Modification of Rubber Particle filled Thermoplastic with High Energy Electrons

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Gutachter: Prof. Dr.-Ing. Michael Gehde
Prof. Dr. rer. nat. habil. Gert Heinrich

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Modification of rubber particle filled thermoplastic with high energy electrons

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Abstract

In present study, high energy electrons were used to modify blends based on RP and PP under two conditions: stationary and in-stationary conditions. Modification of blend under stationary condition is a process which is established in industrial application and where required absorbed dose is applied to form parts (after molding) at room temperature and in solid state. On the contrary, the modification of blend with high energy electrons under in-stationary condition is a new process (electron induced reactive processing) where required absorbed dose is applied to a molten state during melt mixing process. The modification of blend based on RP and PP under stationary condition resulted in slightly enhancement of tensile properties while the modification of this blend under in-stationary condition resulted in deterioration of tensile properties due to degradation of the PP matrix. Thus, special grafting agent (GA) is required for improving the tensile properties. The effect of different GAs on tensile, thermal, dynamic mechanical as well as morphological properties and melt flow properties of blends based on RP and PP were determined. The optimum absorbed dose for modification of blend based on RP and PP under both conditions was evaluated. In addition, the effect of treatment parameters of electron induced reactive processing was investigated.

Keywords: Rubber recycling, Rubber particle, Polypropylene, Grafting agent, Blend, Interfacial adhesion, Compatibility, High energy electrons, Stationary condition, In-stationary condition (electron induced reactive processing)
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Chemnitz, February 2010                                          Kunlapaporn Sritragool
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<tr>
<td>AAc</td>
<td>Acrylic Acid</td>
</tr>
<tr>
<td>AAm</td>
<td>Acrylamine</td>
</tr>
<tr>
<td>AN</td>
<td>Acrylonitrile</td>
</tr>
<tr>
<td>A-TMMT</td>
<td>Tetramethylolmethane Tetraacrylate</td>
</tr>
<tr>
<td>ATU</td>
<td>1-Allyl-2-Thiourea</td>
</tr>
<tr>
<td>BDDA</td>
<td>1,4-Butabediol Diacrylate</td>
</tr>
<tr>
<td>BDK</td>
<td>Benzyl Dimethyl Ketal</td>
</tr>
<tr>
<td>CPE</td>
<td>Chlorinated Polyethylene</td>
</tr>
<tr>
<td>DCP</td>
<td>Dicumyl Peroxide</td>
</tr>
<tr>
<td>DEGDMA</td>
<td>Diethylene Glycol Dimethacrylate</td>
</tr>
<tr>
<td>DHBP</td>
<td>2,5-dimethyl-2,5-di(tert-butylperoxy)hexane</td>
</tr>
<tr>
<td>DPGDA</td>
<td>Dipropylene glycol Diacrylate</td>
</tr>
<tr>
<td>DTMPTA</td>
<td>Dtrimethylol Propane Tetraacrylate</td>
</tr>
<tr>
<td>EAA</td>
<td>Ethylene-Acrylic Acid</td>
</tr>
<tr>
<td>EA</td>
<td>Elastomeric Alloy</td>
</tr>
<tr>
<td>EB</td>
<td>Electron Beam</td>
</tr>
<tr>
<td>ENR/LLDPE-g-VM</td>
<td>Epoxidized Natural Rubber/Vinyl Monomer-grafted-Linear Low Density Polyethylene</td>
</tr>
<tr>
<td>EPDM</td>
<td>Ethylene Propylene Diene Monomer rubber</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron Spectroscopy for Chemical Analysis</td>
</tr>
<tr>
<td>EVA</td>
<td>Ethylene Vinyl Acetate copolymer</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>GA</td>
<td>Grafting Agent</td>
</tr>
<tr>
<td>GRT</td>
<td>Ground Rubber Tire</td>
</tr>
<tr>
<td>HDDA</td>
<td>1,6-Hexanediol Diacrylate</td>
</tr>
<tr>
<td>HDPE</td>
<td>High Density Polyethylene</td>
</tr>
<tr>
<td>HVA-2</td>
<td>N, N'-m-phenylenebismaleimide</td>
</tr>
<tr>
<td>IBE</td>
<td>Ethylene-co-Glycidyl Methacrylate copolymer</td>
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<tr>
<td>IIR</td>
<td>Butyl Rubber</td>
</tr>
<tr>
<td>iPP</td>
<td>Isotactic Polypropylene</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low Density Polyethylene</td>
</tr>
<tr>
<td>MA</td>
<td>Maleic Anhydride</td>
</tr>
<tr>
<td>MAA</td>
<td>Methacrylic Acid</td>
</tr>
<tr>
<td>MFI</td>
<td>Melt Flow Index</td>
</tr>
<tr>
<td>MIBK</td>
<td>Methyl Isobutylketone</td>
</tr>
<tr>
<td>NR</td>
<td>Natural Rubber</td>
</tr>
<tr>
<td>NR/SBR</td>
<td>Natural Rubber/Styrene Butadiene Rubber</td>
</tr>
<tr>
<td>PCs</td>
<td>Functionalized Plastic Resin Comptibilizers</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PF</td>
<td>Phenol Formaldehyde</td>
</tr>
<tr>
<td>PFM</td>
<td>Polyfunctional Monomers</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PO</td>
<td>Peroxide</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene random copolymer</td>
</tr>
<tr>
<td>PP*</td>
<td>Modified PP random copolymer</td>
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<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
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</tr>
<tr>
<td>PP-g-MA</td>
<td>Maleic Anhydride grafted Polypropylene</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PVC</td>
<td>Poly(vinyl chloride)</td>
</tr>
<tr>
<td>rHDPE</td>
<td>recycled High Density Polyethylene</td>
</tr>
<tr>
<td>RP</td>
<td>Rubber Particle</td>
</tr>
<tr>
<td>SBR</td>
<td>Styrene Butadiene Ruber</td>
</tr>
<tr>
<td>SEBS</td>
<td>Styrene-Ethylene-Butylene-Styrene</td>
</tr>
<tr>
<td>SEBS-g-MA</td>
<td>Maleic Anhydride grafted Styrene-Ethylene-Butylene-Styrene</td>
</tr>
<tr>
<td>SSSE</td>
<td>Solid-State Shear Extrusion</td>
</tr>
<tr>
<td>TAC</td>
<td>Triallyl Cyanurate</td>
</tr>
<tr>
<td>TAIC</td>
<td>Triallyl Isocyanurate</td>
</tr>
<tr>
<td>TCI</td>
<td>Trichloroisocyanuric</td>
</tr>
<tr>
<td>TMPTA</td>
<td>Trimethylpropane Triacrylate</td>
</tr>
<tr>
<td>TMPTMA</td>
<td>Trimethylolpropane Trimethacrylate</td>
</tr>
<tr>
<td>TPE</td>
<td>Thermoplastic Elastomer</td>
</tr>
<tr>
<td>TPV</td>
<td>Thermoplastic Vulcanizate</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>WBR</td>
<td>Waste Butyl Rubber</td>
</tr>
<tr>
<td>WLDPE</td>
<td>Waste Low Density Polyethylene</td>
</tr>
</tbody>
</table>

**Symbols**

\[ a_{CN} \quad [kJ/m^2] \quad \text{Charpy Impact Strength} \]

\[ E \quad [MPa] \quad \text{Modulus} \]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Description</th>
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<tbody>
<tr>
<td>E'</td>
<td>[MPa]</td>
<td>Storage Modulus</td>
</tr>
<tr>
<td>E''</td>
<td>[MPa]</td>
<td>Loss Modulus</td>
</tr>
<tr>
<td>L₁</td>
<td>[mm]</td>
<td>Initial Length</td>
</tr>
<tr>
<td>L₂</td>
<td>[mm]</td>
<td>Final Length</td>
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<tr>
<td>Tan δ</td>
<td>[1]</td>
<td>Loss Tangent</td>
</tr>
<tr>
<td>Tc</td>
<td>[°C]</td>
<td>Crystallization Temperature</td>
</tr>
<tr>
<td>Tg</td>
<td>[°C]</td>
<td>Glass Transition Temperature</td>
</tr>
<tr>
<td>Tm</td>
<td>[°C]</td>
<td>Melting Temperature</td>
</tr>
<tr>
<td>ΔHₘ</td>
<td>[J/g]</td>
<td>Melting Enthalpy/Heat of Fusion</td>
</tr>
<tr>
<td>σ</td>
<td>[MPa]</td>
<td>Stress</td>
</tr>
<tr>
<td>σₘ</td>
<td>[MPa]</td>
<td>Tensile Strength</td>
</tr>
<tr>
<td>ε</td>
<td>[%]</td>
<td>Strain</td>
</tr>
<tr>
<td>εₜ</td>
<td>[%]</td>
<td>Elongation at Break</td>
</tr>
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1 Introduction

Properties of polymers can be improved by adding of polymers (polymer blends) as well as inorganic or organic filling or reinforcing components (hybrid compounds, composites). The modification of thermoplastic commodities (e.g. polypropylene) via generation of polymer blends containing an entropy elastic soft phase offers large opportunities for improvement of material properties. These blends (Thermoplastic vulcanizate (TPV)) consist of a thermoplastic (hard phase) and disperse rubber phase (soft phase). They are produced by reactive processing which combines simultaneously melt mixing and cross-linking of rubber within a thermoplastic at elevated temperature. Generally, the rubber phase is crosslinked by peroxides or by activated phenol formaldehyde resins. Both radical generation systems have their own limitations. Thus, the peroxide system results in an unpleasant smell or a blooming effect. Furthermore, the generation rate of peroxide radicals at constant temperature depends on time. The properties of TPVs (e.g. elongation at break, toughness) can be controlled by content, crosslinking yield, particle size and dispersion of rubber phase. The sizes of their crosslinked rubber domains amount to 0.5 µm to 5 µm.

Another possibility of generation of blends of thermoplastics with disperse crosslinked rubber particles offers the addition of rubber particle (RP), ground waste rubber, to thermoplastics during melt mixing process. The size of rubber particles used in blending with thermoplastic depends on type of grinding process. Normally, it is around 30 µm to 400 µm. Using melt compounding with dynamic stabilization at the interface elastomeric alloy (EA) can be produced. Their properties are closed to those of thermoplastic elastomer (TPE), especially TPV based on polypropylene and ethylene propylene diene rubber (EPDM). The EA is a dynamic stabilized blend of polypropylene copolymer with RP, especially RP based on natural rubber (NR)/styrene butadiene rubber (SBR). Dynamic stabilization process is a reactive melt mixing process using organic peroxide for compatibilizing of RP with polypropylene copolymer via interphase grafting reaction between RP and polypropylene copolymer. Therefore, it is possible to use EA instead of TPV in certain application such as in automotive industry for parts exposed to impact loads at lower temperature and also in leisure and sports industry. The use of dynamic stabilization is limited to blends of polypropylene.
copolymers with RP based on NR/SBR or NR. When the dynamic stabilization process was applied to blend of polypropylene copolymer with another type of RP such as EPDM, it resulted in no improvement of mechanical properties.

Further, polymers can be modified by high energy electrons. Polymer modification with high energy electrons can cause e.g. degradation (main chain scission), functionalization or crosslinking and result in changed properties of polymers such as chemical, physical, thermal, and mechanical properties. In rubber recycling, high energy electrons can be used to modify surface of RP, graft monomer onto RP and compatibilize of RP with thermoplastic. In present study, high energy electrons have been introduced for compatibilizing the blend of RP with polypropylene copolymer instead of dynamic stabilization process in order to develop a novel method which is not limited to a small number of polymers as well as type of RP. The blend of RP with polypropylene copolymer has been modified in presence of grafting agents (GAs) under stationary and in-stationary conditions at different doses.

Polymer modification with high energy electrons under stationary conditions characterizes a process which is established in industry and where required absorbed dose is applied to form parts (after molding) in solid state and at room temperature. Polymer modification with high energy electrons under in-stationary conditions is a novel process where required radicals are generated via high energy electrons without any use of additional additive during melt mixing process. This novel process is comparable with that of dynamic stabilization, but uses another radical generation system.

In the next chapter, state of the art, the earlier studies in the field of utilization of RP in polypropylene and polyethylene (PE), use of ionizing radiation in rubber recycling as well as electron induced reactive processing are surveyed. The detailed aims as well as the tasks to be solved in this study are presented in chapter 3 and 4, respectively. In chapter 5, materials used and experimental procedures are described. Chapter 6 contains results of characterization of modified polypropylene copolymer, the effect of modified polypropylene copolymer on properties of the blend of RP with polypropylene copolymer, the effect of type of grafting agents as well as high energy electrons on properties of
blends. Finally, the comparison of properties of blends compatibilized by high energy electrons with EA is also shown in chapter 6. This study ends with conclusions and further studies (chapter 7).
2 State of the Art

Disposal of rubber wastes, discarded tires and other rubber goods is challengeable. There are about five main approaches used in disposal of rubber wastes: landfills and use in civil engineering, incineration for fuel value, pyrolysis, reclaiming process as well as devulcanization and utilization of rubber wastes in thermoplastics and rubber compounds. De summarized that the utilization of rubber wastes in thermoplastics and rubbers is the most economic alternative than other approaches [1]. Moreover, the utilization of rubber wastes in the thermoplastics is more favorable than that in rubber compounds because rubber wastes cannot be utilizes in large amount in the rubber compounds and addition of rubber wastes into rubber compounds results in poor mechanical properties as well as processability [2].

2.1 Size reduction techniques used in production of rubber particle

Before utilization of rubber wastes in thermoplastics, rubber wastes are ground into powder or particle by various grinding processes. These grinding processes are ambient grinding, cryogenic grinding, wet grinding and solid-state shear extrusion (SSSE) pulverization. Firstly, rubber wastes are cut and then shredded into small chips with size of 1” x 1” or 2” x 2” and then ground into powder [3 – 4].

The ambient grinding is the simplest size reduction process and a mechanical grinding technique. These rubber waste chips are passed through a conventional high-powered rubber mill set at close nip at room temperature. The particle size and particle size distribution of rubber particle (RP) depend on time that rubber chips spent in a mill and the type of mill used. The higher the time of rubber wastes chips spent in a mill, the greater the size reduction. Thus, price of RP increases with decreasing particle size. In the ambient grinding process, heat is generated during grinding process so that the RP can be degraded. The ambient grinding process produces RP that has irregular shape with high surface roughness, fibril features and cavities in the surfaces.

The cryogenic grinding process was developed in the mid 1960s in order to reduce size of rubber waste chips. It was commercialized in the late 1960s [5 – 6]. In cryogenic grinding, rubber waste chips are cooled by liquid nitrogen or liquid...
carbon dioxide so that they are frozen. Then, the frozen chips are ground into particles by an impact mill such as a hammer or a pin mill. Then the RP is dried as well as fiber and metal are separated. Lastly, the RP is sorted into various mesh sizes. The cryogenic grinding process produced RP with relatively smooth fracture surface, low specific surface area and broader particle size distribution. Heat is also generated in the cryogenic grinding process but due to low temperature less degradation occurred in RP. Moreover, almost all fibers and steel are liberated from the RP so that yield of usable product is high and loss of rubber is little.

The wet grinding process is a modified ambient grinding process for reducing size of rubber wastes chips by grinding them in a liquid medium, generally water. It involves in passing these chips in water through a series of grinding wheels that move concurrently and are lubricated by water. After ending of grinding process, water is separated from the RP. Then, RP is dried. The particle size of RP is controlled by time spent in the wet grinding process. The RP produced by this process has a very small particle size with obtained range of 400 – 500 mesh [5]. Drawbacks of the wet grinding process are a high energy consumption caused by drying step and inadequate separation of RP and fiber as well as steel [7].

The SSSE pulverization process is a mechano–chemical process for producing RP. In the SSSE pulverization process, a modified co-rotating twin screw extruder from Berstorff Maschinenbau GmbH, Germany, with extensive cooling for removing frictional heat had been used to pulverize rubber wastes [8]. The chips are fed into a hopper and then conveyed into a compression zone. In the compression zone, the chips are subjected to high compressive shear and pressure. Under simultaneous action at compressive shear, pressure and tension from rotating screw, the rubber wastes chips are ground into powder. Particle size of RP can be controlled by varying screw configuration and processing parameters such as feeding speed and screw speed. In SSSE pulverization process, chemical bonds in rubber wastes are broken so that partial devulcanization is occurred. The RP produced from SSSE process has large surface area and “cauliflower-like” morphology [8].
2.2 Utilization of rubber particle in thermoplastics

From blending of RP with thermoplastic, impact-resistant plastics and thermoplastic elastomers (TPEs) can be obtained. The most thermoplastic matrixes used in blending with RP are polypropylene, polyethylene (PE) and poly(vinyl chloride) (PVC) [9 – 12]. Mechanical properties of blends based on RP and thermoplastic depend on nature of RP, content of RP, polymer matrix type, dispersion and interaction between RP and thermoplastic matrix as well as interfacial adhesion between RP and thermoplastic matrix [13 – 15]. The interfacial adhesion between RP and thermoplastic matrix is a main factor for controlling the mechanical properties of those blends. Many studies reported that incorporation of RP into thermoplastic results in lowering of mechanical properties of blends because of poor interfacial adhesion between RP and thermoplastic matrix as well as lack of reactive sites on surface of RP [16 – 18]. The interfacial adhesion between RP and thermoplastic matrix is poor due to crosslinked structure of RP which blocks molecular entanglement [19]. The addition of RP ground by cryogenic grinding process into polypropylene resulted in lowering tensile properties and impact strength of polypropylene because of poor adhesion between RP and polypropylene [16]. McKirahan reported that tensile strength, elongation at break and hardness of recycled high density polyethylene (HDPE) were decreased when RP was added [20].

As mentioned above, poor interfacial adhesion between RP and thermoplastic impairs the mechanical properties of blend. Many approaches such as compatibilization technique and surface modification have been applied to overcome this problem.

2.2.1 Enhancement of interfacial adhesion via compatibilization technique

Compatibilization technique is an approach used to improve the interfacial adhesion between thermoplastic matrix and RP. Various polymeric materials and fresh rubbers are used as compatibilizers. Natural rubber (NR) was used as a compatibilizer in blend of polypropylene with RP [16]. The impact strength of RP/polypropylene blend was improved when NR was added into that blend. According to the study of Choudhury and co-worker, chlorinated polyethylene (CPE) was added as a compatibilizer into blend of RP with low density
polyethylene (LDPE) [17]. The CPE was selected because its structure is similar to LDPE phase and CPE is an elastomeric material. Addition of CPE into blend of LDPE with RP, ground rubber tire (GRT), resulted in enhancement of tensile strength, elongation at break and impact strength as well as lowering of melt flow index (MFI). The decrease in MFI of LDPE/RP blend showed the improvement of interfacial adhesion between LDPE matrix and RP. It was reported that ethylene propylene diene rubber (EPDM) was also used as compatibilizer in blend of RP with HDPE because the structure of EPDM is similar with HDPE and EPDM is rubbery in nature [21]. Not only EPDM but also dicumyl peroxide (DCP) and dimethyl silicone oil were added in HDPE/RP blend to improve compatibility. The impact strength and elongation at break of HDPE/RP blend increased when EPDM of 10 wt%, DCP of 0.2 wt%, and dimethyl silicone of 4 wt% were added. According to the study of Mészáros and co-workers, ethylene vinyl acetate copolymer (EVA) was chosen to compatibilize blend of LDPE with RP because EVA has rubber-like properties and good interfacial adhesion to RP and LDPE [22]. Phinyocheep and co-workers reported that addition of styrene-ethylene-butylene-styrene (SEBS) and maleic anhydride-grafted-styrene-ethylene-butylene-styrene (SEBS-g-MA) in blend of polypropylene with RP obtained from buffing process in sport shoe soles manufacture resulted in increasing impact strength and elongation at break [23]. The improvement of impact strength and elongation at break is due to reduction of interfacial tension between RP and polypropylene matrix as well as decrease of particle size of RP. Isayev and co-worker used various compatibilizers along with sulfur or phenolic resin curing systems in RP/polypropylene blends and ultrasonically devulcanized RP/polypropylene blend [15]. Among various compatibilizers, incorporation of maleic anhydride-grafted polypropylene (PP-g-MA) into blends enhanced tensile strength and Young’s modulus. Later, Isayev and co-worker added PP-g-MA or CPE in blends of HDPE with ultrasonically devulcanized RP and sulfur curing system [24]. They reported that mechanical properties of blend were little improved when PP-g-MA or CPE were added into blend. The SEBS-g-MA was added in blends of untreated or ultrasonically treated RP with polyolefins, PP-g-MA and LDPE [25]. The addition of SEBS-g-MA into these blends resulted in enhancement of mechanical properties. The mechanical properties of untreated RP/polyolefin blend were improved more than those of ultrasonically treated RP/polyolefin blend. It was reported that the incorporation of
epoxidized natural rubber/vinyl monomer-grafted-linear low density polyethylene dual compatibilizer (ENR/LLDPE-g-VM dual compatibilizer) into RP/LLDPE blend improved the interfacial adhesion between RP and LLDPE matrix and resulted in increase of mechanical properties, especially elongation at break [26]. The polymeric compatibilizers, functionalized plastic resin compatibilizers (PCs) and elastomeric compatibilizers, were chosen to improve compatibility between RP and waste thermoplastic matrix, waste HDPE, waste LDPE as well as mixed waste polypropylene with PE [27].

The interfacial adhesion or compatibility between RP and thermoplastic matrix can also be enhanced by the addition of peroxide. Michael and co-workers developed the process named dynamic stabilization, a reactive melt mixing process with \textit{in-situ} compatibilization between RP and polypropylene copolymer phases [11, 28 – 31]. In the dynamic stabilization process, peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (DHBP), was added in order to initiate grafting reaction between RP and polypropylene copolymer matrix [28, 31]. Dynamic stabilized RP/polypropylene copolymer blend is called elastomeric alloy (EA). Compared to blend, mechanical properties of EA are improved and close to those of TPV. According to study of Sonnier and co-workers, the blends of recycled high density polyethylene (rHDPE) with RP were compatibilized by using DCP [32]. The elongation at break and impact strength values of rHDPE/RP blend were improved when DCP was added due to improvement of interfacial adhesion between RP and rHDPE. Liu and co-workers used t-butyl hydroxide to compatibilize blend of polypropylene with waste EPDM powder [33 – 35]. Compatibilized waste EPDM powder/polypropylene blend with t-butyl hydroxide has better tensile strength and elongation at break than uncompatibilized waste EPDM powder/polypropylene blend. The addition of DCP along with SEBS-g-MA into blends of LLDPE with RP improved mechanical properties of these blends [36]. Awang reported that addition of DCP and N, N’-m-phenylenebismaleimide (HVA-2), a coagent, into polypropylene/RP blends resulted in enhancement of tensile properties, swelling resistance and interfacial adhesion [37]. The DCP and maleic anhydride (MA) were added together for compatibilizing LLDPE/RP composites [13]. It was resulted in improvement of impact energy of LLDPE/RP composites.
2.2.2 Enhancement of interfacial adhesion via surface treatment

Surface treatment of RP is another approach applied to improve interfacial adhesion and compatibility between RP and thermoplastic matrix. Oliphant and co-worker coated RP with ethylene-acrylic acid (EAA) copolymer and then the coated RP was compounded with LLDPE [38]. Compared to uncoated RP/LLDPE blend, impact strength and tensile properties of coated RP/LLDPE blend were higher because the functional groups on the surface of RP interacted with carboxylic acid groups on the EAA copolymer. Various functional monomers were used to treat RP in order to improve interfacial adhesion [13]. The treated RP were blended with LLDPE in presence of ethylene-co-glycidyl methacrylate copolymer (IBE). Among blends based on different treated RPs, blend based on treated RP with methacrylic acid (MAA) and 1-allyl-2-thiourea (ATU) had highest impact energy due to interaction between treated RP and IBE. Pramanik and co-worker reported that the impact strength of composites based on LLDPE was improved when RP was modified with a solution of DCP and triallyl cyanurate (TAC) in methyl isobutylketone (MIBK) [13]. It was reported that RP was treated by a solution of potassium permanganate (KMnO₄) in aqueous acetone for generation of hydroxyl group on surface of RP [33, 39]. According to the study of Colom and co-workers, RP was modified by sulphuric acid, γ-methacriloxypetyl-trimethoxysilane (silane A-174) and chlorination with trichloroisocyanuric (TCI) to enhance compatibility between RP and HDPE [40]. Among various treatment processes, the blend based on modified RP by chlorination with TCI has poorest properties. Later, Colom and co-workers treated RP with sulfuric acid (H₂SO₄), nitric acid (HNO₃) and perchloric acid (HClO₄) [41]. Then, the treated RP were compounded with HDPE. Compared to composites based on different treated RP, composite based on treated RP with H₂SO₄ has the highest tensile strength and modulus. SEM study revealed that treated RP with H₂SO₄ has rough surface which confirmed the improvement in tensile strength and modulus due to mechanical adhesion. According to the study of Shanmugharaj and co-workers, allylamine was functionalized onto surface of RP in presence of benzoyl peroxide [42]. Allylamine functionalized RP was compounded with polypropylene and PP-g-MA. Non-functionalized RP/polypropylene/PP-g-MA composites had lower tensile strength and elongation at break than allylamine functionalized RP/polypropylene/PP-g-MA.
composites. Shanmugharaj and co-workers also used ultraviolet (UV) radiation to graft allylamine onto RP in presence of benzophenone, a radiation sensitizer [43]. The mechanical properties were improved when allylamine grafted RP used instead of non-grafted RP in blends with polypropylene and PP-g-MA due to increase in compatibility between RP and polypropylene through chemical reaction of allylamine grafted RP with PP-g-MA, compatibilizer. The RP was modified with acrylamine (AAm) by also using UV radiation in presence of benzophenone and then modified RP, RP-g-AAm, were blended with HDPE and PP-g-MA [44]. The mechanical properties of HDPE/RP-g-AAm/PP-g-MA composite were higher than those of HDPE/RP/PP-g-MA composite due to the interfacial reaction between RP-g-AAm and PP-g-MA.

2.3 Polymer modification with high energy electrons

High energy electrons are a directly ionizing radiation and have been used to modify polymeric materials. The high energy electrons are produced by acceleration of electrons in electron accelerator. When the high energy electrons enter the polymeric material, they lose energy due to their interactions of them with the atomic electrons as well as atomic nuclei of the polymeric materials and are scattered [45 - 46]. The interactions with atomic electrons result in generation of excited atoms or molecules as well as ionization. In contrast, the interactions with atomic nuclei result e.g. in generation of x-rays (Bremsstrahlung) [45 – 49]. The schema of principle of interaction of high energy electrons with matter are shown in figure 2.1.

Figure 2.1: Schema of principle of high energy electrons [45].
The main primary reactions that are induced in the so called physical phase are:

1. Ionization: \( AB \rightarrow AB^+ + e^- \)
2. Excitation: \( AB \rightarrow AB^* \)
3. Capture of electron: \( AB + e^- \rightarrow AB^- \)

These reactive species lead preferentially to generation of radicals via excitation and charge transfer reaction (48).

4. Dissociation of ionized or excited molecules into free radicals and radical ions: \( AB^+ \rightarrow A^+ + B^+ \), \( AB^- \rightarrow A^- + B^- \) and \( AB^* \rightarrow A^+ + B^- \)

These free radicals will initiate chemical reactions resulting in change in the properties of polymeric materials. The chemical reactions occurred are main chain scission (degradation), crosslinking, functionalization, formation of small molecular products and structural rearrangement [48 – 50].

In polymeric materials, crosslinking and main chain scission are the most important processes. It was suggested that polymers with a single or no side chain (-CH₂-CR₁H- or –CH₂-CH₂-) are predominant to crosslinking whereas those with two side-chains attached to a single backbone carbon (-CH₂-CR₁-R₂-) are predominant to main chain scission [47 – 48]. PE, PVC, polystyrene (PS), NR, and styrene butadiene rubber (SBR) are polymers that tend to crosslinking [48 – 49, 51 – 52]. In contrast, poly(methyl methacrylate) (PMMA) and butyl rubber (IIR) are sample of polymers predominantly to chain scission [48, 52].

When polypropylene is subjected to high energy radiation, both crosslinking and degradation occur simultaneously [53 – 56]. Predominance of crosslinking or degradation relies on various factors such as degree of crystallinity, isotacticity, morphology and conditions of irradiation [53, 55, and 57]. Compared to isotactic polypropylene, atactic polypropylene tends more to crosslinking due to a predominantly amorphous structure [58]. Nevertheless, polypropylene tends to degradation by \(\beta\)-chain scission after high energy radiation in air [58– 61]. Further, ethylene-propylene block copolymer and ethylene-propylene random copolymer tend to less degradation than polypropylene homopolymer because ethylene units in the main chain of the copolymer mainly tend to crosslinking [54, 59].
In order to promote crosslinking in polypropylene, various polyfunctional monomers (PFMs) were used [61 – 63]. Unsaturated sites contained in the PFMs will react rapidly with macroradicals generated by high energy radiation. Thus, necessary radiation dose is lowered and possibility of crosslinking is increased. It was reported that the crosslinking of polypropylene in presence of PFMs by high energy radiations is different from other polymer [62]. Type of PFMs and the mechanism of molecular changes play an important role in radiation crosslinking of polypropylene.

High energy radiation is not used only to crosslink of polypropylene but also to functionalize polypropylene. Both high energy electrons and gamma irradiation were used to functionalize polypropylene at room temperature in air without adding of monomers [64 – 66]. The carbonyl, carboxyl, ether, and hydroxyl groups were generated on treated polypropylene. The treated polypropylene was used to improve compatibility between isotactic polypropylene and talc [65]. Only Young’s modulus increased when treated polypropylene of 10 wt% was added into 70/20 isotactic polypropylene/talc blends. The compatibility of polyamide-6 (PA6) with polypropylene was increased when polypropylene was treated with gamma irradiation or high energy electrons in air [66]. It was reported that polypropylene homopolymer and polypropylene copolymer were modified by high energy electrons under air atmosphere in order to improve compatibility between RP based on NR/SBR as well as EPDM and polypropylene copolymer and polypropylene homopolymer [67]. Not only polypropylene but also PE was modified by high energy radiation [64]. The PE was modified by \( \gamma \)-irradiation, high energy electrons, ultraviolet as well as microwave irradiation for improving the compatibility between engineering plastics and inorganic fillers. Moreover, it was reported that the compatibility between HDPE and polyethylene terephthalate (PET) was enhanced when HDPE was treated by gamma irradiation [68].

In addition, high energy electron has been used to improve melt strength of polypropylene. Polypropylene with long-chain branching has high melt strength. Yoshii and co-workers used high energy electrons to modify polypropylene in presence of various types of PFMs in order to improve melt strength of polypropylene [69]. The 1, 4 – butanediol diacrylate (BDDA) and 1, 6 – hexanediol diacrylate (HDDA), two functionality, are the most effective in improvement of melt
strength of polypropylene. It was also reported that gamma irradiation was used to enhance melt strength of polypropylene in presence of triallyl isocyanurate (TAIC) and trimethylolpropane trimethacrylate (TMPTMA) [70]. According to the study of Krause and co-workers, isotactic polypropylene homopolymer was treated by high energy electrons in molten state without adding of PFMs for generation of long-chain branching [71].

Further, high energy electrons and other ionizing radiations such as gamma irradiation had been applied to modify the surface of RP, graft monomers on to RP and compatibilize RP with thermoplastic matrix. It was reported that different type of RP, GRT prepared by ambient, ambient and then cryogenic, cryogenic and wet-ambient grinding processes, were modified by high energy electrons, plasma and corona [72]. From electron spectroscopy for chemical analysis (ESCA), it was revealed that modified RP by high energy electrons had higher oxygen content than modified RP by corona or plasma treatments. Some oxygen containing functional groups were generated on surface of modified RP by high energy electrons. The modified RP were compounded with LLDPE and IBE, the compatibilizer. The impact energy of composites based on modified RP by high energy electrons was higher than that of composites based on modified RP by corona or plasma treatments. The improvement of impact energy or ductility of composites based on modified RP by high energy electrons is due to the interaction between IBE and functional groups generated on surface of RP. The MFI values of composites based on modified RP were higher than MFI value of composite based on unmodified RP. This is due to low molecular weight moieties formed on the surface of RP. Recently, Sonnier and co-workers modified RP by gamma irradiation under air atmosphere [39]. The RP was modified at 15, 25, 50, 75, and 100 kGy. It was reported that carbonyl groups are formed on modified RP. The unmodified and modified RP were blended with HDPE and maleic anhydride-grafted PE (PE-g-MA), the compatibilizer. When modified RP was added into composites, there is no improvement in mechanical properties of composites.

The gamma irradiation has been used to graft ethyl acrylate (EA) onto RP [73 – 74]. The RP-g-EA was blended with polyacrylic rubber compounds. According to the study of Abdel-bary and co-workers, different vinyl monomers, acrylamide (AAm), acrylic acid (AAc) and acrylonitrile (AN), were grafted onto RP via gamma
irradiation [75]. Currently, Tolstov and co-workers had also grafted AAm onto RP by gamma irradiation at absorbed dose of 10 kGy [76]. In their study, maleic anhydride (MAH) was grafted onto HDPE by gamma irradiation. The maleic anhydride-grafted HDPE (HDPE-g-MA) was compounded with EPDM and RP-g- AAm. Compared to TPE based on both non-grafted RP and non-grafted HDPE, the mechanical properties based on both grafted RP and grafted HDPE were enhanced.

Lately, Sonnier and co-workers used gamma irradiation to in-situ compatibilize rHDPE with RP [77]. The blends of rHDPE and RP were treated at 15, 25, 50, and 100 kGy under air atmosphere. Mechanical properties of rHDPE/RP blend, especially elongation at break and charpy impact strength, were improved when a dose of 25 kGy to 50 kGy was applied. The possible reaction mechanism occurred associated with formation of free radicals leading to chain scission within RP, crosslinking of PE matrix, and grafting at the interface of RP and rHDPE. Maziad and co-worker also used gamma irradiation to modify the blend of waste low density polyethylene (wLDPE) with waste butyl rubber (wBR) in presence of various compatibilizers [78]. The wBR/wLDPE blends with compatibilizers were modified at 100, 150, 200, and 400 kGy under air atmosphere. Up to doses of 200 kGy, the tensile strength increases while elongation at break decreases. The increase in tensile strength indicated that crosslinking is predominantly. Among various compatibilizers, diethylene glycol dimethacrylate (DEGDMA) resulted in highest gel fractions of blends.

2.4 Electron induced reactive processing

High energy electrons have been applied to modify polymers, polymer blends or polymer composites under in-stationary conditions during melt mixing process. This process is designated as electron induced reactive processing. According to the study of Wagenknecht and co-workers, a 1.5 MeV electron accelerator was coupled to a banbury mixing chamber for studying the effect of dose and grafting agent (GA) on processing behavior as well as mechanical and thermal properties of polymer compounds [79]. The schematic representation of experimental equipment is shown in figure 5.8 in experimental part. The composite of polypropylene copolymer and magnesium hydroxide (Mg(OH)\textsubscript{2}) in presence of
TAC was also modified by high energy electrons under in-stationary and stationary condition [80]. For stationary condition, high energy electrons modify polymer or polymer blends that were already molded into form parts in solid state and at ambient temperature. The tensile and thermal properties as well as MFI values of polypropylene composites prepared by high energy electrons under in-stationary condition were compared with those of composites prepared by high energy electrons under stationary condition.

Recently, the modification of blend based on polypropylene homopolymer and EPDM by electron induced reactive processing resulted in TPV [81]. The best balance of mechanical properties of TPV based on polypropylene and EPDM was obtained at electron energy of 1.5 MeV, treatment time of 15 s, absorbed dose of 50 kGy and rotor speed of 45 rpm (rotation per minute). There are two reactions occurred under this modification: in-situ compatibilization of polypropylene with EPDM as well as in-situ crosslinking of EPDM phase. The blend of polypropylene with epoxidized natural rubber (ENR) and TAC was also modified by electron induced reactive processing [82].

In conclusion, from literature review in state of the art, it is revealed that the various compatibilizers or surface modification of RP have been applied for improvement of interfacial adhesion/compatibility between RP and thermoplastic, especially polypropylene and PE. Moreover, it is shown that the ionizing radiation have been used to modify RP and thermoplastics. Those modifications result in improved properties of RR/thermoplastic blends. However, there is no publication about the use of high energy electrons for modification of blend based on RP and thermoplastic resulting in mechanical properties of modified blend of RP with thermoplastic comparable to those of EA as well as TPV.
3 Aim of Study

Melt mixing of RP and thermoplastics results in incompatible physical blend. Using melt compounding with dynamic stabilization at the interface, a compatible blend with improved properties can be produced. Melt compounding with dynamic stabilization is a radical controlled process based on thermal induced decay of peroxide. Nevertheless, this process is limited to a blend made from random polypropylene copolymer and RP based on NR/SBR. Thus, the aim of this work is focused on evaluation of polymer modification with high energy electrons and electron induced reactive processing regarding compatibilization of blend components as well as generation of phase coupling in order to overcome the disadvantage of melt compounding with dynamic stabilization.

That means compatibility and interfacial adhesion between polypropylene copolymer and RP, especially RP based on NR/SBR, is to enhance through high energy electrons instead of dynamic stabilization in order to improve the properties of blend which should be closed to those of EA as well as TPV. The high energy electrons can be applied to modify polypropylene copolymer/RP blend under two conditions, stationary and in-stationary conditions. The difference between both types of modifications is that modification of polymer blend with high energy electrons under stationary condition is a process which is already used in industry and where required absorbed dose is applied to form parts of polymer blends at ambient temperature and in solid state while modification of polymer blend with high energy electrons under in-stationary condition (so called electron induced reactive processing) is a novel process where required absorbed dose is applied to polymer blend in molten state during melt mixing process [79]. The latter process is comparable to dynamic stabilization. The only difference is the way radicals are generated. In electron induced reactive processing radicals are generated without any use of additives via energy transfer of high energy electrons to matter. Thus radical generation is controlled by electron current and not by the amount of peroxide and temperature.
4 Tasks of Study

In order to fulfill the aim of this study, experimental setups have to be designed and calibrated for electron treatment under stationary and in-stationary conditions. Thus the depth dose profile as function of electron energy has to be determined for both processes in order to ensure that same dose is applied in both processes and to study the influence of the new processing parameters of electron induced reactive processing. In case of design for electron induced reactive processing, the parameters of mixing process (e.g. mixing temperature, rotor speed) for dynamic stabilization have to take over for better comparison. Due to the main objective of this study, the raw materials used are same as in dynamic stabilization, polypropylene copolymer and RP based on NR/SBR. Due to use of high energy electrons peroxide (PO) is not required in both processes.

Based on literature data, the electron treatment should be done in air in order to generate oxygen containing functional groups for required compatibilization. Thus, high energy electrons were used to modify polypropylene copolymer. The modified polypropylene copolymer (PP*) was characterized and used in this study for improving compatibility between RP and polypropylene copolymer. It acts as compatibilizer. Further, the influence of electron treatment on properties of materials used in this study was investigated as function of absorbed dose in order to fix the common dose range for both processes to be investigated. Finally, the influence of different polyfunctional monomers (PFMs) on phase coupling was studied. In the study, the PFMs are called grafting agent (GA). Therefore, the role and effect of GA used in stationary and electron induced reactive processing were studied and compared to those of peroxide used in dynamic stabilization by using different analyzing methods.
5 Experimental

5.1 Materials used

Polypropylene

Polypropylene random copolymer used in the study is Moplen RP 220M supplied by Basell Deutschland GmbH, Frankfurt, Germany. According to ISO 1183 and ISO 1133, density and melt flow (230 °C/2.13 kg) are 0.900 g/cm³ and 8 g/10 min, respectively.

In order to prevent a confusion of abbreviation between polypropylene random copolymer and other type of polypropylene, only polypropylene random copolymer is abbreviated to PP while the other type of polypropylene is not abbreviated.

Rubber particle based on NR/SBR

Rubber particle (RP) based on NR/SBR is Ecorr®RNM 45 obtained from Rubber Resources B. V., Maastricht, The Netherlands. RP is produced by ambient grinding of truck tire tread peelings and buffings. Characteristics of RP based on NR/SBR are listed in table 5.1.

**Table 5.1: Characteristics of RP based on NR/SBR**

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>acetone-extract [%]</th>
<th>&lt; 13</th>
</tr>
</thead>
<tbody>
<tr>
<td>ashes [%]</td>
<td></td>
<td>&lt; 6</td>
</tr>
<tr>
<td>carbon black [wt%]</td>
<td></td>
<td>31 ± 2</td>
</tr>
<tr>
<td>polymer content [wt%]</td>
<td></td>
<td>56 ± 4</td>
</tr>
<tr>
<td>Sieve analysis [wt% retained]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 mesh (600 µm)</td>
<td></td>
<td>&lt; 0.8</td>
</tr>
<tr>
<td>40 mesh (425 µm)</td>
<td></td>
<td>&lt; 16</td>
</tr>
<tr>
<td>50 mesh (300 µm)</td>
<td></td>
<td>&lt; 52</td>
</tr>
<tr>
<td>60 mesh (250 µm)</td>
<td></td>
<td>&lt; 66</td>
</tr>
<tr>
<td>100 mesh (150 µm)</td>
<td></td>
<td>&lt; 85</td>
</tr>
</tbody>
</table>
Modified Polypropylene

Polypropylene random copolymer (PP) was modified by high energy electrons at 200 kGy at electron accelerator ELV-2 (manufactured by Budker Institute of Nuclear Physics, Novosibirsk, Russia) of Leibniz Institute of Polymer Research, Dresden, Germany. The modified polypropylene is abbreviated to PP*.

Grafting agent

Grafting agents (GAs), polyfunctional monomers, used in this study are dipropylene glycol diacrylate (DPGDA), triallyl cyanurate (TAC), trimethylpropane triacrylate (TMPTA) and ditrimethylol propane tetraacrylate (DTMPTA). The GAs are obtained from Cytec Surface Specialties, The Netherlands.

![Molecular structure of DPGDA (a), TAC (b), TMPTA (c) and DTMPTA (d).](image)

**Figure 5.1:** Molecular structure of DPGDA (a), TAC (b), TMPTA (c) and DTMPTA (d).
Peroxide

Peroxide (PO) used in dynamic stabilization is 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (DHBP). DHBP was supplied by Degussa Initiator GmbH & Co. KG., Pullach, Germany.

![Molecular structure of DHBP](image)

**Figure 5.2:** Molecular structure of DHBP.

### 5.2 Preparation of blends

For all blends prepared in the study, the contents of RP were kept constant at 50 wt%. The RP/PP blend modified by high energy electrons under stationary condition and in-stationary are designated as RP/PP e-blend_stat and RP/PP e-blend_dyn, respectively. The formulas of RP/PP blend, RP/PP e-blend_stat, RP/PP e-blend_dyn, and elastomeric alloy (EA) are summarized in table 5.2. In addition, the formulas of RP/PP/PP* blend (RP/PP e-blend_comp) are listed in table 5.3.

**Table 5.2:** Formulas of RP/PP blend, RP/PP e-blend_stat, RP/PP e-blend_dyn, and EA

<table>
<thead>
<tr>
<th>Sample</th>
<th>Formula</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blend</td>
<td>RP/PP</td>
<td>50/50</td>
</tr>
<tr>
<td>EA</td>
<td>RP/PP/PO</td>
<td>50/50/2</td>
</tr>
<tr>
<td>E-blend_stat with DPGDA</td>
<td>RP/PP/DPGDA</td>
<td>50/50/2</td>
</tr>
<tr>
<td>E-blend_dyn with DPGDA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-blend_stat with TAC</td>
<td>RP/PP/TAC</td>
<td>50/50/1.37</td>
</tr>
<tr>
<td>E-blend_dyn with TAC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-blend_stat with TMPTA</td>
<td>RP/PP/TMPTA</td>
<td>50/50/1.63</td>
</tr>
<tr>
<td>E-blend_dyn with TMPTA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-blend_stat with DTMPTA</td>
<td>RP/PP/DTMPTA</td>
<td>50/50/1.93</td>
</tr>
<tr>
<td>E-blend_dyn with DTMPTA</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
It should be noted that calculation of content of GA used in blends can be seen in chapter 6 (6.1.3 Processing parameters, Grafting agents)

**Table 5.3:** Formulas of RP/PP/PP* blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (RP/PP/PP*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP/PP/PP* blend</td>
<td>50.0/46.5/3.5</td>
</tr>
<tr>
<td></td>
<td>50.0/43.0/7.0</td>
</tr>
<tr>
<td></td>
<td>50.0/40.0/10.0</td>
</tr>
<tr>
<td></td>
<td>50.0/35.0/15.0</td>
</tr>
<tr>
<td></td>
<td>50.0/32.5/17.5</td>
</tr>
<tr>
<td></td>
<td>50.0/30.0/20.0</td>
</tr>
<tr>
<td></td>
<td>50.0/27.5/22.5</td>
</tr>
<tr>
<td></td>
<td>50.0/25.0/25.0</td>
</tr>
</tbody>
</table>

**Rubber particle/polypropylene blends**

In the study, blend of RP and PP were prepared by using an internal mixer (Brabender Plastograph model PL2000, Brabender® GmbH & Co. KG, Duisburg, Germany) or a co-rotating twin screw extruder (twin screw extruder ZE25, Hermann Berstorff Maschinenbau GmbH, Hannover, Germany).

For preparation of blend by using the internal mixer, temperature and rotor speed used were 170 °C and 30 rpm as well as 50 rpm, respectively. Firstly, PP was added into internal mixer. When the torque became constant, RP was added into internal mixer. The blending was continued for additional three minutes. Then, the blend was taken out and pelletized by granulator (Wanner Technik GmbH, Wertheim, Germany). The sequence of adding PP and RP is shown in figure 5.3.
For preparation of blend by using the co-rotating twin screw extruder, the temperature from zone 1 to zone 8 were set at about 35/170/170/170/170/170/165/160 °C. The screw speed was about 87 rpm. RP and PP were firstly mixed and then fed into a hopper of the co-rotating twin screw extruder. After that the compounds were extruded. The extrudate were cooled by water and then pelletized by pelletizer (Scheer Pelletizing Machinery, Reduction Engineering GmbH, Stuttgart, Germany). The pellets were dried at room temperature for about 2 days and then in an incubator (Memmert Co. KG, Schwabach, Germany) at temperature of 105 °C for 1 hour.

Rubber particle/polypropylene/modified polypropylene blend

The RP/PP/PP* blends were prepared by using the internal mixer. The temperature and rotor speed used were set same as in preparation of blend. The PP and PP* were firstly added. Finally, RP was added when torque was constant. The blending was continued for additional three minutes. The blend was taken out and pelletized into granulate by granulator.
Rubber particle/polypropylene e-blend_stat

The PP and RP or the PP, RP, and GA were firstly mixed and then fed into the hopper of the co-rotating twin screw extruder. The temperatures that were set from zone 1 to zone 8 were same as in blend. The screw speed used in the study was around 99 rpm for RP/PP blend with all GAs except TAC and 121 rpm for RP/PP blend with TAC. The compound of e-blend_stat was extruded, then cooled by water and cut into pellets by granulator. The e-blend_stat was dried at room temperature for two days and then in the incubator for one hour at temperature of 105 °C for 1 h.

For recyclability study, e-blend_stat with DTMPTA modified at absorbed dose of 80 kGy was prepared by using Banbury mixer (Werner & Pfleiderer GmbH, Stuttgart, Germany). Firstly, PP was added and then the mixture of RP with DTMPTA was added. The duration of mixing is approximately 9 minutes.

It should be noted that RP/PP e-blends _stat with or without GA were modified by high energy electrons after molding.

Rubber particle/polypropylene e-blend_dyn

For preparation of e-blend_dyn, a 1.5 MeV electron accelerator was directly coupled to the chamber of the internal mixer. PP was firstly added and then RP and GA were added into internal mixer which has a mixing chamber volume of 50 cm³. During the melt mixing, the blend was modified by high energy electrons at a rotor speed of 30 or 39 rpm. The total time of blending process was around 10 minutes. The overall blending process included also the time for leaving the irradiation room and the time for starting the electron accelerator. Example of sequence of adding PP, RP, and GA is listed in table A.1 (see Appendix A) and shown in figure 5.5.
5 Experimental

Figure 5.5: Plastograph of 50/50/1.93 RP/PP/DTMPTA blend prepared at rotor speed of 30 rpm and opened mixing chamber.

**Elastomeric alloy**

In this study, EAs were the reference material. They were prepared in accordance to the work of Wießner and Sritragool [83 - 84] by using the internal mixer or the co-rotating twin screw extruder. The processing parameters of dynamic stabilization used in an internal mixer are given in table 5.4 and were overtaken for all blend preparation in order to minimize systematic uncertainties and to ensure good conditions for comparison with new procedures to be developed.

**Table 5.4:** Processing parameters of dynamic stabilization for batch process

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>rotor speed [rpm]</td>
<td>50</td>
</tr>
<tr>
<td>total processing time [min.]</td>
<td>9</td>
</tr>
<tr>
<td>temperature [°C]</td>
<td>170</td>
</tr>
<tr>
<td>total time of radical generation [min.]</td>
<td>~ 3</td>
</tr>
<tr>
<td>number of radicals depends on</td>
<td>peroxide content/type</td>
</tr>
<tr>
<td>volume of radical generation</td>
<td>total mixing volume</td>
</tr>
</tbody>
</table>

For preparation of EA by using the internal mixer, the temperature and rotor speed used were set same as in table 5.4 and also same as in preparation of
RP/PP blend. PP was firstly added and then a large portion of RP was added when the torque was constant. The rest of RP with PO were added when the torque became constant. The blending was continued for additional three minutes in order to guaranty the same total time of radical generation as given in table 5.4. After that, EA was taken out and ground into granulate by granulator. The sequence of adding PP, RP, and PO is shown in figure 5.6.

![Plastograph of 50/50/2 RP/PP/PO EA prepared at rotor speed of 50 rpm.](image)

**Figure 5.6**: Plastograph of 50/50/2 RP/PP/PO EA prepared at rotor speed of 50 rpm.

For preparation of EA by using the co-rotating twin screw extruder, the temperature from zone 1 to zone 8 were same as in preparation of blend. The screw speed was approximately 99 rpm. The RP, PP, and PO were firstly mixed and then fed into the hopper of the co-rotating twin screw extruder. After that the compound were extruded. The extrudate of EA were cooled by water and then pelletized by pelletizer. The pellets were dried at room temperature for around 2 days and then in the incubator at the temperature of 105 °C for 1 h.

**5.3 Electron treatment**

**Electron treatment under stationary condition**

Electron accelerator ELV-2 of Leibniz Institute of Polymer Research was used to modify dumbbell-shaped specimens of RP/PP e-blends_stat at absorbed dose of 20, 25, 40, 50, 60, 80, 100, and 120 kGy under air atmosphere and at ambient temperature.
Electron induced reactive processing

Electron accelerator ELV-2 was used to modify RP/PP e-blend_dyn at absorbed dose of 40, 60 and 80 kGy at an electron energy of 1.0 and 1.5 MeV for 15, 30 and 60 seconds. Schematic representation of electron induced reactive processing is shown in figure 5.8.

Figure 5.7: Schematic diagram of preparation of RP/PP e-blend_stat.

Figure 5.8: Schematic representation of electron induced reactive processing for preparing e-blend_dyn.
5.4 Preparation of dumbbell-shaped specimens

An injection molding machine (BOY 22D) was used to produce dumbbell-shaped specimens type 1A in accordance to DIN EN ISO 3167. The injection molding machine has a screw diameter of 22 mm, a screw L/D ratio of 17.5 and clamping force of 220 kN. The process parameters are summarized in table 5.5.

Table 5.5: Injection molding process parameter

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feeding zone temperature [°C]</td>
<td>170</td>
</tr>
<tr>
<td>Barrel temperature [°C]</td>
<td>170</td>
</tr>
<tr>
<td>Nozzle temperature [°C]</td>
<td>25</td>
</tr>
<tr>
<td>Mold temperature [°C]</td>
<td>30</td>
</tr>
<tr>
<td>Injection pressure [%]</td>
<td>65</td>
</tr>
<tr>
<td>Holding pressure [%]</td>
<td>50</td>
</tr>
<tr>
<td>Screw speed [%]</td>
<td>50</td>
</tr>
<tr>
<td>Holding time [s]</td>
<td>10</td>
</tr>
<tr>
<td>Cooling time [s]</td>
<td>15</td>
</tr>
</tbody>
</table>
5.5 Characterization methods

**Tensile properties**

According to DIN EN ISO 527-1, a TiraTest 27025 machine was used to determine the tensile properties of blend, e-blend_comp, EA, e-blend_stat, and e-blend_dyn. The tensile test was performed at room temperature with a crosshead speed of 100 mm/min. The modulus was measured within the strain limit from 0.25 to 0.50 %. The results reported in this study are the average value of three or five specimens.

**Charpy impact strength**

Charpy impact strength of the e-blends_stat with DTMPTA modified at absorbed dose of 80 kGy was investigated in accordance to DIN EN ISO 179 on Izod-Charpy impact testing machine (CEAST Resil 25). The pendulum used has an impact energy of 1 J and an impact velocity of 2.9 m/s. The specimens used had a dimension of 80 x 10 x 4 mm$^3$ with a notch depth of 2 mm and notch tip radius of 0.25 mm. The Charpy impact test was performed at temperature of -28 °C. The specimens were placed horizontally on two supports having a distance of 62 mm. The position of notch is opposite side to the pendulum. The results reported in the study are the average value of five specimens.

**Hardness**

According to DIN 53505, hardness of e-blends_stat with DTMPTA modified at 80 kGy was determined by using shore A and Shore D durometers. The hardness was measured in the middle of specimen and of both shoulders of the tensile specimen. The readings were taken 10 s after indentation when firm contact of durometer had been established with the tensile specimens.

**Tension set**

According to the definition of TPE in DIN 7724, a tension set of TPE should be less than 50 %. The tension set values of e-blend_stat with DTMPTA modified at absorbed dose of 80 kGy were determined in accordance to DIN 7724 on a TiraTest 27025 machine. First, the initial length ($L_1$) of tensile specimen was measured. The tension set measurement was done at room temperature with a
crosshead speed of 100 mm/min. When elongation was reached 100 %, the specimen was held for one minute. Finally, the crosshead moved back with speed of 100 mm/min. When the force was zero N, the specimen was released from the crosshead. The final length \( L_2 \) of specimen was measured after one minute. The tension set was calculated as follows:

\[
\text{Tension set} = \frac{L_2 - L_1}{L_1} \times 100 \%
\]  

(5.1)

The tension set values in this report is the average value of three specimens.

**Differential Scanning Calorimetry (DSC)**

The DSC (Q2000, TA Instrument) was used to study thermal properties of blend, e-blend_comp, EA, e-blend_stat, and e-blend_dyn. A sample used should have a weight of about 5 to 10 mg. The sample was put into pre-weighted aluminium (Al) pan. Then the pan was covered by lid and finally sealed with a press. The samples was firstly heated, then cooled and heated again in the temperature range between -90 °C and 200 °C under nitrogen atmosphere with heating and cooling rate of 10 K/min. The glass transition temperatures, crystallization temperatures, melting temperatures, and heat of fusion values were determined from melting endotherms and cooling exotherms.

**Dynamic Mechanical Analysis (DMA)**

Dynamic mechanical properties of blend, EA, e-blends_stat, and e-blendsDyn were investigated by using a dynamic mechanical analyzer (DMA Q800, TA Instruments, Delaware, USA) in dual cantilever bending mode in a temperature range from -75 °C to 100 °C with a heating rate of 1 K/min at a frequency of 1 Hz. The result obtained from DMA is the change of storage modulus \( E' \) and loss modulus \( E'' \) as function of the temperature. The tangent delta \( \tan \delta \) was calculated by dividing \( E'' \) by \( E' \). The \( \tan \delta \) peak maxima correspond to \( T_g \) of RP and PP, respectively.

**Melt flow index (MFI) measurement**

According to DIN 53735-MFI-B, MFI of blend, e-blend_comp, EA, e-blend_stat, and e-blend_dyn were measured by Goettfert machine from Goettfert Werkstoff-
Prüfmaschinen GmbH, Buchen, Germany. The MFI was measured under a loading of 5 kg and at a temperature of 190 °C. The MFI values reported in this study are the average value of three measurements.

**Morphological study**

The tensile fracture surfaces of blend, EA, e-blend_stat, and e-blend_dyn were investigated by a LEO 435 VP Ultra plus Scanning Electron Microscope (SEM) from Carl Zeiss SMT (Jena, Germany) in order to get information on structure of fracture surface. The fracture surfaces were coated with platinum with a thickness of 3 nm.
6 Results and Discussion

6.1 Experimental setup

6.1.1 Stationary treatment

In general, there are six components used in processing of high energy electrons [85]. These are electron accelerator, product conveyor system, radiation shielding system, ventilation system, safety system, and control system. Figure 6.1 shows the scanner of electron accelerator and product conveyor with pallet. In the study, the dumbbell-shaped specimens of RP/PP blends with or without GAs are placed on the pallet for modifying with high energy electrons at various doses. This modification of RP/PP blends is called stationary treatment.

![Scanner of electron accelerator and pallet on conveyor.]

In the stationary treatment, electron energy and atomic composition of polymeric material play an important role for interaction of high energy electrons with polymeric material [85]. It is stated that depth dose profile is the energy deposition produced by high energy electrons of a given energy in a material and the depth dose profile can be revealed as a function of depth, the atomic number, and the atomic weight of the absorber [48]. Figure 6.2 represents the charge specific depth dose profile in polyethylene as function of area density for different electron energy. The charge specific depth dose profile results from the normalization of absorbed dose to electron current as well as electron treatment time. It can be seen that the penetration depth of electrons into material as well as the maximum
value of charge specific dose increases with increasing electron energy. Further, the charge specific dose firstly increases and then decreases with increasing area density. The scattering of high energy electrons results in the initial increase of dose whereas the final decrease of dose is related to the limited penetration path of high energy electrons in matter [86].

**Figure 6.2:** Charge specific depth dose profile in polyethylene for electron energies of 0.6, 1.0, and 1.5 MeV (dose calibration; From Leibniz Institute of Polymer Research Dresden, Germany).

### 6.1.2 Electron induced reactive processing

Electron induced reactive processing (in-stationary treatment) is different from stationary treatment. For the in-stationary treatment, an internal mixer is fixed on the conveyer in order to modify RP/PP blends with or without GA during mixing process with high energy electrons. Figure 6.3 represents the main components used in the in-stationary treatment.
Figure 6.3: Scanner of electron accelerator, and internal mixer on conveyor.

Figure 6.4: Charge specific depth dose in polyethylene for electron energy of 0.6, 1.0, and 1.5 MeV (dose calibration; From Leibniz Institute of Polymer Research Dresden, Germany).

Figure 6.4 shows charge specific depth dose in PE at difference electron energies. It can be seen the same correlations as in the stationary treatment. Maximum of charge specific dose as well as the penetration depth of electrons into PE increase with increasing electron energy. However, the absolute value of charge specific dose under in-stationary condition is much higher due to reduced working width in comparison to electron treatment under stationary condition.
6.1.3 Processing parameters

The design of required compounding procedure (in case of stationary treatment or preparation of physical blends) as well as the novel electron induced reactive processing (dynamic (in-stationary) treatment) based on the batch procedure for the preparation of EA in accordance to the work of Wießner [83]. The main processing parameters to be overtaken are given in table 5.4 in chapter 5 (see Experiment). Due to some special features of electron treatment, it was not possible to simply overtake all processing parameters of EA batch procedure. Thus additional experimental tests were required. Electron treatment during melt mixing is connected with an additional energy input and results in an additional temperature increase. Further, the melt mixing process had to be done with an opened mixing chamber in order to allow high energy electrons to enter the mixing volume. The required tests as well as their results are reported in this chapter.

**Fixed temperature and processing time**

During the preparation of e-blend_dyn, controlling of mixing temperature is important due to the additional energy input via high energy electrons. Due to low coefficients of thermal transfer of polymers, rising of temperature can be occurred by absorption of high energy electrons [49]. Thus, in preparation of e-blend_dyn, the properties of polymer might be dramatically changed due to thermal degradation, if the processing temperature increases too much.

**Figure 6.5:** Temperature – time diagram of 50/46.5/3.5 RP/PP/PP* with and without TAC (b) at different conditions.
The temperature curve of RP/PP/PP* e-blend_dyn with or without TAC are represented in figure 6.5. It can be clearly seen that the temperature of polymer melt increases during electron treatment in comparison to melt mixing process without any electron treatments at the same condition. Further, it is shown that there is no effect of TAC, grafting agent, on temperature of e-blend_dyn. The temperature of e-blend_dyn was reduced when setting temperature regime was changed from 180 °C/130 °C to 190 °C/140 °C and cooling water was started at the time of 0.30 minute or 0.35 minute instead of 3.50 minutes. Thus the temperature regime had been fixed to 190 °C/140 °C and the starting of cooling was 30 s after adding the polypropylene. Thus the average temperature during melt mixing amounts to about 160 °C. This lower average temperature was used since the total processing time had to be fixed to 11 minutes instead of 7 minutes for the EA batch procedure due to safety requirements for electron accelerator.

**Rotor speed**

The rotor speed during melt mixing process influences on torque as well as temperature. The torque-time curve and temperature-time curve of blends compounded at rotor speed of 30, 39 and 50 rpm are represented in figure 6.6 and 6.7, respectively. It can be observed that the torque-time and temperature-time curves of blend prepared at 30 rpm have similar appearance to those of blends prepared at 39 and 50 rpm. It can be seen from figure 6.6 that the torque quickly rose when PP was added into internal mixer. The increase of torque when PP was added is because of resistance applied to rotors by non-molten PP and reduction of the temperature of chamber of internal mixer [87 - 88]. The temperature in mixing chamber reached a minimum value of about 145 °C. The melting point of PP amounts to 140 °C. After that the torque decreased while the temperature increased. The reduction of torque is due to the increase of temperature inside the chamber of the internal mixer [87]. The temperature rose to higher temperature because PP started to melt and was mechanically sheared. After adding of RP, the torque firstly rose sharply, then decreased and finally leveled off. This indicated that the RP is well dispersed in PP.
Results and Discussion

Figure 6.6: Torque-time diagram of 50/50 RP/PP blend mixed at different rotor speed.

Figure 6.7: Temperature-time diagram of 50/50 RP/PP blend mixed at different rotor speed.

The effect of rotor speed on tensile properties of 50/50 RP/PP blends is shown in figure 6.8. It can be seen that the tensile strength, elongation at break, and modulus of blend mixed at 30 rpm are comparable to those of blends mixed at 39 and 50 rpm. Thus in this study, the rotor speed has no effect on tensile properties of RP/PP blend and it is possible to use rotor speed of 30 rpm as well as 39 rpm in electron induced reactive processing.
Figure 6.8: Tensile strength, elongation at break and modulus of 50/50 RP/PP blends prepared at 30, 39, and 50 rpm.

Gas atmosphere

Electron induced reactive processing requires that the melt mixing process takes place with intensive contact to surrounding gas atmosphere. It is known, that melt mixing of PP in presence of air results in degradation of PP. Thus, melt mixing was studied in presence of air and nitrogen atmosphere in order to study their influence on properties of RP/PP e-blend_dyn. The results of this experiment are shown in figure 6.9 for 50/50 RP/PP e-blend_dyn. It can be seen that the e-blends_dyn prepared in presence of nitrogen atmosphere have less improvement of tensile properties. Nevertheless, all experiments were done in presence of air atmosphere, since electron treatment in air results in oxygen containing functional groups improving compatibility between RP and PP.
Figure 6.9: Tensile strength, elongation at break, and modulus of 50/50 RP/PP e-blend_dyn prepared under different gas atmosphere.

Dose

The dose is defined as absorbed energy per unit of mass. Further, the G-value characterizes the amount of radicals generated per 100 eV absorbed energy. Thus both parameters control the total number of radicals generated in our blend. The G-value of PP amounts to 0.4 ... 2.9 radicals per 100 eV. Assuming that one chemical bonding between PP molecule and RP is required for improvement of interfacial adhesion so that one radical has to be generated on PP molecule. Thus the required dose range follows from the calculation of that dose which is required to generate one radical per PP molecule. Figure 6.10 represents the dependence of this dose value on molecular mass. Taking into account a molecular weight of 250,000 g/mol and a G-value of 0.4 ... 2.9 radicals per 100 eV, a dose range from 13 kGy up to 100 kGy can be determined. Thus the range of dose to be studied in this work was fixed from 20 kGy to 100 kGy.
6 Results and Discussion

Figure 6.10: The relationship between absorbed dose and molecular mass of polymer (From Leibniz Institute of Polymer Research Dresden, Germany).

**Grafting agents**

In the study, the main aim was the development of e-blend material which has properties close to or higher than EA. The composition of selected EA is 50/50/2 RP/PP/PO. It means that the content of PP and RP in e-blend is 50 wt%. Molecular structure of DHBP was shown in figure 5.2 (See experimental). It can be seen that DHBP composes of two peroxides. The content of PO used in dynamic stabilization is 2 wt%. Crosslinking of PP via high energy electrons requires the use of additional crosslinking agents. These agents contain different amount of double bonds per molecule. Further it is known, that the number of double bonds per molecule influences on the efficiency of grafting and crosslinking. It was assumed that the total number of double bonds in GA should be equal to the total number of PO-bonds in DHBP used in preparation of EA. Number of PO in DHBP is two so that it is equal to two double bonds in DPGDA, the grafting agent. Thus, the content of DPGDA used is 2 wt%. In case of GA having more than two double bonds, the required content of GA can be calculated in following way on the base of number of double bonds and molecular weight of GA. The content of DTMPTA amounts to:

\[
\frac{2 \text{ (double bonds in DPGDA)}}{242 \text{ (molecular weight of DPGDA)}} \times \frac{466 \text{ (molecular weight of DTMPTA)}}{4 \text{ (double bonds in DTMPTA)}} \times 2 \text{ wt\%} = 1.93 \text{ wt\%}
\]
It is noted that the molecular weight of DPGDA and DTMPTA are 242 and 466 g/mol, respectively. In brief, the content of DPGDA, TAC, TMPTA and DTMPTA are 2, 1.37, 1.63, and 1.93 wt%, respectively.

Finally, the main processing parameters of electron induced reactive processing are shown in table 6.1 in comparison to EA procedure (dynamic stabilization).

**Table 6.1:** Comparison of processing parameters of dynamic stabilization and electron induced reactive processing

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Dynamic stabilization</th>
<th>Electron induced reactive processing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotor speed [rpm]</td>
<td>50</td>
<td>30, 39 and 50</td>
</tr>
<tr>
<td>Total processing time [min]</td>
<td>9</td>
<td>11 (due to safety regulations)</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>170</td>
<td>165</td>
</tr>
<tr>
<td>Total time of radical generation [s]</td>
<td>~ 180</td>
<td>15, 30, 60</td>
</tr>
<tr>
<td>Number of radicals depends on Peroxide content/type</td>
<td>Total mixing volume</td>
<td>Total mixing volume depending on electron energy (1.0, 1.5 MeV)</td>
</tr>
</tbody>
</table>

**6.2 Comparison of blend prepared by twin screw extruder and internal mixer**

Blend and EA can be prepared by using a twin screw extruder as well as by using an internal mixer with closed mixing chamber volume. However, blends prepared by electron induced reactive processing can be only produced by an internal mixer with opened mixing chamber. Otherwise, high energy electrons cannot enter the mixing volume due to their absorption in metal. Further, it is known that the different preparation methods are influencing on mechanical properties. That is why the tensile properties of 50/50 RP/PP blends prepared by internal mixer with opened and closed mixing chamber as well as blend prepared by twin screw extruder were investigated. The tensile properties of these blends are shown in figure 6.11. It can be seen in figure 6.11 that the tensile strength, elongation at break, and modulus values of blends prepared by internal mixer at both conditions
are comparable to those of blends prepared by twin screw extruder. Thus preparation of e-blend_stat can be done by twin screw extruder in order to save time for the comprehensive study of the influence of dose as well as type of grafting agent on mechanical properties.

6.3 Rubber particle/polypropylene/modified polypropylene blend

It is known from the literature that PP modified with ionizing radiation improves the mechanical properties of RP/PP blend. In the following chapter, the influence of modified PP on different properties is represented.

6.3.1 Characterization of modified PP (PP*)

The appearances of neat PP and PP* are shown in figure 6.12. It can be seen in figure 6.12(b) that PP* has yellow color. Discoloration of PP results from the generation of conjugated double bonds during degradation process. A further
result of this degradation process is the generation of carbonyl and hydroperoxide groups in PP* influencing on crystallization and compatibility [60, 89 – 90].

Figure 6.12: Appearance of PP (a) and PP* (b).

Figure 6.13: Tensile properties of PP and PP*.

Tensile strength, elongation at break, and modulus of PP and PP* are illustrated in figure 6.13. It is clearly seen that the elongation at break of PP is dramatically decreased when PP was treated by high energy electrons at 200 kGy under air atmosphere. It is suggested that the reduction of elongation at break of PP* results from the high energy radiation induced degradation of PP [59, 91 - 92].

6.3.2 Effect of modified polypropylene on properties of blend

Tensile properties

In the study, PP was treated by high-energy electrons at absorbed dose of 200 kGy in order to generate a compatibilizer for the incompatible RP/PP blend. The treated PP is called electron modified PP and labeled as PP*. PP* was added into
blend of PP with RP at different contents. The RP/PP blends with PP* are designated as RP/PP e-blend_comp. The tensile properties of all e-blend_comp with different content of PP* are shown in figure 6.14.

**Figure 6.14:** Tensile strength (a), elongation at break (b), modulus (c) of 50/50 – X/X RP/PP/PP* blends (e-blend_comp) as function of content of PP*.
It can be seen in figure 6.14 that tensile strength and elongation at break increase with increasing loading of PP* up to 17.5 wt%. Higher contents of PP* result in a slightly decrease of tensile strength and dramatically decrease of elongation at break. In addition, modulus values increase with increasing loading of PP* within uncertainty level.

The optimum content of PP* in e-blend_comp is about 17.5 wt%. At this concentration, the tensile strength, elongation at break, and modulus of e-blend_comp are 11.70 MPa, 111 %, and 303 MPa, respectively. The increase in tensile properties, especially elongation at break, indicates the improvement of interfacial adhesion between RP and PP.

It was reported that modified PP by high energy electrons at room temperature under air atmosphere contains carbonyl, carboxylic, ether as well as hydroxyl groups [64, 66]. Thus, it is expected that the functional groups generated in PP* will be grafted on to RP and then result in enhancement of compatibility/interfacial adhesion between PP and RP.

**Melt flow index**

Figure 6.15 shows the effect of PP* on MFI of e-blend_comp. The MFI of e-blend_comp firstly decreases with increasing dose up to loading of PP* of 3.75 wt%, then slightly increases up to loading of PP* of 15 wt% in order to reach minimum value at optimum concentration of PP* of 17.5 wt%. When the content of
PP* is higher than 17.5 wt%, MFI increases. The decrease of MFI of 50/32.5/17.5 RP/PP/PP* blend indicates the improvement of interfacial adhesion between RP and PP [17].

![Figure 6.15](image_url)

**Figure 6.15:** Melt flow index of 50/50 – X/X RP/PP/PP* blends (e-blend_comp) as function of loading of PP*.

**Thermal properties**

In this study, e-blend_comp contained PP* of 17.5 wt% was selected to determine thermal properties and to compare with those of blend.

![Figure 6.16](image_url)

**Figure 6.16:** DSC curves of 50/50 RP/PP blend and 50/32.5/17.5 RP/PP/PP* e-blends_comp registered during 2nd heating (a) and cooling (b).
The thermal properties of blend and e-blend_comp containing PP* of 17.5 wt% are shown in figure 6.16 and listed in table 6.2. The incorporation of PP* into blend of PP with RP results in slightly increase in melting temperature and an increase in crystallization temperature due to self nucleation effect.

Table 6.2: Glass transition temperature ($T_g$), crystallization temperature ($T_c$), melting temperature ($T_m$), and heat of fusion ($\Delta H_m$) of 2nd heating of 50/50 RP/PP blend and 50/32.5/17.5 RP/PP/PP* e-blends_comp

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$ [$^\circ$C]</td>
</tr>
<tr>
<td>Blend (50RP/50PP)</td>
<td>-61.3</td>
</tr>
<tr>
<td>E-blend-comp (50RP/32.5PP/17.5PP*)</td>
<td>-61.0</td>
</tr>
</tbody>
</table>

Morphology of blend and e-blend_comp

Figure 6.17 shows the SEM Photomicrographs of fracture surfaces from blend and e-blend_comp. Figure 12(c) is the SEM photomicrograph of e-blend_comp at high magnification. It is observed in figure 6.17(b and c) that fibril structure is formed. The formation of fibril structure on tensile fracture surface confirms the enhancement of tensile properties of blends when PP* is added.
Figure 6.17: SEM photomicrographs of tensile fracture surfaces of 50/50 RP/PP blend (a) and 50/32.5/17.5 RP/PP/PP* e-blends_comp (b) and (c).

6.4 Rubber particle/polypropylene e-blend_stat

6.4.1 Effect of dose on properties of e-blend_stat without grafting agent

At beginning of the study, the 50/50 RP/PP blend without grafting agent was treated by high energy electrons at absorbed doses of 0, 25, 50, and 100 kGy. It should be noted that the tensile properties and MFI values showed in figure 6.18 are the average values of three specimens.
Figure 6.18: Tensile strength, elongation at break, modulus, and MFI values of 50/50 RP/PP blend without GA modified at dose of 25, 50 and 100 kGy.

It can be seen that tensile strength values of blend increase slightly with increasing absorbed dose while modulus values of blends are nearly constant within experimental uncertainty. Moreover, it can be seen that elongation at break and MFI values of blend increase with increasing absorbed dose. The increase of elongation at break of blend modified by high energy electrons under stationary condition (e-blend_stat without GA) indicates the improvement of compatibility between RP and PP. However, the elongation at break of e-blend_stat without GA is still lower than that of RP/PP blend containing PP* of 17.5 wt%. Compared to MFI of unmodified blend, MFI values of e-blend_stat without GA dramatically increase with increasing absorbed dose due to chain scission in PP, especially at absorbed dose of 100 kGy. It is known that crosslinking and degradation occur simultaneously in PP when it is subjected to ionizing radiation [63, 93]. Finally, the degradation is dominant in irradiation of PP [61]. Moreover, it was also reported that irradiation of PP by electron beam in air resulted in degradation of PP [63]. Hence, a suitable grafting agent (GA) is required to enhance mechanical properties of blend.
6.4.2 Effect of grafting agent on properties of e-blend_stat modified at absorbed dose of 40 kGy

**Tensile properties**

There are four GAs selected in this study: DPGDA, TAC, TMPTA, and DTMPTA. These GAs are different in number of functional groups (functionality – double bond) and type of monomers. Type of monomers of DPGDA, TMPTA, and DTMPTA is an acrylate whereas that of TAC is an allyl. DPGDA, TMPTA, and DTMPTA have 2, 3, and 4 functionality, respectively. The functionality of TAC is equal to that of TMPTA.

![Stress strain diagram](image)

**Figure 6.19:** Stress – strain diagram of 50/50 RP/PP blend and 50/50 RP/PP e-blends_stat in presence of TAC, DPGDA, TMPTA as well as DTMPTA modified at absorbed dose of 40 kGy.

It can be seen from figure 6.19 showing tensile properties of blend and e-blend_stat in presence of different GAs modified at absorbed dose of 40 kGy that e-blend_stat with DTMPTA has highest tensile properties whereas e-blend_stat with TAC has lowest tensile properties. The total amount of double bounds added is the same for all e-blend_stat. The tensile properties of e-blend_stat with DPGDA are comparable to those of e-blend with TMPTA. Sawasaki and co-worker reported that a graft reactivity of PFMs having acrylate groups is greater than that of PFMs having allyl groups [62 - 63]. Besides, they also reported that the PFMs having more than two functionalities had higher effectiveness to generate large gel fraction to polypropylene [62]. The larger gel fraction, the
higher crosslinking efficiency. In crosslinking of polypropylene, polypropylene with tetramethylolmethane tetraacrylate (A-TMMT) had elongation of about 600 % for gel fraction of 75 % while polypropylene with TAC had elongation less than 100 % when gel fraction was more than 50 % [63]. It is also reported that, for irradiation crosslinking of EVA, PFMs having allyl or hydroxyl groups have lower crosslinking efficiency than PFMs having methacrylate and acrylate groups [94]. It was also reported that, among three type of polypropylene, polypropylene random copolymer (PP) is the most suitable for crosslinking by ionizing radiation [70]. In the study, the polypropylene used is polypropylene random copolymer. The most efficient PFMs for promoting of crosslinking of polypropylene random copolymer is PFMs containing acrylate and methacrylate grouprs such as trimethylolpropane trimethacrylate (TMPTMA) and TMPTA [54, 61]. In contrast, TAC, PFMs containing allyl groups, is suitable to use in enhancement of crosslinking of polypropylene homopolymer [61]. Accordingly, DPGDA, TMPTA, and DTMPTA which all of them contain acrylate groups are more suitable than TAC for use not only in improvement of crosslinking of polypropylene copolymer but also in coupling RP with polypropylene copolymer. In addition, among three GA having acrylate groups, DTMPTA containing four acrylate groups (tetrafunctional monomer) has highest reactivity to coupling RP with polypropylene copolymer.

Moreover, compared to the tensile properties of unmodified blend without GA, the tensile properties of e-blends_stat with DPGDA, TMPTA and DTMPTA are much higher. Thus, we concluded that the modification with high energy electrons in presence of grafting agents except TAC can improve the compatibility/the interfacial adhesion between RP and PP. The improvement of interfacial adhesion is expected to occur via the formation of copolymer such as PP-RP or PP-GA-RP.

**Melt flow index**

MFI values of blend and e-blends_stat in presence of different GAs modified at 40 kGy are shown in figure 6.20. It was observed that MFI of e-blend_stat with DTMPTA is the lowest and also lower than that of blend. This indicates that crosslinking or coupling of PP to RP is dominating over chain scission occurred in PP matrix. The e-blend_stat with TAC has highest MFI due to higher degradation yield in PP matrix. The highest MFI of e-blend_stat with TAC supports the lowest
tensile properties of e-blend_stat with TAC which are also lower than that of e-blend without GA and are comparable with blend.

![Graph of MFI for 50/50 RP/PP blend and 50/50 RP/PP e-blends_stat in presence of TAC, DPGDA, TMPTA, and DTMPTA modified at 40 kGy.](image)

**Figure 6.20**: MFI of 50/50 RP/PP blend and 50/50 RP/PP e-blends_stat in presence of TAC, DPGDA, TMPTA, and DTMPTA modified at 40 kGy.

**Thermal properties**

The thermal properties of blend and e-blend_stat with different GAs are presented in figure 6.21 and listed in table 6.3. It is noted that a dose of 40 kGy has been applied to e-blend_stat. The incorporation of various GAs results in small differences in DSC curve. It is seen that, compared with melting temperature of 50/50 RP/PP blend, the melting temperature of e-blends_stat with different GAs only slightly decreases while crystallization temperature little increases. Higher heat of fusion results in higher crystallinity if the type of crystallinity has not changed. Compared to neat RP/PP blend, heat of fusion values of PP phase in e-blend_stat with different GAs are lower, especially in e-blend_stat with DPGDA. The $T_g$ values of e-blends_stat with GAs are nearly constant and just only slightly increase except $T_g$ of e-blend_stat with TAC when compared to $T_g$ of neat blend.
Figure 6.21: DSC curves of 50/50 RP/PP blend and 50/50 RP/PP e-blends_stat in presence of TAC, DPGDA, TMPTA as well as DTMPTA modified at absorbed dose of 40 kGy and registered during 2nd heating (a) and cooling (b).
Table 6.3: Glass transition temperature (T\textsubscript{g}), crystallization temperature (T\textsubscript{c}), melting temperature (T\textsubscript{m}), and heat of fusion (\Delta H\textsubscript{m}) of 2\textsuperscript{nd} heating of blend and e-blends_stat with different GAs modified at absorbed dose of 40 kGy

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dose [kGy]</th>
<th>T\textsubscript{g} [°C]</th>
<th>T\textsubscript{c} [°C]</th>
<th>T\textsubscript{m} [°C]</th>
<th>\Delta H\textsubscript{m} [J/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blend</td>
<td>0</td>
<td>-61.3</td>
<td>102.0</td>
<td>139.9</td>
<td>29.31</td>
</tr>
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<td>E-blend_stat with TAC</td>
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<td>-61.4</td>
<td>102.4</td>
<td>138.2</td>
<td>26.65</td>
</tr>
<tr>
<td>E-blend_stat with DPGDA</td>
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<td>-60.8</td>
<td>102.4</td>
<td>138.6</td>
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<td>E-blend_stat with TMPTA</td>
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<td>103.6</td>
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<td>-60.3</td>
<td>102.9</td>
<td>138.7</td>
<td>26.93</td>
</tr>
</tbody>
</table>

Dynamic mechanical properties

It is known that dynamic mechanical analysis can be used to investigate the compatibility of components in polymer blends. The dynamic mechanical properties, especially tangent delta (\tan\ \delta), are used to indicate the compatibility of components in polymer blend. In \tan\ \delta vs temperature curve, the appearance of more than one \tan\ \delta peaks which correspond to T\textsubscript{g} of each component indicates that the polymer blend is incompatible whereas the appearance of single \tan\ \delta peak indicates that the polymer blend is compatible. When the T\textsubscript{g} value of component shifts inward, it means that the compatibility of components may be enhanced.
Figure 6.22: Tan δ vs temperature curves for 50/50 RP/PP e-blends_stat with different GAs modified at absorbed dose of 40 kGy compared with tan δ vs temperature curves for 50/50 RP/PP blend.

Figure 6.22 shows the tan δ of blend and e-blends_stat in presence of various GAs modified at absorbed dose of 40 kGy as function of temperature. Table 6.4 lists the T_g values of RP and PP in blend and e-blends_stat in presence of various GAs modified at absorbed dose of 40 kGy. It is seen in figure 6.22 that there are three tan δ peaks appeared in blend and all e-blends_stat with various GAs. The tan δ peak (relaxation peak) at lowest temperature corresponds to T_g of RP component whereas the second tan δ peak corresponds to T_g of PP component. In addition, there are third tan δ peaks between 30 °C and 80 °C in blend and all e-blends_stat with various GAs which may be possible α-relaxation peaks. The α-relaxation peaks relate to a slip mechanism of polymer chain in crystal phase [95 – 96]. The T_g values of RP and PP in blend are -59.7 °C and -5.9 °C, respectively. Only T_g value of RP in e-blend_stat with TAC shifts slightly to lower temperature around 0.4 K when compared with that of RP in blend. In contrast, T_g values of other e-blends_stat with DPGDA, TMPTA or DTMPTA shift slightly to higher temperature around 0.2, 0.2, and 0.7 K, respectively. The inward slightly shift of T_g values of RP in e-blends_stat with DPGDA, TMPTA, and DTMPTA can indicates the improvement of compatibility between RP and PP. The highest inward shift of T_g value of RP in e-blend_stat with DTMPTA supports that DTMPTA is the most effective for improving the interfacial adhesion between RP
and PP. Moreover, the outward slightly shift of $T_g$ value of RP in e-blend_stat with TAC confirms that TAC is unsuitable to use for improvement of the interfacial adhesion between RP and PP in e-blend_stat. From table 6.4, the $T_g$ values of PP in e-blend_stat in presence of various GAs except TMPTA increase slightly when compared with $T_g$ of PP in blend while $T_g$ of PP in e-blend_stat with TMPTA is comparable with that of PP in blend.

**Table 6.4:** Glass transition temperature ($T_g$) of RP and PP in 50/50 RP/PP blend and 50/50 RP/PP e-blends_stat with GAs modified at absorbed dose of 40 kGy

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dose [kGy]</th>
<th>$T_g$/RP [°C]</th>
<th>$T_g$/PP [°C]</th>
</tr>
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<tr>
<td>Blend</td>
<td>0</td>
<td>-59.7</td>
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<tr>
<td>E-blend_stat with TAC</td>
<td>40</td>
<td>-60.1</td>
<td>-5.5</td>
</tr>
<tr>
<td>E-blend_stat with DPGDA</td>
<td>40</td>
<td>-59.5</td>
<td>-5.5</td>
</tr>
<tr>
<td>E-blend_stat with TMPTA</td>
<td>40</td>
<td>-59.5</td>
<td>-6.0</td>
</tr>
<tr>
<td>E-blend_stat with DTMPTA</td>
<td>40</td>
<td>-59.0</td>
<td>-5.4</td>
</tr>
</tbody>
</table>

**Morphology**

The morphology of tensile fracture surface of 50/50 RP/PP e-blends_stat with various GAs modified at absorbed dose of 40 kGy is shown in figure 6.23. Figure 6.23(b), 6.23(d), 6.23(f), and 6.23(h) show SEM photomicrographs at high magnification of tensile fracture surfaces of e-blends_stat with TAC, DPGDA, TMPTA, and DTMPTA, respectively. It is seen in figure 6.23 that there are two zones appeared in all SEM photomicrographs: bright zone and relatively dark zone. In the dark zone, the cavities were formed due to the pullout of RP during tensile testing. The number of cavities appeared in SEM photomicrographs of e-blend_stat with TAC seems relatively highest. It means that a lot of RPs was removed from the PP matrix. Moreover, the interface between RP and PP matrix is clearly seen in figure 6.23(b). It can be indicated that interfacial adhesion between RP and PP in blend and e-blend_stat with TAC is poor. Thus, TAC is ineffective to improve interfacial adhesion between RP and PP.
Figure 6.23: SEM photomicrographs of tensile fracture surfaces of e-blends_stat with GAs modified at 40 kGy: (a) and (b) 50/50 RP/PP e-blend_stat with TAC, (c) and (d) 50/50 RP/PP e-blend_stat with DPGDA, (e) and (f) 50/50 RP/PP e-blend_stat with TMPTA, and (g) and (h) 50/50 RP/PP e-blend_stat with DTMPTA.
In contrast, it is seen in SEM photomicrographs of tensile fracture surface of e-blend_stat with DTMPTA at low and high magnifications that fibril structure (see circle) are formed which indicates the improvement of interfacial adhesion between RP and PP. This SEM photomicrograph of e-blend_stat with DTMPTA confirms the greatest improvement of tensile properties of e-blend_stat when DTMPTA was added.

6.4.3 Effect of dose on e-blend_stat with different grafting agents

In this study, the e-blends_stat with DPGDA, TAC, TMPTA, and DTMPTA were modified by high energy electrons at absorbed doses of 20, 40, 60, 80, 100, and 120 kGy. The tensile properties and MFI values of e-blend_stat with different GAs were evaluated. It is noted that the results showed here are the average values of three samples.

Tensile properties

Tensile properties of e-blends_stat with various GAs as function of dose are illustrated in figure 6.24. It can be seen in figure 6.24(a) that the tensile strength increases with increasing dose for e-blend_stat with DPGDA as well as TMPTA and only slightly increases for e-blend_stat with TAC while the tensile strength of e-blend_stat with DTMPTA increases with increasing dose up to 80 kGy and then levels off. Moreover, it can be seen in figure 6.24(b) that elongation at break values of e-blend-stat with TMPTA and DTMPTA as well as DPGDA increase up to dose of 80 kGy or 100 kGy (in the case of e-blend_stat with DPGDA) and then decrease. The highest elongation at break values of e-blends_stat with DPGDA, TMPTA or DTMPTA are obtained for a dose of about 80 to 100 kGy. On the other hand, the elongation at break of e-blend_stat with TAC decreases with increasing dose. Finally, modulus values of e-blends_stat with different GAs slightly change when dose increases. The modulus values of e-blends_stat with DPGDA and TMPTA increase with increasing dose up to 100 kGy and then level off.
Figure 6.24: Tensile strength (a), elongation at break (b), and modulus (c) of e-blends_stat in presence of different GAs as function of dose.
From figure 6.24, it is clear that e-blend_stat with DTMPTA has highest tensile strength and elongation at break while e-blend_stat with TAC has lowest tensile strength and elongation at break. Thus, DTMPTA is the most efficient GA for enhancement the compatibility as well as interfacial adhesion between RP and PP. The optimum dose for achieving maximum elongation at break in e-blend_stat with DTMPTA amounts to about 80 kGy.

**Melt flow index**

Figure 6.25 shows the effect of dose and type of grafting agent on MFI of e-blend_stat. Among e-blend_stat in presence of various type of GAs, e-blend_stat with DTMPTA has lowest MFI whereas e-blend_stat in presence of TAC has highest MFI. It is obviously clear that compared with e-blends_stat with other GAs, less chain scission occurs in PP phase in e-blend_stat with DTMPTA as the absorbed dose increases. The MFI values of e-blends_stat with TAC and TMPTA increase with increasing dose. For e-blend_stat with DPGDA, MFI are nearly constant upto a dose of 20 kGy and then increases with increasing dose. In contrast to this, for e-blend_stat with DTMPTA, MFI firstly decreases, reaches a minimum value at about 20 kGy, and then increases with increasing dose. At doses of 20, 40, and 60 kGy, MFI values of e-blend_stat with DTMPTA are lower than MFI of blend with DTMPTA at 0 kGy.

![Figure 6.25: Melt flow index of e-blends_stat with DPGDA, TAC, TMPTA, and DTMPTA as function of dose.](image-url)
Thermal properties

In this work, only 50/50 RP/PP e-blend_stat with DTMPTA of 1.93 wt % of DTMPTA was selected to study the effect of dose on thermal properties of e-blend_stat with DTMPTA.

![DSC curves of 50/50 RP/PP e-blends_stat in presence of DTMPTA modified at different absorbed doses registered during 2nd heating (a) and cooling (b).](image)

**Figure 6.26:** DSC curves of 50/50 RP/PP e-blends_stat in presence of DTMPTA modified at different absorbed doses registered during 2\textsuperscript{nd} heating (a) and cooling (b).

It can be seen in figure 6.26 that the DSC curves of e-blends_stat with DTMPTA modified at different doses are similar. Table 6.5 summarized the thermal properties of blend and e-blend_stat with DTMPTA modified at different doses. Incorporation of DTMPTA into blend results in slightly increases of melting temperature as well as crystallization temperature and decrease of heat of fusion.
Compared with melting temperature and crystallization temperature values of blend with DTMPTA, melting temperature and crystallization temperature of e-blends_stat with DTMPTA modified at different doses are lower. The reduction of melting temperature of e-blend_stat with DTMPTA modified at different dose could result from chain scission occurred in PP matrix and reduction of crystal size upon treatment with high energy electrons [97]. The e-blends_stat with DTMPTA modified at different doses except e-blend_stat with DTMPTA modified at 60 kGy have lower melting temperature than blend. The heat of fusion of e-blends_stat with DTMPTA modified at different doses lower compared to the heat of fusion of blend.

Table 6.5: Glass transition temperature ($T_g$), crystallization temperature ($T_c$), melting temperature ($T_m$), and heat of fusion of 2$^{nd}$ heating of blend and e-blends_stat with DTMPTA modified at different absorbed doses

<table>
<thead>
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<th>Sample</th>
<th>Dose [kGy]</th>
<th>$T_g$ [°C]</th>
<th>$T_c$ [°C]</th>
<th>$T_m$ [°C]</th>
<th>$\Delta H_m$[J/g]</th>
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<td>Blend</td>
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<td>-61.3</td>
<td>102.0</td>
<td>139.9</td>
<td>29.31</td>
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<td>E-blend_stat with DTMPTA</td>
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<td>-59.1</td>
<td>101.2</td>
<td>137.9</td>
<td>25.41</td>
</tr>
</tbody>
</table>

6.4.4 Recyclability of e-blend_stat with DTMPTA modified at absorbed dose of 80 kGy

In this study, the 50/50 RP/PP e-blend_stat with DTMPTA modified at absorbed dose of 80 kGy was selected to study recyclability.
Tensile properties

Figure 6.27 shows tensile strength, elongation at break, and modulus of e-blend_stat with DTMPTA modified at absorbed dose of 80 kGy and at different reprocessing cycle.

**Figure 6.27:** Tensile strength (a), elongation at break (b), and modulus (c) of 50/50 RP/PP e-blend_stat with DTMPTA modified at absorbed dose of 80 kGy as function of number of cycle of reprocessing.
It is seen in figure 6.27(a) and 6.27(b) that the tensile strength and elongation at break values of 50/50 RP/PP e-blend_stat with DTMPTA modified at 80 kGy after the first and second reprocessing are higher than those of 50/50 RP/PP e-blend_stat with DTMPTA modified at 80 kGy that was not reprocessed. It is known that there are remaining radicals trapped in irradiated polymer, especially for polymer irradiated in the solid state [98 – 99]. These trapped radicals will cause further chemical reactions over a period of time. The chemical reactions occurred are called post-irradiation effects. The reaction rate depends on the reactivity of trapped radicals, the mobility of the matrix and the diffusion of oxygen into the sample. Moreover, the irradiation of polymers in air results in formation of peroxides. The peroxides are decomposed at elevated temperature so that the polymers irradiated in air will be rapidly degraded if they are heated. Therefore, in this study, it is assumed that these trapped radicals induced further reactions during the first and second reprocessing resulting in improved tensile strength and elongation at break. The tensile properties of 50/50 RP/PP e-blend_stat with DTMPTA modified at absorbed dose of 80 kGy after the third reprocessing are comparable to those of 50/50 RP/PP e-blend_stat with DTMPTA modified at absorbed dose of 80 kGy that was not reprocessed. After 5th reprocessing, the elongation at break reduces to about 15% while tensile strength and modulus are comparable. After 10th reprocessing cycle, the elongation at break and modulus decrease dramatically while tensile strength decreases slightly.
Charpy impact strength

Figure 6.28 shows the influence of recycling on Charpy impact strength of 50/50 RP/PP e-blend_stat with DTMPTA modified at absorbed dose of 80 kGy. It is seen in figure 6.28 that the Charpy impact strength of e-blend_stat with DTMPTA after first and second reprocessing are lower than the original value of RP/PP e-blend_stat with DTMPTA that was not reprocessed. In contrast, the Charpy impact strength values of e-blend_stat with DTMPTA after 3rd or 10th reprocessing are comparable to e-blend_stat with DTMPTA that was not reprocessed.

![Figure 6.28: Charpy impact strength of 50/50 RP/PP e-blend_stat with DTMPTA modified at absorbed dose of 80 kGy as function of number of cycle of recycling.](image)

Hardness

The result of hardness of 50/50 RP/PP e-blend_stat with DTMPTA modified at absorbed dose of 80 kGy that was reprocessed for 10 cycles are represented in figure 6.29. It is clear that there is no effect of reprocessing on hardness of e-blend_stat with DTMPTA modified at 80 kGy within the experimental uncertainty.
6 Results and Discussion

Figure 6.29: Shore A and Shore D Hardness of 50/50 RP/PP e-blend_stat with DTMPTA modified at absorbed dose of 80 kGy as function of number of cycle of recycling.

**Tension set**

Figure 6.30 shows the tension set of e-blend_stat with DTMPTA modified at absorbed dose of 80 kGy and at different reprocessing cycle. It is seen in figure 6.30 that there is no influence of reprocessing on tension set of e-blend_stat with DTMPTA modified at 80 kgy

Figure 6.30: Tension set of 50/50 RP/PP e-blend_stat with DTMPTA modified at absorbed dose of 80 kGy as function of number of cycle of recycling.
Melt flow index

The influence of recycling on MFI of 50/50 RP/PP e-blend_stat with DTMPTA modified at absorbed dose of 80 kGy is shown in figure 6.31. It is seen that the MFI values increase with increasing number of reprocessing. After 10 cycle, the MFI amounts to 12.56 g/10 min.

![Figure 6.31: MFI of 50/50 RP/PP e-blend_stat with DTMPTA modified at 80 kGy as function of number of cycle of recycling.](image)

6.5 Rubber particle/polypropylene e-blend_dyn

6.5.1 Effect of high energy electrons on properties of e-blend_dyn without grafting agent

![Figure 6.32: Tensile strength, elongation at break, and modulus of 50/50 RP/PP blend and 50/50 RP/PP e-blend_dyn without GA modified at absorbed dose of 40 kGy.](image)
Figure 6.32 shows the tensile properties of RP/PP blend and RP/PP e-blend_dyn without GA modified at absorbed dose of 40 kGy. Compared with RP/PP blend, tensile properties of RP/PP e-blend_dyn are lower. The reduction of tensile properties of e-blend_dyn shows no enhancement in interfacial adhesion between RP and PP. Therefore, it is possible to assume that only high energy electrons cannot improve the interfacial adhesion between RP and PP. Thus, a specific GA is required for improving the tensile properties of RP/PP blend.

6.5.2 Effect of grafting agent on properties of e-blend_dyn modified at absorbed dose of 40 kGy

Tensile Strength

The GAs and contents of GA used in e-blends_dyn prepared by electron induced reactive processing are the same as used in e-blend_stat modified by high energy electrons under stationary condition.

Figure 6.33: Stress-strain diagram of 50/50 RP/PP blend and 50/50 RP/PP e-blends_dyn in presence of TAC, DPGDA, TMPTA as well as DTMPTA modified at absorbed dose of 40 kGy.

It can be seen in figure 6.33 that tensile properties of e-blends_dyn in presence of different GAs modified at absorbed dose of 40 kGy are similar to those of e-blends_stat (figure 6.19). The e-blend_dyn with DTMPTA has highest tensile properties because DTMPTA having four acrylate groups has highest reactivity in
grafting reaction. On the other hand, compared to e-blend_dyn with other GAs, e-blend_dyn with TAC has lowest tensile properties. Moreover, the tensile properties of e-blend_dyn with TAC modified at 40 kGy are close to neat RP/PP blend due to low reactivity of TAC which has allyl monomers.

**Melt flow index**

The effect of GAs on MFI values of e-blends_dyn modified at absorbed dose of 40 kGy are represented in figure 6.34. It can be seen that the effect of TAC and DTMPTA on MFI of e-blend_dyn are similar to those on MFI of e-blend_stat (figure 6.20). The MFI of e-blend_dyn with DTMPTA is the lowest as well as lower than for neat blend while the MFI of e-blend_dyn with TAC is the highest. Because e-blend_dyn with DTMPTA has MFI lower than neat blend, it is expected that not only coupling of PP to RP but also crosslinking in PP dominate.

![Figure 6.34: MFI of 50/50 RP/PP blend and 50/50 RP/PP e-blendsDyn in presence of TAC, DPGDA, TMPTA, as well as DTMPTA modified at absorbed dose of 40 kGy.](image)

**Thermal properties**

The effect of GAs on thermal properties of e-blend_dyn modified at absorbed dose of 40 kGy is shown in figure 6.35 and listed in table 6.6. It can be seen that melting temperature and crystallization temperature of all e-blends_dyn in presence of different GAs shift to higher temperature when compare to those of neat blend. The e-blend_dyn with DTMPTA has highest T_m and T_c. The heat of fusion and T_g of all e-blend are slightly changing. The increasing T_c indicates a
nucleation effect. The increase in $T_m$ of PP phase in e-blend_dyn indicates that polymer build-up processes are dominating during electron induced reactive processing. In comparison to neat 50/50 RP/PP blend, only heat of fusion values of e-blend_dyn with DTMPTA are lower. It was reported that increase of melting temperature as well as lowering of crystallization temperature, heat of crystallization and heat of fusion indicate the formation of crosslinking of PP when PP was treated by $\gamma$-irradiation at dose up to 25 kGy [100]. Thus, it is possible to assume from thermal study of e-blendsDyn with various GAs modified at absorbed dose of 40 kGy that both crosslinking and degradation occurred in all PP matrix of e-blendsDyn, especially in e-blendDyn with DTMPTA.

**Figure 6.35:** DSC curves of 50/50 RP/PP blend and 50/50 RP/PP e-blendsDyn in presence of DPGDA, TAC, TMPTA as well as DTMPTA modified at absorbed dose of 40 kGy registered during 2nd heating (a) and cooling (b).
Table 6.6: Glass transition temperature ($T_g$), crystallization temperature ($T_c$), melting temperature ($T_m$), and heat of fusion ($\Delta H_m$) of 2nd heating of blend and e-blends_dyn with different GAs modified at absorbed dose of 40 kGy

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<tr>
<th>Sample</th>
<th>Dose [kGy]</th>
<th>Thermal properties</th>
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</thead>
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<td>$T_g$ [°C]</td>
<td>$T_c$ [°C]</td>
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<tr>
<td>Blend</td>
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<td>-61.3</td>
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<tr>
<td>E-blend_dyn TAC</td>
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<tr>
<td>E-blend_dyn DTMPTA</td>
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<td>-60.0</td>
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</table>

Dynamic mechanical properties

The tan δ curves of blend and e-blends_dyn in presence of various GAs modified at absorbed dose of 40 kGy as function of temperature are shown in figure 6.36. The $T_g$ values of RP and PP in blend and e-blends_dyn in presence of various GAs modified at 40 kGy are summarized in table 6.7. It is seen that there are three tan δ peaks present in both blend and e-blends_dyn with various GAs. The tan δ peaks in the range from $-70$ °C to $-40$ °C, from $-30$ °C to 10 °C, and from 30 °C to 80°C are referred to $\alpha$-transition and $T_g$ of RP, $\beta$-transition and $T_g$ of PP, and $\alpha$-relaxation peak of PP, respectively. In blend, the $T_g$ values for RP and PP are $-59.7$ °C and $-5.9$ °C, respectively. The $T_g$ of RP in e-blend_dyn with TAC shifts slightly to lower temperature while $T_g$ of RP in e-blend_dyn with TMPTA or DTMPTA slightly increases. Moreover, $T_g$ of RP in e-blend_dyn with DPGDA is same as that of RP in blend. The decrease of $T_g$ of RP in e-blend_dyn with TAC indicates that TAC is not effective in compatibilization. The $T_g$ values of PP matrix in all e-blends_dyn are slightly higher than that of PP matrix in blend.
Figure 6.36: Tan δ vs temperature curves for 50/50 RP/PP e-blends_dyn with various GAs at dose of 40 kGy compared with tan δ vs temperature curves for 50/50 RP/PP blend.

Table 6.7: Glass transition temperature ($T_g$) of RP and PP in 50/50 RP/PP blend and 50/50 RP/PP e-blends_dyn with GAs modified at absorbed dose of 40 kGy

<table>
<thead>
<tr>
<th>Sample</th>
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<th>$T_g$/PP [°C]</th>
</tr>
</thead>
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<td>Blend</td>
<td>0</td>
<td>-59.7</td>
<td>-5.9</td>
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<td>E-blend_dyn TAC</td>
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<td>-60.1</td>
<td>-5.7</td>
</tr>
<tr>
<td>E-blend_dyn DPGDA</td>
<td>40</td>
<td>-59.7</td>
<td>-5.0</td>
</tr>
<tr>
<td>E-blend_dyn TMPTA</td>
<td>40</td>
<td>-59.3</td>
<td>-5.1</td>
</tr>
<tr>
<td>E-blend_dyn DTMPTA</td>
<td>40</td>
<td>-59.3</td>
<td>-5.2</td>
</tr>
</tbody>
</table>

Morphology

The SEM photomicrographs of tensile fracture surfaces of e-blends_dyn in presence of various GAs modified at absorbed dose of 40 kGy are shown in figure 6.37. Figure 6.37(b), 6.37(d), 6.37(f) and 6.37(h) show SEM photomicrographs in high magnifications of tensile fracture surface of e-blends_dyn with TAC, DPGDA, TMPTA, and DTMPTA, respectively.
Figure 6.37: SEM photomicrographs of tensile fracture surfaces of e-blendsDyn with GAs modified at 40 kGy: (a) and (b) 50/50 RP/PP e-blendDyn with TAC, (c) and (d) 50/50 RP/PP e-blendDyn with DPGDA, (e) and (f) 50/50 RP/PP e-blendDyn with TMPTA and (g) and (h) 50/50 RP/PP e-blendDyn with DTMPA.
It can be seen in SEM photomicrographs at high magnification that the fibril structure (see circle) are observed in the tensile fracture surface of e-blends_dyn with DPGDA, TMPTA and DTMPTA. The fibril structure indicates the occurrence of plastic formation at the interface between RP and PP matrix. In SEM photomicrographs at low magnification, the fibril structure can be observed only in the tensile fracture surface of e-blend_dyn with DTMPTA. There is no formation of fibril between the phases in e-blend_dyn with TAC. The formation of fibril structure indicates the improvement of interfacial adhesion between RP and PP which results in increasing of the tensile properties of e-blend_dyn with DPGDA, TMPTA and DTMPTA modified at absorbed dose of 40 kGy.

6.5.3 Effect of dose on properties of e-blend_dyn with DTMPTA

In this study, only e-blend_dyn with DTMPTA was selected to investigate the effect of dose on properties of e-blend_dyn. The e-blend_dyn with DTMPTA was modified by high energy electrons during mixing at dose of 40, 60, and 80 kGy. The effect of dose on tensile as well as thermal properties and MFI of e-blend_dyn are reported.

**Tensile properties**

Figure 6.38 shows the effect of dose on tensile properties of e-blend-dyn in presence of DTMPTA. The tensile strength and elongation at break of e-blend_dyn with DTMPTA increase up to a dose of 40 kGy and then decrease as dose increase. It can be seen that at 40 kGy the tensile strength and elongation at break are maximum, 13.1 MPa and 205.61 %, respectively. The modulus values of e-blend_dyn with DTMPTA also increase up to dose of 40 kGy and then slightly decrease with increasing dose.

In electron induced reactive processing, not only dose and type of GA but also temperature, rotor speed, and absorbed dose per rotation have an influence on the properties of e-blend_dyn. In electron modification under stationary condition, dose and type of GA are the main parameters influencing on the properties of e-blend_stat. It is clear that the optimum dose for e-blend_dyn is in the range of 40 kGy.
Figure 6.38: Tensile strength (a), elongation at break (b), and modulus (c) of e-blends_dyn in presence of DTMPTA as function of dose.
6 Results and Discussion

**Melt flow index**

The effect of dose on MFI of e-blend\_dyn in presence of DTMPTA is shown in figure 6.39. The MFI of e-blend\_dyn with DTMPTA decrease up to a dose of 60 kGy and then increase. Compared to MFI of blend with DTMPTA, MFI values of e-blend\_dyn with DTMPTA modified at 40 and 60 kGy are lower. The lower MFI values indicate that polymer build-up or grafting processes are dominating.

![Melt flow index of e-blend\_dyn with DTMPTA as function of dose.](image)

**Figure 6.39**: Melt flow index of e-blend\_dyn with DTMPTA as function of dose.

**Thermal properties**

The effect of dose on thermal properties of e-blend\_dyn in presence of DTMPTA is shown in figure 6.40. The glass transition temperature, crystallization temperature, melting temperature, and heat of fusion values of blend as well as e-blends\_dyn in presence of DTMPTA modified at 0, 40, 60, and 80 kGy are summarized in table 6.8. It can be seen from table 6.8, that melting temperature and crystallization temperatures of e-blend\_dyn in presence of DTMPTA are higher than those of blend while heat of fusion of e-blend\_dyn in presence of DTMPTA are lower than that of blend. It is seen in figure 6.40 and in table 6.8 that melting temperature and crystallization temperature values of e-blend\_dyn in presence of DTMPTA modified at 40, 60, and 80 kGy shift to higher temperature. The heat of fusion of e-blend\_dyn with DTMPTA firstly increases and then decrease when absorbed dose increases. The melting temperature and crystallization temperature values of e-blend\_dyn in presence of DTMPTA
modified at 40, 60, and 80 kGy are higher than those of blend while heat of fusion values of e-blend_dyn in presence of DTMPTA modified at 40, 60, and 80 kGy are lower than heat of fusion of blend. Moreover, it is seen in figure 6.40 that there are two melting peaks in DSC curve of e-blend_dyn with DTMPTA modified at 60 kGy. The first melting temperature is around 125 °C which may correspond to melting temperature of β-phase and the second melting temperature is around 144.3 °C which may correspond to melting temperature of α-phase [101]. This can be indicated that the transition from α-phase to β-phase occurred.

![DSC curves of 50/50 RP/PP e-blends_dyn in presence of DTMPTA modified at different absorbed doses registered during 2nd heating (a) and cooling (b).](image)

**Figure 6.40**: DSC curves of 50/50 RP/PP e-blends_dyn in presence of DTMPTA modified at different absorbed doses registered during 2nd heating (a) and cooling (b).
6 Results and Discussion

Table 6.8: Glass transition temperature ($T_g$), crystallization temperature ($T_c$), melting temperature ($T_m$), and heat of fusion ($\Delta H_m$) of 2nd heating of blend and e-blends_dyn with DTMPTA modified at different absorbed doses

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dose [kGy]</th>
<th>Thermal properties</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$T_g$ [°C]</td>
<td>$T_c$ [°C]</td>
<td>$T_m$ [°C]</td>
<td>$\Delta H_m$[J/g]</td>
</tr>
<tr>
<td>Blend</td>
<td>0</td>
<td>-61.3</td>
<td>102.0</td>
<td>139.9</td>
<td>29.31</td>
</tr>
<tr>
<td>E-blend_dyn DTMPTA</td>
<td>0</td>
<td>-60.8</td>
<td>103.5</td>
<td>141.1</td>
<td>24.53</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-60.0</td>
<td>109.1</td>
<td>142.3</td>
<td>27.00</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>-58.5</td>
<td>112.4</td>
<td>144.3</td>
<td>21.33</td>
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<tr>
<td></td>
<td>80</td>
<td>-58.1</td>
<td>108.2</td>
<td>144.2</td>
<td>21.21</td>
</tr>
</tbody>
</table>

6.5.4 Effect of new processing parameters on properties of e-blend_dyn with DTMPTA

Due to highest tensile properties of e-blend_dyn with DTMPTA, this blend was selected for further study. In order to investigate the influence of treatment parameters as well as content of GA on tensile properties of e-blend_dyn with DTMPTA, the RP/PP/DTMPTA blend ratio selected was 50/46/4.

Electron treatment time

The electron treatment time was varied from 15, 30, to 60 seconds at fixed electron energy of 1.5 MeV as well as fixed absorbed dose of 40 kGy.

Tensile properties

The effect of electron treatment time on tensile properties of RP/PP e-blend_dyn with DTMPTA modified at absorbed dose of 40 kGy is shown in figure 6.41. It is seen in figure 6.41(a) and 6.41(b) that tensile strength and elongation at break were enhanced when the electron treatment time was increased from 15 seconds to 60 seconds. In contrast, the modulus is nearly constant when electron treatment time increases. When compared with unmodified blend with DTMPTA, all e-blends_dyn with DTMPTA modified at absorbed dose of 40 kGy and different
electron treatment times have greatly higher tensile properties which are indicated that improvement in the interfacial adhesion between RP and PP.

**Figure 6.41:** Tensile strength (a), elongation at break (b), and modulus (c) of 50/46 RP/PP e-blend_dyn with DTMPTA of 4 wt% modified at absorbed dose of 40 kGy as function of electron treatment time.
It was shown that the electron treatment time influences on tensile properties, especially elongation at break, of e-blend_dyn with DTMPTA. Higher electron treatment time results in maximum tensile properties. Thus, further experiments are required at higher electron treatment times to get optimum tensile properties.

**Melt flow index**

Figure 6.42 shows the effect of electron treatment time on MFI of RP/PP e-blend_dyn with DTMPTA modified at absorbed dose of 40 kGy. It is observed that all e-blends_dyn with DTMPTA have lower MFI than unmodified blend with DTMPTA. This indicates that build-up processes and grafting to RP is dominating. The MFI of e-blend_dyn with DTMPTA modified for 15 seconds are comparable to that of e-blend_dyn with DTMPTA modified at 30 seconds. With increasing electron treatment time to 60 seconds, the MFI increases. Thus increasing MFI values correlate with improved tensile properties.
6 Results and Discussion

**Figure 6.42:** MFI of 50/46 RP/PP e-blend_dyn with DTMPTA of 4 wt% modified at absorbed dose of 40 kGy as function of electron treatment time.

**Electron Energy**

In this study, the electron energies used were 1.0 and 1.5 MeV and the electron treatment time as well as absorbed dose were fixed at 30 seconds and 40 kGy, respectively.

**Tensile properties**

Figure 6.43 shows the effect of electron energy on tensile properties of e-blend_dyn with DTMPTA modified at absorbed dose of 40 kGy for 30 seconds. It is observed that the tensile strength and modulus increase with increasing electron energy whereas elongation at break reduces with increasing electron energy. Thus, it was shown that electron energy also influences on elongation at break of e-blend_dyn with DTMPTA.
Figure 6.43: Tensile strength (a), elongation at break (b), and modulus (c) of 50/46 RP/PP e-blend_dyn with DTMPTA of 4 wt% modified at absorbed dose of 40 kGy for 30 seconds as function of electron energy.
Melt flow index

The effect of electron energy on MFI of e-blend_dyn with DTMPTA modified at absorbed dose of 40 kGy for 30 seconds is shown in figure 6.44. It is observed that there is no influence of electron energy on MFI within the experimental uncertainty.

![Melt flow index graph]

Figure 6.44: MFI of 50/46 RP/PP e-blend_dyn with DTMPTA of 4 wt% modified at absorbed dose of 40 kGy for 30 seconds as function of electron energy.

6.6 Comparison of e-blend_stat as well as e-blend_dyn with EA

In order to compare e-blend_stat as well as e-blend_dyn with EA, e-blend_stat with DTMPTA and e-blend_dyn with DTMPTA (1.5 MeV, 30 s) are selected because both e-blend_stat with DTMPTA and e-blend_dyn with DTMPTA have highest tensile strength and elongation at break.

Tensile properties

The tensile properties of both e-blends with DTMPTA as function of dose are shown in figure 6.45. The blue line represents the property level of EA. It can be seen that at 40 kGy tensile strength and elongation at break of e-blend_dyn with DTMPTA are comparable to those of e-blend_stat with DTMPTA. The optimum tensile strength and elongation at break of e-blend_dyn with DTMPTA were obtained when absorbed dose is 40 kGy whereas the optimum tensile strength and elongation at break of e-blend_stat with DTMPTA were obtained when absorbed dose is approximately 80 kGy. At 80 kGy, the tensile strength and
elongation at break values of e-blend-stat with DTMPTA is higher than those of e-blend_dyn with DTMPTA and reaches the level of EA. At all absorbed doses, the modulus values of e-blend_dyn are higher than those of e-blend_stat and EA.

It can be seen that e-blend_dyn with DTMPTA has lower tensile strength and elongation at break than EA while e-blend_stat with DTMPTA has tensile strength and elongation at break comparable to EA when absorbed dose amounts to 80 kGy.

![Graphs showing tensile strength, elongation at break, and modulus vs. dose](image)

**Figure 6.45:** Tensile strength (a), elongation at break (b), and modulus (c) of 50/50 RP/PP e-blend_stat with DTMPTA and e-blend_dyn with DTMPTA as function of dose in comparison to EA.
Figure 6.45: (Continued from previous page).

Melt flow index

Figure 6.46 shows comparison of MFI of e-blend_dyn with DTMPTA and e-blend_stat with DTMPTA as function of dose in comparison with EA. It can be seen that at 40 kGy, MFI of e-blend_dyn with DTMPTA is slightly higher than that of e-blend_stat with DTMPTA. Moreover, at 50 kGy, MFI of e-blend_dyn with DTMPTA is equal to that of e-blend_stat with DTMPTA. At higher doses, e-blend_dyn with DTMPTA has lower MFI than e-blend_stat with DTMPTA. In addition, MFI of both e-blends with DTMPTA are lower than that of EA. At 40 kGy, compared to both e-blends with DTMPTA, the MFI of EA is around five times higher. Nevertheless, tensile strength and elongation at break of EA are higher compared to e-blend_stat at 40 kGy and e-blend_dyn at 40 kGy. In contrast to this, lower values of MFI correlate with higher E modulus.
6 Results and Discussion

Figure 6.46: MFI of e-blend_stat with DTMPTA and e-blend_dyn with DTMPTA as function of dose in comparison to EA.

Thermal properties

Thermal properties of both e-blend_stat and e-blend_dyn with DTMPTA at 40 kGy as well as EA are shown and summarized in figure 6.47 and in table 6.9, respectively.

Figure 6.47: DSC curves of 50/50 RP/PP e-blends_dyn with DTMPTA modified at absorbed dose of 40 kGy and e-blend_stat with DTMPTA modified at absorbed dose of 40 kGy as well as EA registered during 2nd heating (a) and cooling (b).
It is clearly seen that the melting temperature and crystallization temperature of e-blend_dyn with DTMPTA is higher than both e-blend_stat with DTMPTA and EA. In addition, the melting temperature of EA is lowest. This is due to peroxide induced degradation in PP matrix [102]. It can be indicated that higher degradation occurred in PP matrix of EA than in that of both types of e-blends with DTMPTA modified at 40 kGy. On the other hand, the glass transition temperature and heat of fusion of both e-blends with DTMPTA are comparable to those of EA.

Table 6.9: Glass transition temperature ($T_g$), crystallization temperature ($T_c$), melting temperature ($T_m$), heat of fusion of 2nd heating of e-blends_dyn with DTMPTA modified at modified at absorbed dose of 40 kGy and e-blend_stat with DTMPTA modified at modified at absorbed dose of 40 kGy as well as EA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dose [kGy]</th>
<th>$T_g$ [°C]</th>
<th>$T_c$ [°C]</th>
<th>$T_m$ [°C]</th>
<th>$\Delta H_m$ [J/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA (50RP/50PP/2PO)</td>
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<td>-60.6</td>
<td>100.2</td>
<td>134.7</td>
<td>26.90</td>
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<tr>
<td>E-blend_stat with DTMPTA (50RP/50PP/1.93DTMPTA)</td>
<td>40</td>
<td>-60.3</td>
<td>102.9</td>
<td>138.7</td>
<td>26.93</td>
</tr>
<tr>
<td>E-blend_dyn with DTMPTA (50RP/50PP/1.93DTMPTA)</td>
<td>40</td>
<td>-60.0</td>
<td>109.1</td>
<td>142.3</td>
<td>27.00</td>
</tr>
</tbody>
</table>
In this study, RP was compounded with polypropylene copolymer in order to achieve the RP/PP blend which has properties, especially elongation at break comparable to TPV or EA. However, RP/PP blend cannot classify as TPV and EA because the elongation at break is lower than 100%. This is due to low interfacial adhesion or compatibility between RP and PP. High energy electrons can be used for modification of RP/PP blend to enhance compatibility/interfacial adhesion.

The modification of polymeric materials by high energy electrons will result in changed properties. The chemical reactions occurred in polymeric materials are crosslinking, branching, and grafting as well as degradation, functionalization and formation of small molecular products. In this study, high energy electrons were used to modify RP/PP blends with or without GAs under two conditions: stationary and in-stationary conditions. The modification of RP/PP blend with high energy electrons under stationary condition is a process where required absorbed dose is applied to form parts in solid state at room temperature while the modification of RP/PP blend with high energy electrons under in-stationary condition is a novel process where required absorbed dose is applied during melt mixing process. The latter process is comparable with that of dynamic stabilization, but uses another radical generating system. Finally, high energy electrons were used to modify PP for generation of a self-compatilizer.

The modification of PP with high energy electrons results in degradation, discoloration of PP, and extreme decrease of elongation at break due to degradation. The modified PP was added into RP/PP blend in order to improve interfacial adhesion between RP and PP. It acts as a compatibilizer. The incorporation of modified PP into RP/PP blend results in enhancement of tensile properties due to functional groups generated in modified PP. The optimum content of modified PP (200 kGy) added into RP/PP blend amounts to about 17.5 wt%. At this optimum content, the tensile strength, elongation at break, and modulus of e-blend_comp are 11.70 MPa, 111 %, and 303 MPa, respectively.

Firstly, the 50/50 RP/PP blend without adding any GA was modified by high energy electrons under stationary condition at absorbed dose of 25, 50, and 100 kGy. The tensile strength, elongation at break and MFI values increased with
increasing dose. At absorbed dose of 100 kGy, tensile properties and MFI of 50/50 RP/PP e-blend_stat are highest. However, the elongation at break of e-blend_stat at 100 kGy is lower than 100% and that of RP/PP*/PP blend containing 17.5 wt% of modified PP (PP*). The dramatic increase of MFI of e-blend_stat at 100 kGy indicates degradation of PP matrix. This means, pure radical generation via high energy electrons in RP/PP blend does not result in desired tensile properties.

Thus, specific GA is required. In this study, four GAs were tested: DPGDA, TAC, TMPTA, and DTMPTA. Among various GAs, DTMPTA is the most effective while TAC is unsuitable for promoting interfacial adhesion between RP and PP. The 50/50 RP/PP e-blend_stat in presence of DTMPTA has highest tensile properties and lowest MFI while the 50/50 RP/PP e-blend_stat in presence of TAC has lowest tensile properties which are close to tensile properties of 50/50 RP/PP blend as well as highest MFI. In crosslinking of polypropylene, PFMs containing acrylate groups and having more than two functional group are more suitable for use in promoting crosslinking of polypropylene copolymer while PFMs containing allyl groups is more suitable for use in improving crosslinking of polypropylene homopolymer. Therefore, it is clear that DTMPTA having four acrylate groups is the most effective to improve interfacial adhesion between RP and PP. It is expected that RP-PP copolymer and RP-GA-PP copolymer are formed during modification with high energy electrons under stationary condition. Compared with melting temperature, heat of fusion and crystallization temperature of 50/50 RP/PP blend, the melting temperatures and heat of fusion values of all e-blend_stat in presence with various GAs are lower while the crystallization temperatures are slightly higher. From DMA study, it can be indicated that the 50/50 RP/PP blend and 50/50 RP/PP e-blends_stat with various GAs are incompatible. The addition of DPGDA, TMPTA, and DTMPTA into 50/50 RP/PP e-blend_stat at 40 kGy results in a small shift of glass transition temperature to higher temperature whereas addition of TAC into 50/50 RP/PP e-blend_stat at 40 kGy results in slightly shift of glass transition temperature to lower temperature. The decreasing of glass transition temperature of RP in e-blend_stat with TAC at 40 kGy supports that TAC is unsuitable for promoting interfacial adhesion. The glass transition temperature of RP in e-blend_stat with DTMPTA is highest. This
confirms that DTMPTA is the most effective for promoting interfacial adhesion between RP and PP. In addition, the greatest efficiency of DTMPTA in enhancement of interfacial adhesion between RP and PP was supported from the photomicrograph of tensile fracture surface of 50/50 RP/PP e-blend_stat with DTMPTA which shows fibril structure. At an optimum dose of about 80 kGy, tensile strength and elongation at break values of 50/50 RP/PP e-blends_stat with DPGDA, TMPTA, and DTMPTA are highest. In addition, e-blend_stat with DTMPTA modified at 80 kGy shows tensile properties which are comparable with those of EA as well as high recyclability. After 5th reprocessing, there is a slightly decrease in tensile properties and little increase in MFI.

The modification of 50/50 RP/PP blend with high energy electrons under in-stationary condition results in decreased tensile properties and increased of MFI. This means that degradation is dominating and specific grafting agent is required for improved tensile properties. The same GAs added into e-blend_stat were used. The 50/50 RP/PP e-blend_dyn in presence of DTMPTA at 40 kGy has highest tensile properties whereas the 50/50 RP/PP e-blend_dyn in presence of TAC at 40 kGy has lowest tensile properties. Compared with melting and crystallization temperatures as well as heat of fusion of 50/50 RP/PP blend, the melting and crystallization temperatures of all 50/50 RP/PP e-blend_dyn in presence of various GA are higher while heat of fusion of them is nearly constant. From DMA study, compared with glass transition temperature of RP in blend, glass transition temperature of e-blend-dyn with TAC shifts slightly to lower temperature while glass transition temperature of e-blend_dym with DTMPTA shifts a little to higher temperature. Further, the results from morphological study also support that DTMPTA is the most effective GA for use in modification of RP/PP blend with high energy electrons under in-stationary condition. The optimum dose used in modification of RP/PP blend with high energy electrons under in-stationary condition is 40 kGy. Moreover, tensile properties of e-blend_dyn with DTMPTA depend not only on absorbed dose but also on treatment time and electron energy.

The e-blend_stat with DTMPTA and e-blend_dyn with DTMPTA are compared with EA. Only e-blend_stat with DTMPTA at 80 kGy has tensile strength and elongation at break values comparable to EA. The modulus values of both
e-blend\_stat with DTMPTA and e-blend\_dyn with DTMPTA are greater than that of EA. Moreover, the modulus of e-blend\_dyn with DTMPTA is higher than that of e-blend\_stat with DTMPTA. The MFI values of both e-blend\_stat with DTMPTA and e-blend\_dyn with DTMPTA is lower than MFI of EA. Further, e-blend\_dyn with DTMPTA has lowest MFI. EA has lower melting temperature as well as crystallization temperature than e-blend\_stat with DTMPTA at 40 kGy and e-blend\_dyn with DTMPTA at 40 kGy. The lowest melting temperature of EA can be indicated that the degradation of PP matrix in EA is higher than in both e-blends with DTMPTA modified at 40 kGy. Heat of fusion value of EA is comparable to heat of fusion value of e-blend\_stat with DTMPTA at 40 kGy and e-blend\_dyn with DTMPTA at 40 kGy.

In summary, the e-blend\_stat with DTMPTA modified at 80 kGy as well as e-blend\_dyn with DTMPTA modified at 40 kGy can be used instead of EA and TPV in some application such as in the automotive industry as well as the leisure and sport industry.

**Further study**

In present study, the modification of blend of PP with RP based on NR/SBR in presence of various GAs, especially DTMPTA, with high energy electrons under stationary condition results in best tensile properties which are comparable to those of EA. Thus, this procedure should be transferred to industrial application.

Further investigations are required for the electron induced reactive processing (in-stationary treatment) in order to improve the tensile properties of RP/RR e-blend\_dyn. Due to experimental results, the influence of amount of DTMPTA should be studied for concentrations less than 2 wt%. Further, the influence of treatment time and electron energy should be studied. The experimental results support improved tensile properties for treatment times greater than 60 s as well as electron energy less than 1.5 MeV.

Next, both procedures of electron treatment should be tested for blends based on other type of RP and thermoplastic. Thus, e-blends based on other commodity plastics like polyethylene or isotactic polypropylene and RP based on NR/SBR as well as polypropylene-copolymer and RP based on EPDM should be investigated.
Finally, comprehensive investigation of continuously working process of electron induced reactive processing is required. In the present work, a laboratory internal mixer was used. Thus, e-blend_dyn of only 40 grams was obtained per one batch cycle. Therefore, the electron accelerator should be coupled with other polymer processing machine, especially extruder.
8 References


conditions. Paper presented at the annual meeting of the Polymer Processing Society, Salermo, Italy.


**Appendix A: Sequence of adding PP, RP and GA as well as time began to modify blend in electron induced reactive processing**

**Table A.1:** Sequence of adding PP, RP and GA as well as time began to modify blend in electron induced reactive processing

<table>
<thead>
<tr>
<th>Time [Min]</th>
<th>Note</th>
</tr>
</thead>
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<tr>
<td>0:00</td>
<td>temperature: from 190 °C to 140 °C; internal mixer on</td>
</tr>
<tr>
<td>0:30</td>
<td>water on</td>
</tr>
<tr>
<td>1:00</td>
<td>adding PP_1</td>
</tr>
<tr>
<td>1:20</td>
<td>adding PP_2</td>
</tr>
<tr>
<td>1:40</td>
<td>adding PP_3</td>
</tr>
<tr>
<td>2:00</td>
<td>adding PP_4</td>
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<tr>
<td>2:20</td>
<td></td>
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<tr>
<td>2:30</td>
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</tr>
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<td>adding RP_1</td>
</tr>
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<td>adding RP_2</td>
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<tr>
<td>3:05</td>
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</tr>
<tr>
<td>3:15</td>
<td>adding RP_4</td>
</tr>
<tr>
<td>3:30</td>
<td>adding GA</td>
</tr>
<tr>
<td>5:00</td>
<td>door closed; starting electron accelerator</td>
</tr>
<tr>
<td>6:00</td>
<td></td>
</tr>
<tr>
<td>7:00</td>
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<tr>
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<td>door opened</td>
</tr>
<tr>
<td>10:00</td>
<td>Internal mixer and water off; take off</td>
</tr>
</tbody>
</table>
Curriculum Vitae

Personal data
Name: Kunlapaporn Sriragool
Date of Birth: 3rd July 1980
Birthplace Uttaradit, Thailand
Nationality: Thai
Marital status: Single

Education
1984 – 1992  Tha-It Municipal School, Uttaradit, Thailand
1992 – 1998  Wattana Wittaya Academy, Bangkok, Thailand
1998 – 2002  Suranaree University of Technology, Nakhon Ratchasima, Thailand
             Bachelor of Engineering (Polymer Engineering)
2003 – 2006  Martin - Luther University Halle – Wittenberg, Halle, Germany
             Master of Science (Applied Polymer Science)

Professional experience
05/2006 – today  Scientific Assistant, Institut für Fördertechnik und kunststoffe, Professur Kunststoff, Chemnitz University of Technology, Chemnitz, Germany