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Modification of Particle Filled Polymers with High Energy Electrons Under In-Stationary Conditions of Melt Mixing

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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 and ions for subsequent molecule changes via radical induced chemical reactions. In the present study, high energy electrons have been used to modify polyolefine (polyethylene and polypropylene) systems in presence of a grafting agent under stationary and in-stationary conditions. Polymer modification with high energy electrons under stationary conditions characterizes a process where required absorbed dose is applied to polymers in solid state and at room temperature. Polymer modification with high energy electrons under in-stationary conditions is a novel process where required absorbed dose is applied in molten state during melt mixing process. 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. A 1.5 MeV electron accelerator has been directly coupled to a banbury mixing chamber in order to study this novel process. In comparison to the stationary process, the main differences are working at higher temperature, absence of any crystallinity, intensive macromolecular mobility as well as intensive mixing during dose application. The influence of both processes on mechanical properties and flame resistance of polymer composites is discussed.

Keywords: high energy electrons; polymer modification; polymer processing; polymer composites

Introduction

Polymer Modification with High Energy Electrons

It is well known that effects of high energy electron induced chemical reactions depend on absorbed dose, chemical structure of target materials, and treatment conditions like temperature and aggregate state[1] as well as gas atmosphere.[2] An entirely novel approach is the coupling of polymer modification with high energy electrons and melt-mixing process to generate radical induced chemical reactions for compatibilisation / phase coupling between incompatible polymer-filler-systems in-situ during compounding process. This unique procedure has been developed at Leibniz Institute of Polymer Research Dresden and applied to flame retardant polyolefine-magnesiumhydroxide-composites.

Flame Retardant Polyolefine-Magnesiumhydroxide-Composites

Polyethylene (PE) and polypropylene (PP) are widely used in different fields of

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application because of their material properties. A major drawback of all polyolefines is their poor flame resistance that hinders the practical application in some fields. Magnesium-hydroxide (MH) is a good endothermic flame retardant due to its high decomposition temperature and its smoke supressibility.[3] However, the disadvantage of MH is the high level (about 60 wt%) required to achieve the desired flame-retardant effect. Thus, improvement in flame retardancy is accompanied by dramatic loss in mechanical properties and processability of the composite.[4,5] Further, the mechanical properties of polymer composites depend on filler dispersion as well as interfacial adhesion between filler and matrix.

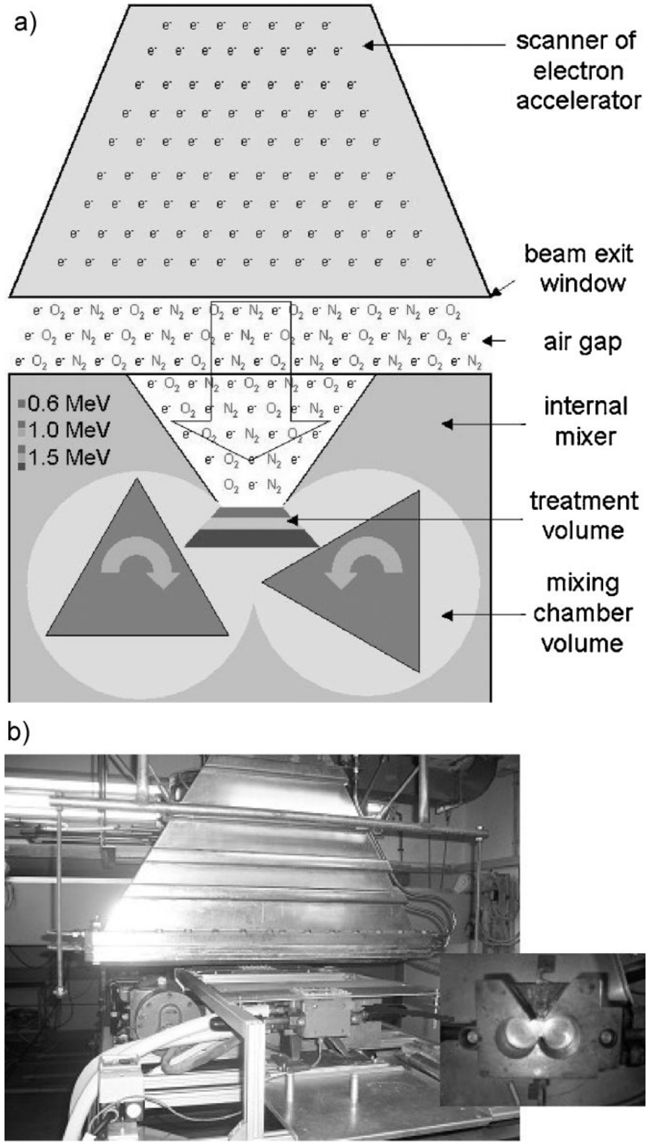

Figure 1.
a) Electron accelerator coupled with internal mixer (principle). b) Electron accelerator coupled with internal mixer (experimental setup).

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 "GD7255" (manufactured by Basell, Frankfurt, Germany) and polypropylene "HD120MO" (manufactured by Borealis, Linz, Austria) were used as matrix polymer.

As a grafting agent trifunctional *triallylcyanurate* (TAC; supplied by Sigma-Aldrich Chemie, Munich, Germany) has been added (2.0 wt%) during polymer processing.

Polymer Composites

Polymer (38 wt%), magnesium hydroxide (60 wt%) and TAC (2 wt%) were mixed in banbury mixing chamber at 165 °C (PE) or 195 °C (PP) and 60 rpm for 11 minutes in order to obtain an adequate homogenization as well as to enable electron treatment.

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

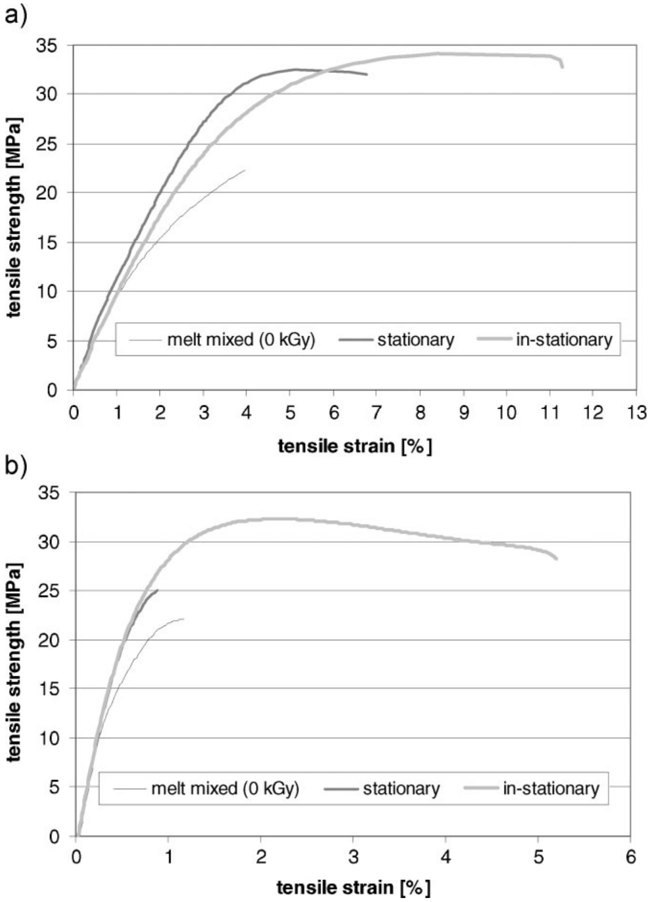

Figure 2.

a) Comparison of stress-strain-behavior of PE/MH/TAC composite. b) Comparison of stress-strain-behavior of PP/MH/TAC composite.

of melt-mixing process. Electron treatment under stationary conditions have been done at room temperature using injection molded samples of polyolefine/MH/TAC-formulation that has been only physically melt mixed. Electron treatment under in-stationary conditions of melt mixing process has been done in an oil heated internal mixer (Brabender Plasticorder, net volume ~ 50 cm^3) equipped with roller type blades (Figure 1a and 1b).

Sample Preparation

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 30 °C.

Material Characterization

The stress-strain behavior has been 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 polyolefine/MH/TAC composites has been 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 has been evaluated using the principle of Limiting Oxygen Index (LOI) measurements. The measurements have been done on the parallel sections of the tensile test specimens using a FTA II LOI-tester (by Stanton Redcraft, Pittsfield, USA).

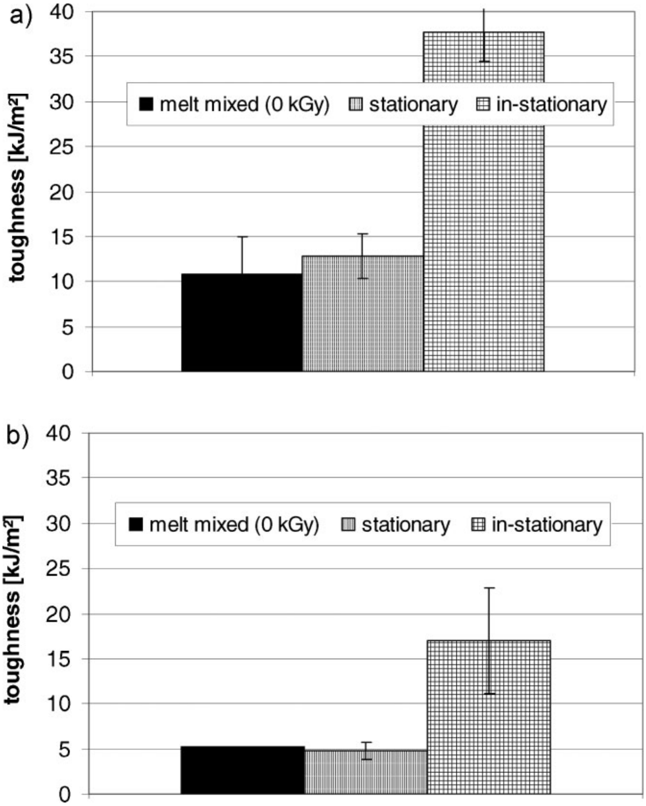

Figure 3.
a) Comparison of Charpy toughness of PE/MH/TAC composite. b) Comparison of Charpy toughness of PP/MH/TAC composite.

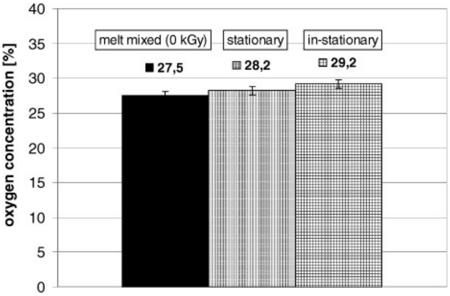

Figure 4.
Comparison of flame retardancy of PE/MH/TAC composite.

Results and Discussion

Tensile Properties and Toughness

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

The unmodified melt mixed samples containing 60 wt% non-modified MH and 2 wt% TAC show poor mechanical properties and reach only small tensile strength at small elongations at break. Electron treatment under stationary as well as in-stationary conditions results in improved tensile strength and in case of PE/MH/TAC composite in improved elongation at break. This indicates improved interfacial adhesion between MH-particles and polyolefine-matrix. However, electron treatment under in-stationary conditions 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 polyolefine-matrix but at the same time the polyolefine-matrix remains deformable in a plastic manner. This indicates higher toughness of these composites that coincides with Figure 3a and 3b. Again, electron treatment under in-stationary conditions leads to composites with highest Charpy toughness. In contrast, electron treatment under stationary conditions does not influence Charpy toughness of composites.

Flame Retardancy

The flame retardancy of PE/MH/TAC composite as ranked by LOI-measurements is shown in Figure 4. It can be seen that the flame resistance of the unmodified melt mixed sample with 60 wt% of non-modified MH is maintained in all composites within the accuracy of LOI-method.

Conclusion

It has been shown that the novel procedure of electron treatment under in-stationary conditions of melt mixing results in composites with best tensile properties as well as highest Charpy toughness in presence of TAC and without any use of additional compatibilizer. In contrast to that, electron treatment of same composite systems under stationary conditions results in small improvement of stress-strain-behavior and does not improve Charpy toughness. Further investigations are required in order to characterize the morphological changes induced during electron treatment under in-stationary conditions of melt mixing as function of its processing parameters. This offers a wide range of application of this novel technology for various polymer composites.

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