network around the rubber matrix. Thus, there are essentially two distinct filler-filler networks: CB-CB and silicate-silicate (Shown in the Fig. 4.43b). Moreover, the AFM observation of nanostructures on the surface of the tip of static crack in NR-EOMt composite under constant elongation revealed breakage of EOMt tactoids into smaller pieces due to critical stress field in the crack. Similar rupture of clay can happen during
“ordinary” mechanical loading of NR-CB30-EOMt composites resulting in high hysteresis and Payne effect as shown in the Fig. 4.43.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E'_0$ (MPa)</th>
<th>$E''_\infty$ (MPa)</th>
<th>$(E'<em>0 - E''</em>\infty)$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR-CB30</td>
<td>5.45</td>
<td>3.73</td>
<td>1.72</td>
</tr>
<tr>
<td>NR-CB30-FA</td>
<td>6.91</td>
<td>3.97</td>
<td>2.94</td>
</tr>
<tr>
<td>NR-CB30-OMt</td>
<td>9.26</td>
<td>4.89</td>
<td>4.37</td>
</tr>
<tr>
<td>NR-CB30-EOMt</td>
<td>24.85</td>
<td>7.65</td>
<td>17.2</td>
</tr>
<tr>
<td>NR-CB50</td>
<td>18.81</td>
<td>7.16</td>
<td>11.65</td>
</tr>
</tbody>
</table>

4.4.5 Tear fatigue analysis (TFA): crack growth behavior

TFA tests were carried out to explicate the crack growth behavior of nanoparticle filled NR-CB composites. One double notched pure-shear test specimen was analyzed for each loading amplitude and details of this experiment can be found in the following references (169-171). The
crack growth rate \((da/dn)\) of different NR-CB composites obtained from this results are plotted against the tearing \((T)\) energy using a log-log scale, and are compared with that of 50 phr carbon black-filled NR composites. The effect of such behavior is depicted in Fig. 4.44. It is interesting to observe that a linear fit can be made for all the cases which indicate that the rate of crack growth \((da/dn)\) can be represented by the power-law relation with the tearing energy \((T)\) as found previously.

A pre-existing cracks or flaws generally considered in the crack growth approach of rubber like materials (163). Griffith (78) pointed out a balanced relationship between the stored mechanical energy of a cracked body and surface energy associated with newly generated fracture surfaces. This approach is only valid for perfectly elastic materials. Later on this approach of fracture was further extended in rubbers (172) and it was observed that this behavior is highly nonlinear in nature. Therefore, in doing such extension it was recognized that the reduction in mechanical energy of the system was balanced, not only by improved surface free energy, but also by work done through dissipative processes arising in material in the vicinity of the crack tip.

Fig. 4. 44. Crack growth rate as a function of tearing energy for different NR composites
Results and discussion

A significant reduction in crack growth behavior is observed from Fig. 4.44 over the all tearing energy employed in the presence of both OMt and EOMt compared to NR-CB30. There is even further improvement in crack growth rate observed in the case of NR-CB30-EOMt compared to NR-CB30-OMt. This improvement can be ascertained from the morphology of this composite. In general the dispersion of OMt nanoparticles in the non-rubber matrix is very poor attributed to the small interlayer spacing of OMt. Therefore the crack growth rate is faster in the case of NR-CB30-OMt compared to NR-CB30-EOMt. Homogeneous dispersion of EOMt nanoparticles in the rubber matrix made this composite better crack resistant. Finally NR-CB30-EOMt composite is compared with NR-CB50. It can be observed from Fig. 4.44 that at low tearing energy the crack growth rate of NR-CB30 is superior compared to NR-CB30-EOMt but at higher tearing energy the crack growth is getting inferior for the same composites compared to NR-CB30-EOMt.

Several mechanisms are put forwarded to understand the stable crack propagation behavior in both filled and unfilled rubber (163, 173). There is a considerable dependence of crack growth behavior noticed and reported in the literature on the strain induced crystallization especially for the crystallizable rubbers (NR, chloroprene rubber etc.) (173). In general strain induced crystallization improves the crack growth rate. Another factor could be the morphology which plays a vital role in the case of filled rubber system. We have observed a significant reduction in crack growth rate in the presence of nanoparticles both OMt and EOMt. A completely different kind of nano-morphology could be perceived in the case of nanoparticle filled NR-CB composites in both TEM and AFM. Additionally the homogeneous dispersion of such nanoparticles in the rubber matrix can help in the dissipation of energy. We already mentioned in the previous section that clay/NR/CB aggregates can form a so called “nano-blocks” attributed to the strong intermolecular interactions between EOMt and CB in the case of NR-CB-EOMt. Such nano-block can acts as micro-barriers to increase the crack path by deviating and branching at the crack tip. It is also interesting to observe that such “nano-blocks” are not prominent in the case NR-CB30-OMt attributed to the poor dispersion of OMt particles in the rubber matrix. Superior dispersion of EOMt particles can also deliver substantial interfacial area. Therefore, the dissipation on the clay-rubber interface contributes to the overall improvement of crack growth rate. Finally we compare the composite NR-CB30-EOMt with NR-
CB50. However, higher crack growth rate is observed in the case of NR-CB50 compared to NR-CB30-EOMt at high tearing energy.

**Fig. 4. 45. Viscoelastic behavior as a function of Temperature**

It has been observed and reported that the crack growth rate in rubber materials depends on the viscoelastic properties of the rubber matrix (173, 174). According to Persson-Brener the tearing energy (T) at the crack velocity v can be expressed by the following equation (173):

$$T(v) = T \left[ 1 - \frac{2}{\pi} \frac{E_0}{a} \int_0^{2\pi} \frac{\bar{F}(\omega)}{\omega} \left( \frac{1}{E^*(\omega)} \right)^{-1} \right]$$

(37)

$E^*(\omega) = E' + i E''$ is the complex modulus, $E_0$ is the storage modulus at zero-velocity in the outer rubber bulk region of the crack tip, $a$ is the crack tip diameter, $\omega$ is the perturbing frequency defined as $v/r$ ($r$ is the distance from the crack tip). The function $F(\omega)$ was defined as

$$F(\omega) = \left[ 1 - \left( \frac{\omega \alpha}{2\pi v} \right)^{0.5} \right]$$

(38)

$Im \left( \frac{1}{E^*(\omega)} \right) = -E''/IE^*F$ designates the imaginary part of the inverse complex modulus $1/E^*(\omega)$ which known as the complex compliance of the material.
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With Eq. 37 a rather direct relationship can be obtained between $T(v)$ and $-E''/\sigma_I\sigma^2$. Although we have no frequency-dependent master curves of the elastic modulus available, some qualitative conclusions and explanations – similar like in (174) – can be drawn from the temperature-sweep data (DMA) due to the time(frequency)-superposition. The values of $-E''/\sigma_I\sigma^2$ for the different NR composites obtained from DMA are plotted against temperature and represented in the Fig. 4.45. The corresponding values are lowest in the case of NR-CB30-OMt and the highest values are obtained in the case of NR-CB30-EOMt which is even comparable with NR-CB50. From such a ranking one can conclude that NR-CB30-EOMt has larger values of $T$ indicating that this compound needs more energy dissipation at the same crack growth velocity during cyclic loading compared to NR-CB30-OMt and NR-CB50. It is well established that energy dissipation affects the fracture properties of a rubber. The higher the energy dissipated, lower the energy available to cause crack growth. In the present work, superior dispersion of EOMt particles can also bring substantial interfacial area. Therefore, the dissipation on the clay-rubber interface contributes to the overall reduction of the crack growth rate. Subsequently, NR-CB30-EOMt has a lower crack growth rate compared to NR-CB30-OMt. Similar observations were also perceived from TFA analysis.

4.4.6 Fracture toughness

Figure 4.46 depicts characteristic examples of the load-extension diagrams from the impact fracture testing. One can see that the variation of the filler type and filler content leads to differences in the deformation behavior. It is interesting to note that when using additionally 5 phr EOMt and OMt respectively, the maximum load increases. In the case of adding 5 phr of OMt also the deformability is enhanced. This behavior results in the highest crack resistance value $J_d$ (see also Table 4.22) of the material containing OMt.

Two reference materials were investigated: NR-CB30 and NR-CB 50 containing 30 and 50 phr CB respectively. Generally, due to the lower reinforcement effect, 30 phr CB results in a principally lower parameter level than 50 phr CB. However, similar to the mechanical properties (Table 4.22), the addition of 5 phr EOMt or OMt can influence also the fracture behavior. Some parameters showed a behavior of the compound containing 30 phr CB and only 5 phr EOMt comparable to the NR-CB50. However, concerning the impact behavior it is stated that the crack
resistance of the material NR-CB30-EOMt is much lower than that of NR-CB50. Latter has a much higher maximum load this means, the contribution of the strength to the general toughness is higher. The large standard deviation of the NR-CB50 material is due to the fact that in some specimens, the cracks showed large deviations from the ideal path perpendicular to the loading direction. This is a hint for high crack toughness and the occurrence of strain crystallization and can be derived also from the special form of the F–l diagram. Because of the self-reinforcing properties due to the strain crystallization, which takes place at a certain deformation and then contributes increasingly to the strength, also the extension at maximum load $l_{\text{max}}$ increases for NR-CB50. Furthermore, the notch sensitivity of the materials can be different, leading to different impact tearing behavior. So, for NR-CB30-EOMt and NR-CB30-OMt the existence of the double-edge notches seems to be more significant due to the morphology and therefore, the values are more influenced than the values of NR-CB50.

**Fig. 4.46. Characteristic load-extension diagrams of all materials investigated**

If the NR-CB50 material is disregarded, the $J_d$ values allows for a similar ranking of the materials crack resistance as it was found by the TFA investigations (see Fig. 4.45). The NR material with 30 phr CB and NR-CB30-FA have the lowest resistance against cyclic crack growth with low initial values of tearing energy as well as the highest crack growth rates. The addition of 5 phr OMt and EOMt respectively leads to a shift of the tearing energy where the
Results and discussion

Crack growth begins to higher values. The slope is slightly higher which is attributed to a little faster crack growth.

Table 4. 22. Measuring values $F_{\text{max}}$ and $l_{\text{max}}$ as well as $J_d$ values

<table>
<thead>
<tr>
<th>Materials</th>
<th>$F_{\text{max}}$</th>
<th>$l_{\text{max}}$</th>
<th>$J_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR-CB30</td>
<td>35.7±1.31</td>
<td>29.7±1.57</td>
<td>79.0±3.8</td>
</tr>
<tr>
<td>NR-CB30-FA</td>
<td>34.1±2.3</td>
<td>28.1±2.7</td>
<td>84.6±8.2</td>
</tr>
<tr>
<td>NR-CB30-OMt</td>
<td>47.4±3.3</td>
<td>31.5±1.9</td>
<td>107.2±6.8</td>
</tr>
<tr>
<td>NR-CB30-EOMt</td>
<td>47.5±2.4</td>
<td>19.0±1.7</td>
<td>89.0±7.2</td>
</tr>
<tr>
<td>NR-CB50</td>
<td>84.9±16.6</td>
<td>41.4±8.0</td>
<td>231.0±95</td>
</tr>
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</table>

During cyclic investigations, the NR-CB50 showed the highest value of tearing energy at low crack growth rates, but when the crack is once initiated, it grows with the highest crack growth rate. This is in contrast to the impact tests and may be accounted to the different conditions for the strain crystallization appearing to a higher content at the large deformation during the impact test.
5 Conclusions and Outlook

Clays are excellent candidates for the preparation of rubber based polymer nanocomposite because of their high specific surface area. The presence of strong electrostatic forces between clay layers restricts the successful preparation of clay-rubber nanocomposites, especially in the case of non-polar rubbers like natural rubber (NR). Most of the earlier efforts have been paid in changing the surface character of clay minerals. This challenge persists even after the organic modification of clay. Albeit the modified clay minerals are fairly compatible with the polar rubber like carboxylated nitrile rubber (XNBR), chloroprene rubber (CR) etc., its dispersion in nonpolar rubbers like NR, styrene-butadiene rubber (SBR), ethylene propylene diene monomer rubber (EPDM), butadiene rubber (BR) etc. is rather unsatisfactory. Thus, the dispersion of clay nanoparticles in such non-polar rubber matrices is one of the difficult tasks when applying melt mixing for nanocomposite preparation.

The present investigation is primarily aimed to investigate the potential of layered silicate based on montmorillonite (Mt) as reinforcing filler in non-polar NR matrix. In this regards, we started with organo-montmorillonite (OMt) as nanofiller. But unfortunately a poor dispersion of OMt was found in the non-polar NR matrix. Large agglomerates were observed with bared eyes as well as from microscopic analysis. Therefore, the prime aim of the present work is to develop a novel way to disperse such clay minerals in the non-polar NR rubber matrix by minimizing the strong van der Wall force between the OMt layers.

To successfully overcome this problem, a new approach called “propping-open” process has been adopted and reported in the presented study. In this work OMt was treated with a series of long alkyl chain fatty acids (C16-C22) and these organic acids expanded the interlayer space between the clay layers and ultimately aided the dispersion. The characterization of the expanded organo-montmorillonite (EOMt) was carried out extensively using various analytical techniques, like WAXD, FTIR, TGA and contact angle measurements. WAXD results confirmed that the silicate layers of the Mt are successfully intercalated by fatty acids. The d-spacing of EOMt was increased from 3.6 to 4.2 nm as the alkyl chain length varied from 16 to 22. FTIR confirmed the intercalation of long alkyl chain fatty acids in the interlayer space of clay. A new peak was
observed in FTIR at 1730 cm$^{-1}$ attributed to the strong interaction between C=O group and interlayer cations via water bridge.

Contact angle measurements revealed that the pre-intercalation of long alkyl chain fatty acids makes the OMt clay more hydrophobic. Effect of intercalation time was studied and reported in this work. Variable temperature WAXD and FTIR were also carried out to get more insight about the structural changes of the fatty acid during melting.

The primary aim of this pre-intercalation of fatty acids in the interlayer was to render it and made suitable for the rubber nanocomposite preparation based on non-polar NR. TEM was utilized to explore the morphology of the nanocomposites and proved that the nanocomposites are composed of a random distribution of intercalated and exfoliated aggregates throughout the rubber matrix. The vulcanization kinetics indicates that the presence of Mt affects the curing process of the NR. The activation energy of the curing reaction of NR is decreased in the presence of both OMt and EOMt, and therefore less energy is required for the curing. NR-C22-EOMt showed the most favorable mechanical and dynamic mechanical properties. Tensile strength has been found to increase by 114% for only 5 phr loading of C22-EOMt, while the modulus at 200% elongation undergoes an increment of 77% for the same filler loading. This enhancement results from a strong interaction between NR and Mt promoted by long alkyl chain fatty acid. Therefore, the excess amount of pre-intercalated fatty acids can additionally expand the interlayer spacing of the OMt and facilitate penetration of polymer chains into the layers, which further aid in dispersion. However, no significant change in the stress-strain properties was observed among NR-EOMt nanocomposites. On the other hand, a smaller interlayer distance of OMt, which is generally used as ‘nanofiller’ does not permit its suitability in rubber application particularly in NR.

C22-EOMt was chosen further in order to understand the underlying reinforcing mechanism of this EOMt in NR matrix attributed to its largest interlayer distance among the entire modified sample prepared. Also C22-EOMt showed higher efficiency of intercalation compared to the other surfactants. Semi-empirical micromechanical models such as Guth-Smallwood and Halpin-Tsai models have been utilized to understand the underlying reinforcement behavior of C22-EOMt nanoparticles in NR nanocomposites. Mechanical percolation threshold of C22-EOMt
particles was decreased compared to OMt particles. This is attributed to the formation of a highly networked structure. Therefore, filler-filler networking can occur even at very low loading of C22-EOMt particles. This novel percolation phenomenon was further understood in terms of mass fractal dimension of the nanoparticle clusters. A vanishing fractal dimension of the C22-EOMt clusters was observed. Non-linear viscoelastic behavior (Payne effect) was observed (even at 4 phr of EOMt content) and was found to increase strongly with increasing amount of EOMt. This further supports the idea of development of a highly networked filler structure. The molecular mobility of the macromolecular rubber chains was calculated and reported in terms of apparent activation energy. Higher activation energy was obtained in the case of NR nanocomposites with 10 phr EOMt content. Exfoliation of EOMt particles in NR matrix was observed by TEM. Finally, a higher value of Kraus parameter (m) further supported the enhanced rubber-filler interaction especially in the case of EOMt. The above observations are discussed in a mostly qualitative way by considering currently available empirical models. The results do form a clear picture that helps us to understand the underlying mechanism of rubber reinforcement, especially when the fillers are non-conventional with high aspect ratio.

The effect of different clay minerals on the CB filled NR composites has been investigated systematically. TFA test confirmed the dramatic improvement in fracture behavior of NR-CB composites in the presence of EOMt. The incorporation of clay also altered the viscoelastic behavior of the resulting composites confirmed from DMA study. A synergy in reinforcement between clay and CB was attested by the marked enhancement in mechanical properties. Enormous filler-filler networking (Payne effect) was perceived in the presence of such highly exfoliated clay particles. Finally, it was observed that at least approximately 30-40% reduction in CB loading in this formulation without sacrificing the other physical properties like tensile strength, modulus, hardness etc. could be obtained. Moreover, the beneficial nano-effects of this formulation are reflected in reducing the rolling resistance of a compound prepared using this simple process.

The main aim of this study was to understand the reinforcement of clay minerals in non-polar NR. The unfavorable thermodynamic compatibility between OMt which is commercially known as nanofil-15 and non-polar NR matrix always acts as a strong barrier not only against the
Conclusions and Outlook

The intercalation of the macromolecular rubber chain within the clay layers, but also against the formation of stable homogeneous distribution of the exfoliated clay layers throughout the matrix. Therefore, the further modification of these clay minerals with some organic materials are mandatory in order to achieve highly exfoliated structures of this clay. The selection of surfactants for organic modification needs more critical attention with respect to their structural and chemical differences. Here, we did modification with the help of organic fatty acids. Other options could be like different non-ionic surfactants such as BRIJ 72. It is expected to have higher interlayer spacing of these clay minerals using these non-ionic surfactants attributed to the bulky structures. The impact of such expanded clays on the strain-induced crystallization of NR could be investigated using on-line detection of deformation and fracture (on-line SAXS/WAXS). Clay assisted dispersion of carbon nanotubes (CNT) in non-polar NR matrix could be another great aspect of these highly exfoliated clay minerals. Use of different secondary particles in dispersing CB and CNT is gaining special attention for the last few years. The CB and CNT has tendency to form agglomerates attributed to the strong van der Waal force of attraction. Apart from the dispersion, one can imagine the synergy of 2-dimensional clay minerals and 1-dimensional CNT in the same rubber matrix.

This presented work is directed towards the way of producing highly exfoliated rubber-clay nanocomposites adopting “propping-open approach” particularly based on non-polar NR. The rubber-clay nanocomposites prepared therefrom might be utilized in a wide range of applications requiring materials with high strength, improved barrier properties, light weight etc. Industrial applications of such clay based rubber nanocomposites include tire, automotive, aircraft and aerospace industries. There is never-ending demand in the tire industry to improve durability of tires, increase safety and to consume less fuel. Those demands can be fulfilled if rolling resistance of a tire is reduced, the wear property is being enhanced and an improvement of wet as well as ice grip is enhanced to avoid skid. These all properties of tire not only depend on the polymer systems but also largely depend on the nature and type of fillers. Therefore, the presented work can be utilized to formulate truck tire recipe with aforesaid desirable properties. Nevertheless, we still have to go long way for the fruitful use of such rubber nanocomposites in various commercial applications.
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