Preparation of epoxy-functionalized methyl methacrylate-butadiene-styrene core-shell particles and investigation of their dispersion in polyamide-6

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Published in: Polymer

DOI: 10.1016/S0032-3861(96)01003-8

Published: 01/01/1997

Citation for published version (APA):
Preparation of epoxy-functionalized methyl methacrylate–butadiene–styrene core–shell particles and investigation of their dispersion in polyamide-6

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(Received 29 October 1996)

Functional core–shell impact modifiers of glycidyl methacrylate (GMA) functionalized methyl methacrylate–butadiene–styrene (MBS) have been prepared via a seeded semi-continuous emulsion polymerization. These functional MBS–GMA particles were blended with polyamide-6. Investigations by transmission electron microscopy showed a very good dispersion of the particles in the polymeric matrix, compared with blends of MBS with polyamide-6 where a third functional polymer styrene–maleic anhydride was added. © 1997 Elsevier Science Ltd.

(Keywords: emulsion polymerization; epoxy-functionalized MBS; blends with polyamide-6)

INTRODUCTION
Multiphase polymer blend systems offer interesting possibilities for obtaining optimum property combinations if proper control of the phase morphology and of the interfacial interactions are to be achieved. These factors are of crucial importance with respect to the mechanical and optical properties of blend materials. Added block or graft copolymers as interfacial agents to control the morphology and to strengthen the interfaces of immiscible blends have been used successfully. However, industrially more interesting would be the formation of the block or graft copolymer in situ during melt-blending through interfacial reaction of added functionalized polymeric components. Even more interesting would be to have graft copolymers with functional groups on the surface. Nevertheless, reactive blending has gained a lot of interest since the commercialization of super-tough nylon. In most cases polyamide-6 (PA-6) is blended in situ with a core–shell impact modifier. The in situ blending can be achieved in three different ways; firstly, the impact modifier can be functionalized so that the functional groups react with the polyamide matrix, secondly, by the functionalization of the matrix, and in the third place by the addition of a third polymer that can react with one polymer phase and that is miscible with the other polymer phase. The most well known examples of the first method are the blends of PA 6 or PA-6,6 containing an ethylene/butene midblock and styrene endblocks elastomer that has been grafted with maleic anhydride (MA). Other examples are the blends of PA-6 with succinic anhydride (SA) or MA grafted ethylene propylene rubber (PA-6/EPM-g-SA, PA-6/EPM-g-MA) or with MA grafted ethylene–propylene–diene monomer rubber (PA-6/EPDM-g-MA). The modification of the elastomers can be accomplished by solution grafting of MA molecules promoted by radical initiator or grafting in an extruder by adding MA. Such materials are now also commercially available. Moreover, the elastomers can be modified with other reactive groups such as glycidyl methacrylate (GMA). An example of this is GMA grafted to ABS (acrylonitrile–butadiene–styrene) and the GMA grafted ABS is then blended with the polyamide. Furthermore, an example of the second method of in situ compatibilization, namely the functionalization of the matrix, is PA-6-g-acrylamide and ABS. The third method of in situ compatibilization is the addition of a third polymer with functional groups that is miscible with the grafted chains of the shell (when a core–shell impact modifier is used) and that can react at the interface with the matrix to provide coupling. Certain styrene–maleic anhydride (SMA) copolymers are miscible with PMMA, PS or SAN, yet through the MA moiety these polymers can react with polyamides during melt-blending. Examples of these systems are: PA-6/PS/SMA, PA-6/PMMA/SMA and PA-6/ABS/SMA. Other reactive polymers that have been used as...
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Table 1 Materials used

<table>
<thead>
<tr>
<th>Material</th>
<th>Commercial name</th>
<th>Supplier</th>
<th>Mₚ</th>
<th>Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBS-A</td>
<td></td>
<td>Kaneka</td>
<td>1/7</td>
<td></td>
</tr>
<tr>
<td>MBS-GMA</td>
<td></td>
<td>DSM</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>PA-6</td>
<td></td>
<td>GE Plastics</td>
<td>108.5</td>
<td></td>
</tr>
<tr>
<td>PBT</td>
<td>PBT315</td>
<td>GE Plastics</td>
<td>46.28</td>
<td></td>
</tr>
<tr>
<td>PPE</td>
<td>PPO803</td>
<td>Bayer</td>
<td>125.000</td>
<td></td>
</tr>
<tr>
<td>SMA-20</td>
<td>SEA-0437</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a* Prepared in Eindhoven Polymer Laboratories
*b* Uncorrected molecular weight related to polystyrene
*c* The number indicates the wt% of maleic anhydride in SMA

Table 2. Seed latex recipe of polybutadiene (PB) and graft polymer MBS GMA 222 (in g)

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>PB</th>
<th>MBS GMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>527</td>
<td>800</td>
</tr>
<tr>
<td>S</td>
<td>36.6</td>
<td>16.1</td>
</tr>
<tr>
<td>MMA</td>
<td>35.2</td>
<td>8.8</td>
</tr>
<tr>
<td>GMA</td>
<td>36.6</td>
<td>12.0</td>
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<tr>
<td>Butadiene</td>
<td>230.8</td>
<td>19.2</td>
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<tr>
<td>KPS</td>
<td>2.868</td>
<td>0.8</td>
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<tr>
<td>KCR</td>
<td>1.45</td>
<td>0.8</td>
</tr>
<tr>
<td>AMA-80</td>
<td>19.2</td>
<td>0.016</td>
</tr>
<tr>
<td>CHP</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>SFS</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>FeSO₄EDTA</td>
<td>0.016</td>
<td></td>
</tr>
</tbody>
</table>

*a* Polybutadiene
*b* Potassium persulfate (initiator)
*c* Potassium carbonate (buffer)
*d* Sodium dihexyl sulfosuccinate (surfactant)

Table 3 List of blends with PA-6 prepared

<table>
<thead>
<tr>
<th>No.</th>
<th>Code</th>
<th>PA-6</th>
<th>SMA-20</th>
<th>MBS-GMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AA25074.1</td>
<td>75</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>AA29074.1</td>
<td>75</td>
<td>1</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>AA29074.1</td>
<td>75</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>10</td>
<td>AA09124.1</td>
<td>75</td>
<td>5</td>
<td>25</td>
</tr>
</tbody>
</table>

Materials

Experimental

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The CHP was used as received, and solutions were prepared of SFS, FeSO₄ and EDTA, all in oxygen-free water at pH 4. The ratio of the components added to the redox system (CHP/EDTA–Fe²⁺/SFS) was 1/0.02/1 (w/w). The latex was dried by the freeze-drying technique.

Blend preparation

Before each processing step, all the materials were dried for at least 12 h at 85°C in a vacuum oven to ensure removal of the sorbed water. The blends were prepared by means of the DSM mini extruder (capacity: 4 g) at a screw speed of 100 rev min⁻¹. The extrusion temperature of the PA-6 blends was 240°C. For the preparation of the PA-6 blends, SMA and MBS were premixed during 2 min whereas the blend of PA-6 and MBS-GMA was not premixed. The extrusion time was recorded from the moment PA-6 was added and was 5 min for all blends. After mixing, the blends were quenched with dry ice and isopropanol (−78°C) to freeze in the morphology.

The PPE/PBT blends were prepared in a mini-extruder with a capacity of 6 g, using an extrusion temperature of 260°C during 3 min after filling (±5 min).

Morphology characterization

Latex particle morphology as well as the blend morphology were determined by TEM.

The latex was diluted 400 times and the butadiene core was stained with a 2% OsO₄ solution for 30 min, and subsequently dried on a copper grid.

Pieces of extruded strands of the blend were trimmed ready for microtoming. Thin sections were obtained by ultramicrotomy at ambient temperature using a Reichert Ultracut E microtome and a diamond knife. The thin sections (thickness 50–100 nm) were stained with OsO₄ vapour during 3 h to generate contrast between the phases. The transmission electron microscope (CM10, Philips) was operated at 60 kV.

RESULTS AND DISCUSSION

The objective of this research is the preparation of a functional graft copolymer of MBS–GMA and evaluation of the morphology in the blend of a MBS–GMA and PA-6. The advantage of emulsion-made core–shell impact modifiers is the accurate control of the size of the particles, in contrast to the compounding of rubber where the size of the particles formed is strongly dependent on the parameters of the mixing process. However, despite the predetermined particle size, some appropriate strategies are required to achieve a uniform stabilized dispersion and adequate particle–matrix adhesion.

The MBS–GMA polymer was prepared via a seeded semi-continuous emulsion polymerization under flooded conditions. This polymerization was performed at room temperature in order to minimize hydrolysis of the epoxy groups to the corresponding difunctional alcohol. Therefore, a redox initiator system was used. In the first step a PB seed latex was prepared with an average particle size of 80 nm and a polydispersity of 1.03. In the second step, the monomers S, MMA and GMA were added to the PB latex according to a certain addition profile which is outlined in Figure 1. First, a mixture of S/MMA (50/50, azotrope) was added under flooded conditions according

![Figure 1](image1.png)

**Figure 1** Schematic representation of the addition profile of the monomers MMA, S and GMA in the semi-continuous graft polymerization of MBS–GMA in emulsion

![Figure 2](image2.png)

**Figure 2** (a) TEM micrograph of the final morphology of the MBS–GMA latex; (b) larger magnification
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Figure 3 TEM micrograph of a PA-6/MBS blend (no compatibilizer) where the butadiene is stained with OsO₄ to the following equation:

$$\Phi_{\nu_{SMMA}} = 1.5e^{-0.02t}$$

$$0 < t < 300 \text{ min} \quad (1)$$

After 240 min, GMA was also added in accordance with the following equation:

$$\Phi_{\nu_{GMA}} = 0.9 \left( 1 - e^{-0.04(t-240)} \right)$$

$$t \geq 240 \text{ min} \quad (2)$$

where $\Phi$ is the addition rate of monomer in ml s⁻¹. This addition scheme of monomer is chosen because of the fact that GMA is the most reactive monomer²⁶. Moreover, GMA has to be at the outer part of the particle in order to react with the polyamide endgroups during melt-compounding. The ratio of the SMMA/GMA is 90:10 wt%. Figure 2 shows the particle morphology of the final latex, as observed by TEM. It is clear from the TEM micrograph that a layer of SMMA–GMA is formed around the rubber particles (having a small particle size distribution of 80 nm). It can also be seen from the same micrograph that secondary nucleation has occurred. This is most probably the result of flooded reaction conditions where the rate of addition is higher than the rate of polymerization.

When the non-reactive MBS-A impact modifier is mixed with PA-6 a very poor dispersion of the MBS particles is obtained. This can be seen from Figure 3, where a TEM micrograph of a PA-6/MBS blend (without compatibilizer) is shown. When a functional copolymer is added as compatibilizer, the degree of dispersion of the impact modifier is improved, as can be seen in Figures 4a and 4b, where 3 and 5% of a SMA copolymer is used. However, there is still some coagulation of MBS particles. It has been reported that the degree of coagulation decreases when larger particles of MBS are mixed with PA-6²⁷. It should be taken into account that the size of non-reactive MBS is rather small, so that comparison of these blend systems with blend systems of the functionalized MBS impact modifier with a core particle size of 90 nm is not completely justified.

The functionalized MBS graft copolymer was also blended with poly(2,6-dimethyl-1,4-phenylene ether) (PPE) and poly(butylene terephthalate) (PBT). Blends of PPE/PBT can be compatibilized using PPE/PBT
copolymers, but also by a variety of other (co)polymers. Some examples of these copolymers contain small amounts of GMA. Too high a GMA content results in a less effective compatibilization of PPE/PBT blends, as mentioned previously for styrene-GMA compatibilizers. In Figure 6a a 40/60 wt% PPE/PBT blend is shown without compatibilizer. When the MBS-GMA is added a much smaller distribution of the PPE in the PBT matrix is achieved (Figure 6b). However, more experiments are necessary in order to have an optimal distribution of the GMA on the surface of the particles so that a stable morphology can be obtained even after annealing.

Changing the monomer addition profile to achieve a more random copolymer of the shell should be successful for the compatibilization of the PPE/PBT blends. Therefore, it is worth mentioning that, depending on the matrix, the location of the GMA groups is very important and can be regulated by means of the monomer addition profile during the graft polymerization.

When there are sufficient reactive groups at the surface, a good compatibilization and dispersion can be achieved. It is expected that the compatibilization reactions at the interface will lead to a decrease in the interfacial tension and some stabilization against coagulation. Steric hindrance against coagulation caused by such graft chains can be an even more important factor influencing the particle size. Another important factor in determining the final blend morphology is the topology of the grafting and the extent of the chemical reaction at the interface.

CONCLUSIONS

Epoxy-functionalized core–shell particles can be prepared in semi-continuous emulsion polymerization processes. Via a specific addition profile of the monomers, the optimum level of the reactive functional groups at the particle surface can be achieved.

The morphology of a blend of MBS–GMA particles and PA-6 indicates a very good dispersion. The blends of MBS (of approximately the same size) and PA-6, into which a third polymer with functional groups (SMA) was added, showed a lower degree of dispersion. The coagulation of the MBS particles is found to decrease when the functional groups are on the surface of these particles. This method of preparing functionalized core–shell particles is very promising in achieving well compatibilized modified thermoplastics. Depending on the type of matrix, the amount of epoxy groups on the surface of the core–shell particles can be regulated during the graft polymerization.

ACKNOWLEDGEMENTS

A. Aerdts wishes to thank in the first place the EC for the grant given and the Laboratory of Macromolecular Structural Chemistry (MSC, KU Leuven), especially Professor G. Groeninckx, for the facilities given to perform a post-doc in his laboratory. Furthermore, thanks go also to Ir. E. van Rijn (TUE, for monomer addition profile), Mrs Ing. A. Spoelstra (TUE, instructions in microtomy) and Mrs B. Vanderschueren (KU Leuven,
instructions in transmission electron microscopy). Ir. P. Koets and Ir. B. Jansen (TUE) are acknowledged for the fruitful discussion.

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