Reactive EB Processing of Polymer Compounds

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Summary: Polymer modification with high energy electrons is well-established in polymer industry and used for degradation, cross-linking, grafting, curing, and polymerization. These applications use local and temporal precise input of energy in order to generate excited atoms or molecules as well as ions for subsequent molecule changes via radical induced chemical reactions. Reactive electron beam (EB) processing combines melt mixing process and chemical reaction simultaneously. For this purpose, a 1.5 MeV electron accelerator was directly coupled to an internal mixer in order to induce chemical reactions by energy input via high energy electrons under dynamic conditions of melt mixing of different polymer compounds. In the present study, reactive EB processing was used for the development of a flame retardant polyethylene composite as well as Thermoplastic Vulcanizate. The influence of absorbed dose as well as electron energy and electron treatment time was studied. Increased values of both tensile strength and elongation at break of polymer compounds indicated in-situ compatibilization upon reactive EB processing.

Keywords: high energy electrons; polymer composites; polymer processing; thermoplastic vulcanizate

Introduction

Polymer Compounds

Material properties of polymers can be specifically designed and changed by addition of fillers or reinforcing substances into polymers (e.g. composites) as well as by mixing of several polymers (polymer blends). Magnesium-hydroxide (MH) is a good endothermic flame retardant.[1] However, a dramatic loss in mechanical properties and processability of those composites[2,3] was observed due to incompatibility between mineral hydrophilic filler and hydrophobic polymer matrix as well as the required high level of MH for achieving the desired flame-retardant effect. Thus, interfacial adhesion between filler and matrix have to be improved. The addition of rubber polymers into thermoplastics leads to the specific adjustment of application relevant properties. Additional cross-linking of the elastomer phase (Thermoplastic Vulcanizate - TPV) is particularly advisable. TPVs were produced by simultaneously mixing and cross-linking a rubber within a thermoplastic at elevated temperature.[5–7] The rubber phase was generally cross-linked either by activated phenol formaldehyde resins or by peroxides. Besides advantages, both resin and peroxide cross-linking systems have their own limitations. The disadvantages of flame retarded polyolefine-MH composites as well as resins and peroxides in dynamic vulcanization create a demand for an alternative.

Polymer Modification with High Energy Electrons

It is well known that high energy electron induced chemical reactions depend on absorbed dose, chemical structure of target materials, and treatment conditions like temperature and aggregate state[7] as well as gas atmosphere.[8] State of the art of

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polymer modification with high energy electron characterizes a process where required absorbed dose is applied to form parts (after molding) in solid state and at room temperature (stationary conditions). The absorbed dose controls the energy input per unit of mass as well as the total number of radicals. Reactive EB processing is a novel procedure where chemical reactions are induced by spatial and temporal precise energy input via high energy electrons under dynamic conditions of melt mixing. In this novel process, the penetration depth of electrons is limited to a part of mixing volume. The total mixing volume is modified due to the change of polymer mass within the penetration depth of electrons during mixing process. Further, electron treatment time and electron energy do not only control dose rate and penetration depth, respectively. In reactive EB processing, electron treatment time also influences the ratio of radical generation rate to mixing rate (dose per rotation) and electron energy controls the ratio of modified volume to total mixing chamber volume (r_{vol}). Mechanical, chemical, and morphological characteristics of various reactive EB processed compounds were studied in order to evaluate the potential of reactive EB processing.

Experimental Part

Materials

A commercial untreated magnesium-hydroxide (MH) grade FR-20-100D-S7 (by ICL-Dead Sea Periclase, Beersheva, Israel) with a specific BET-surface of 7 m^2/g and a mean particle size between 1.45 and 1.8 μm was used as flame retardant filler.

Polyethylene (PE) GD 7255 was obtained from Basell, Frankfurt, Germany. The melt flow rate of the polyethylene, measured at 190 °C and 21.6 kg, amounts to 116 g/10 min. It has a density of 0.955 g/cm^3.

Trifunctional *triallylcyanurate* (TAC; supplied by Sigma-Aldrich Chemie, Munich, Germany) has been used as grafting agent in PE composite.

Buna EP G 6850, the ethylidene norbornene (ENB) containing ethylene propylene diene monomer rubber (EPDM), was obtained from Lanxess, Leverkusen, Germany. The EPDM contains 51 wt % of ethylene and 7.7 wt % of ENB. It has a Mooney viscosity, ML (1 + 4) at 125 °C of 60 and a density of 0.860 g/cm^3.

Polypropylene (PP) HD120MO, a homopolymer, was obtained from Borealis, Düsseldorf, Germany. The melt flow rate of the polypropylene, measured at 230 °C and 2.16 kg, amounts to 8.0 g/10 min. It has a density of 0.908 g/cm^3.

PE Composites

PE (38 wt%), magnesium hydroxide (60 wt%) and TAC (2 wt%) were mixed in banbury mixing chamber at 165 °C and 60 rpm for 11 minutes in order to obtain adequate homogenization as well as to enable electron treatment.

Thermoplastic Vulcanizates

Thermoplastic vulcanisates (TPVs) with 50:50 blend ratio of PP and EPDM were prepared by a batch process in a Brabender mixing chamber, having a mixing chamber volume of 50 cm^3, with a rotor speed of 45 rpm at 175–180 °C in presence of air. The total time of mixing was 16 min due to required homogenization as well as safety regulations of electron accelerator.

Electron Treatments

Electron treatments were done at electron accelerator ELV-2 (manufactured by Budker Institute of Nuclear Physics, Novosibirsk, Russia) at the Leibniz Institute of Polymer Research. Electron treatments have been done under stationary condition as well as in-stationary conditions of melt-mixing process (reactive EB processing). Electron treatments under stationary conditions were done at room temperature using injection molded samples of polyethylene/MH/TAC-formulation that was only physically melt mixed. Electron treatments under in-stationary conditions of melt mixing process were done in an oil heated internal mixer (Brabender Plasti-

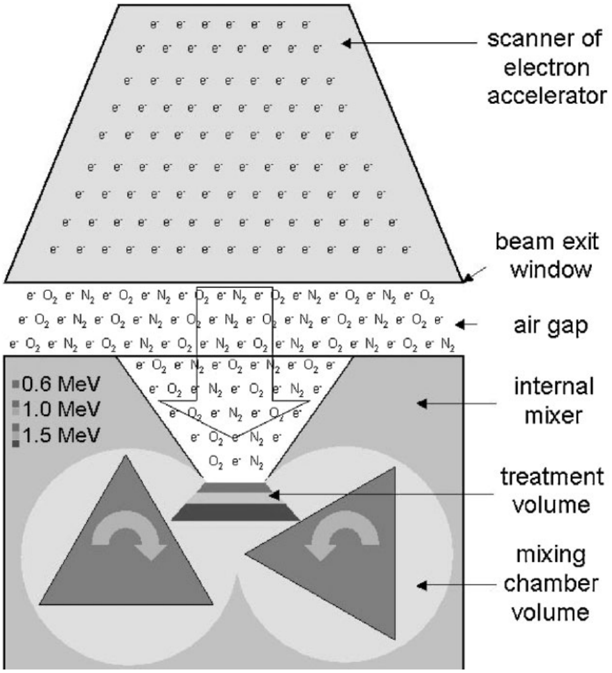

Figure 1.
Electron accelerator coupled with internal mixer (principle).

corder, mixing chamber volume of 50 cm^3) equipped with roller type blades (Figure 1). The friction ratio of the rotors amounts to 1.5.

Preparation of PE Composite Samples

Tensile test specimens according to DIN 53504- Type S2 were injection molded using a BOY 22A HV (Dr. Boy GmbH & Co. KG, Neustadt-Fernthal, Germany) at a temperature on the nozzle of 230 °C and a temperature of the mold of 230 °C.

Preparation of PP/EPDM TPV Samples

Immediately after mixing, the composition was pressed manually by metallic plates without any additional heating to achieve a sheet of about 2 mm thickness. This sheet was cut into small pieces and pressed in a compression molding machine (Rucks Maschinenbau, Glauchau, Germany) at 200 °C, 6 min, and 88 bar pressure. The sheet was then cooled down to room temperature under pressure. Test specimens were die-cut from the compression molded sheet and used for testing after 24 h of storage at room temperature.

Testing Procedure – PE Composite

The stress-strain behavior was characterized in uniaxial tensile test at 23 °C using an universal testing machine (zwicki by Zwick, Ulm, Germany) at a cross-head speed of 10 mm/min. Five samples were tested per formulation.

The impact toughness (Charpy-toughness) of PE/MH/TAC composites was determined in accordance to DIN EN ISO 179-1 at 23 °C and 50% relative humidity using an impact testing machine (PSW 25 J by WPM Leipzig GmbH, Leipzig, Germany).

The flame resistance was evaluated using the principle of Limiting Oxygen Index (LOI) measurements. The measurements were done on the parallel sections of the tensile test specimens using a FTA II LOI-tester (by Stanton Redcraft, Pittsfield, USA).

Testing Procedure – PP/EPDM TPVs

Tensile tests were carried out according to ISO 527-2/S2/50 on dumb-bell shaped specimens using an universal tensile testing machine Zwick 8195.04 at a constant cross-head speed of 50 mm/min. E-modulus was determined in between 0.05 and 0.25% of strain. Gel content of the samples was calculated after extracting out the PP-phase by boiling xylene. Phase morphology was investigated by a LEO 435 VP Ultra plus Scanning Electron Microscope (SEM) from Carl Zeiss SMT (Jena, Germany) after ultracutting of TPV samples at −130 °C in a Leica Ultra-microtome (Wetzlar, Germany).

Results and Discussion

PE Composite

The stress-strain behavior of the polyethylene/MH/TAC composites under uniaxial tension is shown in Figure 2.

The unmodified plasticized samples containing show poor mechanical properties and reach only small tensile strength at small elongations at break. Electron treatment under stationary stationary as well as reactive EB processing result in improved tensile strength and improved elongation at break. This indicates improved interfacial adhesion between MH-particles and polyethylene-matrix. However, reactive EB processing leads to composites with best tensile properties by combining high stresses with high elongations. This indicates that there is a strong interaction between MH and polyethylene-matrix but at the same time the polyethylene-matrix remains deformable in a plastic manner. This indicates higher toughness of these composites that coincides with Figure 3.

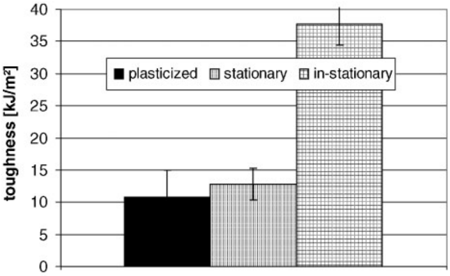

Figure 3.
Comparison of Charpy toughness of PE/MH/TAC composite.

Reactive EB processing results in composites with highest Charpy toughness. In contrast, electron treatment under stationary conditions (state of the art) does not influence Charpy toughness of PE/MH/TAC composites.

The flame retardancy of PE/MH/TAC composite is shown in Figure 4. It can be seen that the flame resistance of the

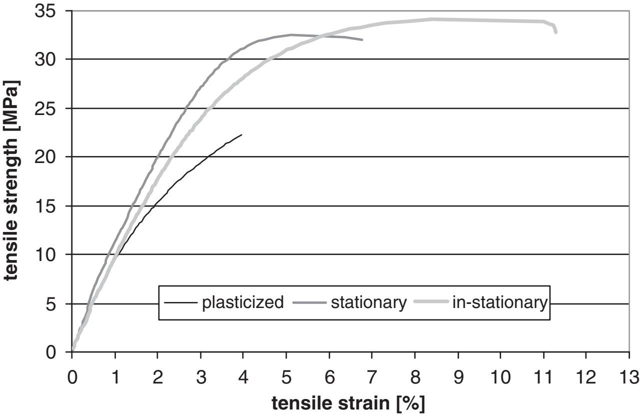

Figure 2.
Comparison of stress-strain-behavior of PE/MH/TAC composite.

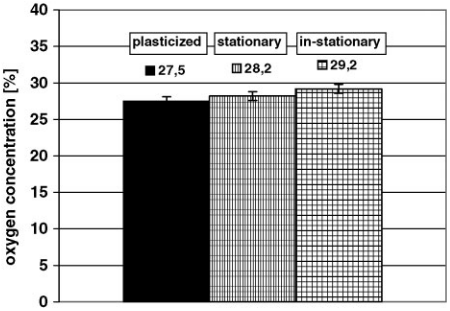

Figure 4.
Comparison of flame retardancy of PE/MH/TAC composite.

unmodified plasticized sample with 60 wt% of non-modified MH is maintained in all composites within the accuracy of LOI-method.

PP-EPDM TPVs

Influence of the various conditions of reactive EB processing on the stress-strain behavior of the PP-EPDM TPVs is shown in Figure 5 (a, b, and c). From experimental data at 1.5 MeV and for an electron treatment of 60 s it was observed that with increasing absorbed dose from 25 kGy to 50 kGy tensile strength, elongation at break, and E modulus of the TPVs were significantly improved. Further increase in dose to 100 kGy resulted in a small increase of tensile strength where as elongation at break is kept constant.

The experimental data at 1.5 MeV and 100 kGy showed that with decreasing electron treatment time from 60 s (16,5 kGy/s and 22 kGy per rotation) to 15 s (66 kGy/s and 88 kGy per rotation), tensile strength and elongation at break were further improved whereas E modulus remained constant. Highest tensile strength and maximum elongation at break were recorded for an electron treatment of 15 s. Thus, electron treatment time influencing on dose rate as well as absorbed dose per rotation is an additional parameter controlling the stress-strain behavior of the PP-EPDM TPVs.

The influence of electron energy on mechanical properties was investigated at an absorbed dose of 50 kGy due to limited dose rate of electron accelerator and for an electron treatment time of 60 s. In comparison to the results at 1.5 MeV (8.2 kGy/s and $r_{vol} = 0.062$) it is seen that at 0.6 MeV (28.8 kGy/s and $r_{vol} = 0.017$) tensile strength and elongation at break were reduced whereas E modulus remained constant. Finally, electron energy influencing penetration depth as well as ratio of modified volume to total mixing chamber volume is controlling the stress-strain behaviour of the PP/EPDM TPVs.

Morphology

Figure 6 (a, b, and c) illustrates SEM photomicrographs of various PP-EPDM blends: both untreated and treated under various conditions. In all cases, a wide distribution of particle sizes is generated due to the mixing under dynamic conditions. It can be seen from the micrographs that for the untreated sample, the particle sizes were much bigger (around 2–3 μm). Reactive EB processing at 1.5 MeV, 100 kGy, and 60 s results in smaller EPDM particle size (even to 0.2 μm) indicating better dispersion due to the dynamic vulcanisation. The smallest EPDM particle sizes (around 0.04 μm) were recorded in case of 100 kGy absorbed dose and 15 s electron treatment time (Figure 6c) at 1.5 MeV, which is in line with the mechanical properties.

Gel Content

With increasing dose the gel content value (Table 1) increases. The gel content values were higher than the EPDM content itself in the blend which indicated high degree of cross-linking in EPDM phase and the formation of *in-situ* PP-EPDM graft-links by reactive EB processing. The PP-EPDM graft-links were not extractable even by boiling xylene and therefore also contribute to the gel contents.

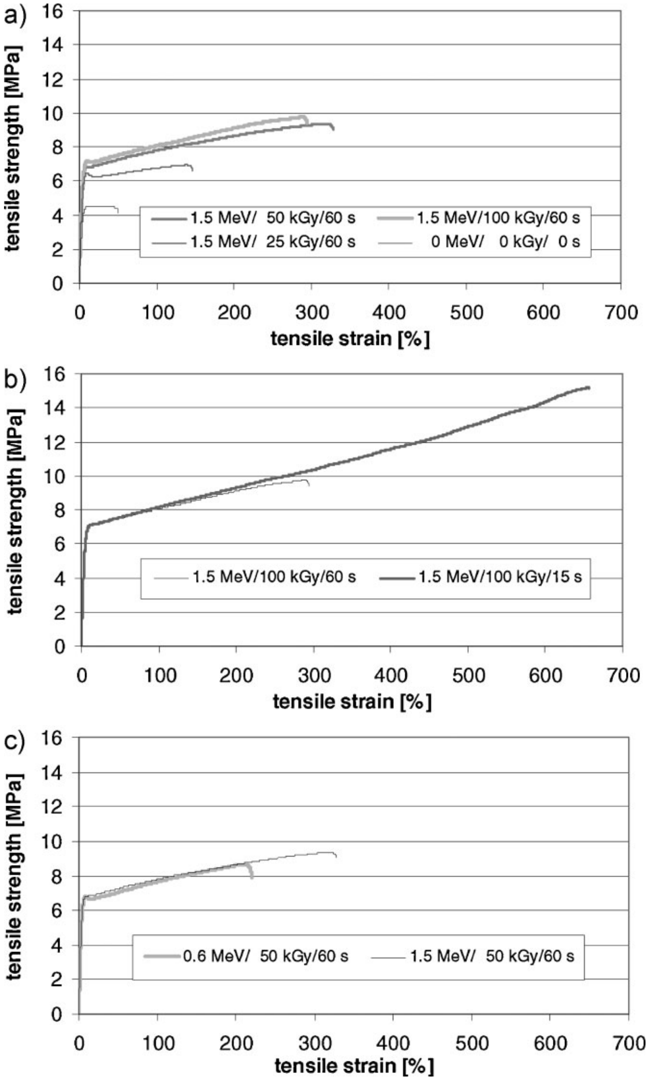

Figure 5.
Influence of dose (a), electron treatment time (b), and electron energy (c) on tensile stress as function of tensile strain.

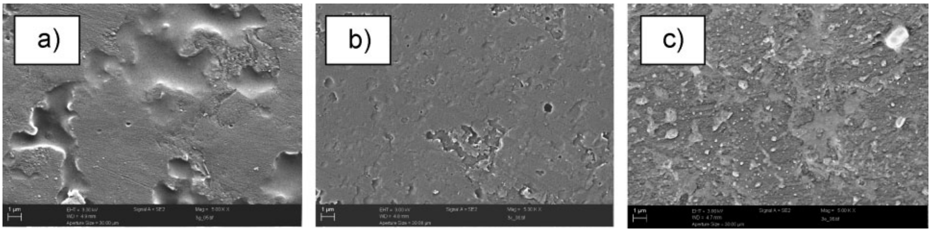

Figure 6.
SEM photomicrograph of sample: 0 MeV, 0 kGy (a), 1.5 MeV, 100 kGy, 60 s (b), and 1.5 MeV, 100 kGy, 15 s (c).

Table 1.
Experimental results of gel content.

electron energy [MeV]	dose [kGy]	treatment time [s]	Gel content [%]
0	0	0	0
1.5	25	60	54.5
1.5	50	60	64
1.5	100	60	65

Conclusion

It has been shown that the reactive EB processing of PE/MH/TAC system results in composites with best tensile properties as well as highest Charpy toughness without any use of additional compatibilizer. In contrast to that, electron treatment of same material system under stationary conditions (state of the art) results in small improvement of stress-strain-behavior and does not improve Charpy toughness.

The preparation of PP-EPDM vulcanizates by reactive EB processing is an alternative to conventional phenolic resin and peroxide cross-linking systems. The experimental results indicated that two processes are simultaneously occurring contributing to enhancement in the mechanical properties: (a) *in-situ* compatibilization of PP and EPDM and (b) cross-linking in the EPDM phase. Both processes do not only depend on absorbed dose like in traditional electron treatment under stationary conditions. Moreover, they depend on electron treatment time as well as electron energy. Electron treatment time correlates with dose rate and radical generation rate. Thus we can conclude that radical generation rate of reactive EB processing controls structure, morphology, and properties of PP-EPDM vulcanizate at fixed mixing rate and fixed mixing temperature range. An influence of reaction rate in relation to mixing rate was already reported by Msakni et al.[9] for cross-linking of ethylene-octene copolymers by peroxide under dynamic conditions.

Further experiments are required to investigate the role of absorbed dose per rotation and electron energy in reactive EB processing as well as to understand the mechanism of reactive EB processing resulting in the observed experimental data. This novel procedure offers a wide range of application for various polymers and their blends or composites.

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