

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

A. M. Aerdts* and G. Groeninckx

Catholic University of Leuven, Department of Chemistry, Laboratory of Macromolecular Structural Chemistry (MSC), Celestijnenlaan 200F, 3001 Heverlee, Belgium

and H. F. Zirkzee, H. A. M. van Aert and J. M. Geurts

Eindhoven University of Technology, Laboratory of Polymer Chemistry and Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

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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.

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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^{1–5}. 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)^{1–3}. 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)⁴ or with MA grafted ethylene–propylene–diene monomer rubber (PA-6/EPDM-*g*-MA)^{5–8}. The modification of the elastomers can be accomplished by solution grafting of MA molecules promoted by radical initiator^{4,9} or grafting in an extruder by adding MA⁸. 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 polyamide¹⁰. Furthermore, an example of the second method of *in situ* compatibilization, namely the functionalization of the matrix, is PA-6-*g*-acrylamide and ABS¹¹. 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/SMA¹², PA-6/PMMA/SMA¹³ and PA-6/ABS/SMA^{14,15}. Other reactive polymers that have been used as

* To whom correspondence should be addressed. Present address: Eindhoven University of Technology, Laboratory of Polymer Chemistry and Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

Table 1 Materials used

Material	Commercial name	Supplier	M_w	Particle size
MBS-A		Kaneka		77
MBS-GMA ^a				90
PA-6		DSM		
PBT	PBT315	GE Plastics	108 500 ^b	
PPE	PPO803	GE Plastics	46 280 ^b	
SMA-20 ^c	SEA-0437	Bayer	125 000	

^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^{22,23} (in g)

Ingredients	PB	MBS GMA
Water	527	800
S		36.61
MMA		35.2
GMA		8
Butadiene	236.8	120 ^a
KPS ^b	2.868	
KCB ^c	1.45	
AMA-80 ^d	19.2	
CHP		0.8
SFS		0.8
FeSO ₄ EDTA		0.016

^a Polybutadiene^b Potassium persulfate (initiator)^c Potassium carbonate (buffer)^d Sodium dihexyl sulfosuccinate (surfactant)**Table 3** List of blends with PA-6 prepared

No.	Code	PA-6	SMA20	MBS-A	MBS-GMA
1	AA25074.1	75	5	20	
2	AA25074.2	75	3	20	
7	AA29074.1	75		25	
10	AA09124.1	75			25

compatibilizers for blends of PA-6 with methyl methacrylate-butadiene-styrene (MBS) graft copolymer are the phenoxy and glycidyl ether of the bisphenol-A type of resins (PA-6/MBS/DGEBA or phenoxy¹⁶).

This paper will mainly focus on the preparation of epoxy-functionalized core-shell particles prepared in a semi-continuous emulsion polymerization process and the investigation of the dispersion of these reactive core-shell modifiers in PA-6. The morphology of the blends has been investigated by transmission electron microscopy (TEM). The morphology of the blends of PA-6 with the functionalized core-shell impact modifier MBS has been compared with that of PA-6/MBS and PA-6/MBS/SMA. Finally, compatibilization of PBT/PPE blends was briefly investigated using various compatibilizers including MBS-GMA to confirm the presence of a high concentration of epoxy groups on the surface of the core-shell particles.

EXPERIMENTAL

Materials

Table 1 summarizes information about the various materials used in this work. The MBS material was

synthesized by emulsion polymerization via the 'grow out' (GO) procedure. The GO procedure involves an emulsion polymerization in which both the styrene-butadiene rubber (SBR) core and the MMA/S shell are synthesized in a two-stage process. The SBR consists of a S-rich nucleus on which a Bd-rich layer is polymerized (the S/Bd ratio is 23/77). The shell is polymerized in two stages. First, PMMA is polymerized on the core and then PS, but the overall MMA/S ratio remains 50/50. The core shell ratio is 70/30. The morphology of this type of MBS is perfectly spherical¹⁷⁻²⁰.

The PA-6 was supplied by DSM, and poly(butylene terephthalate) (PBT315) and poly(2,6-dimethyl-1,4-phenylene ether) (PPE803) were supplied by General Electric Plastics. The styrene-maleic anhydride copolymer (SMA-20, SEA-0437) was supplied by Bayer. This SMA copolymer contained 20 wt% of MA in the copolymer.

Functionalization of MBS with GMA

Functionalization of the MBS polymer with GMA can be achieved in solution using a solvent to swell the MBS and a radical initiator to graft GMA onto the MBS, or in emulsion processes. In the emulsion process a polybutadiene (PB) polymer first has to be synthesized and then, together with S and MMA, GMA is polymerized at the end of the grafting process.

The polybutadiene (PB) seed latex with an average particle size of 90 nm, was prepared as described by Verduren²¹. The polymerization time was 17 h at a temperature of 80°C and at a stirrer speed of 500 rev min⁻¹. The recipe for the PB seed latex is given in Table 2. Before using the PB latex in the graft copolymerizations, the latex was dialysed in a membrane (Medicell International Ltd, London, UK). The water was changed five times every 4 h and this has been found sufficient to remove most inorganic ingredients. After this, the solid content was determined. The seeded semi-continuous emulsion polymerization was performed surfactant free in a 1 l glass reactor under nitrogen at 25°C with a 12-bladed turbine impeller and at a stirrer speed of 350 rev min⁻¹^{22,23}. The recipe is given in Table 2. The monomers S (Merck), methyl methacrylate (MMA, Merck) and GMA (Merck) were distilled under reduced pressure and subsequently stored at 5°C under nitrogen. An oil-soluble initiator, cumene hydroperoxide (CHP), was used in combination with a redox system²⁴. The redox initiator system, CHP (C₉H₁₂O₂, Fluka, 80% pure), sodium formaldehyde sulfoxylate (SFS) (CH₃NaO₃S.2H₂O, Fluka), iron(II) sulfate (FeSO₄, Fluka) and ethylenediamine tetraacetic acid (EDTA, Fluka) were also used without further purification.

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/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 (Table 3) 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 alcohol²⁵. 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

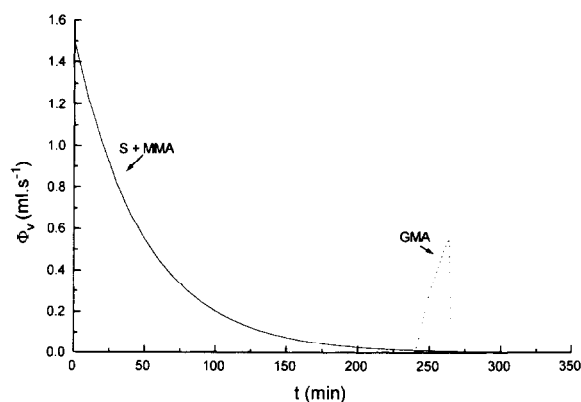


Figure 1 Schematic representation of the addition profile of the monomers MMA, S and GMA in the semi-continuous graft polymerization of MBS-GMA in emulsion

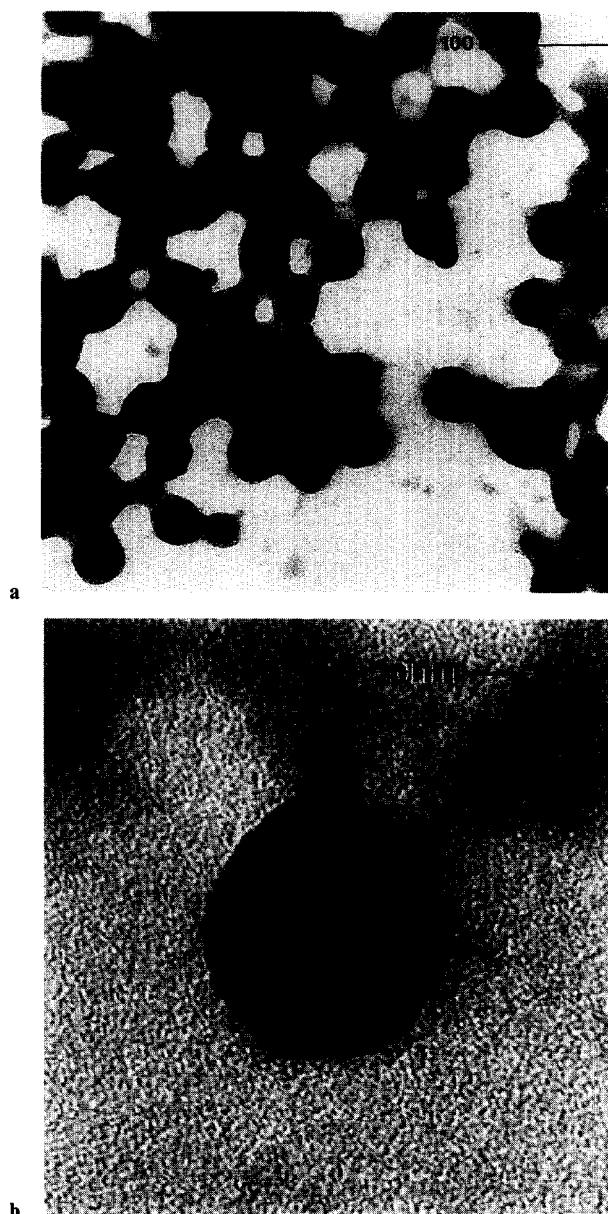


Figure 2 (a) TEM micrograph of the final morphology of the MBS-GMA latex; (b) larger magnification



Figure 3 TEM micrograph of a PA-6/MBS blend (no compatibilizer) where the butadiene is stained with OsO₄

to the following equation:

$$\Phi\nu_{(S-MMA)} = 1.5e^{-0.02t} \quad (1)$$

$$0 < t < 300 \text{ min}$$

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

$$\Phi\nu_{(GMA)} = 0.9\{1 - e^{-0.04(t-240)}\} \quad (2)$$

$$t \geq 240 \text{ min}$$

where Φ 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 *b*, 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.

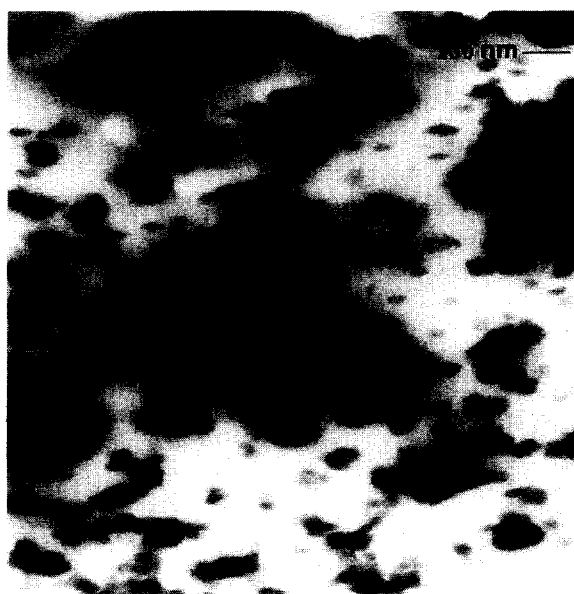
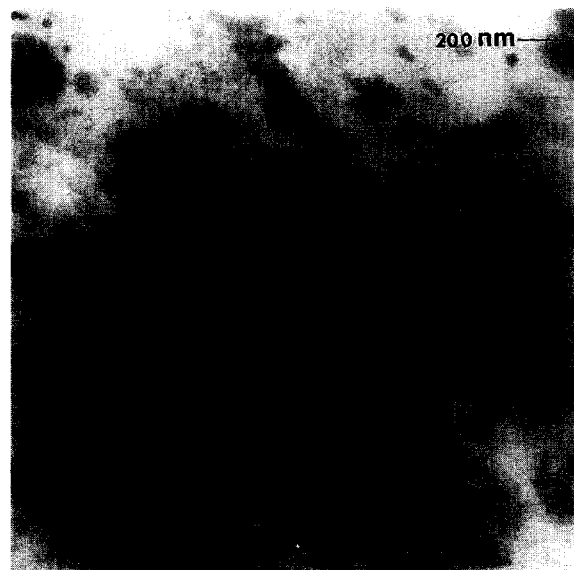


Figure 4 TEM micrograph of a PA-6/MBS blend with (a) 3 wt% of SMA20 and (b) 5 wt% of SMA20 (no. 2)/(no. 3) as compatibilizer. The butadiene is stained with OsO₄

In order to achieve a finer dispersion of the modifiers, the MBS-GMA, having reactive epoxy groups, was dispersed in PA-6. However, the melt-mixing of these polymers with PA-6 in the mini-extruder gave some problems of oxidation and degradation due to the absence of antioxidants and stabilizers. The final morphology of this blend is shown in *Figure 5*. The butadiene in the blend was stained with OsO₄; the background is darkened due to the extrusion process as outlined above. It can be seen from this figure that the degree of dispersion of the MBS-GMA particles in the PA-6 matrix is very high. The MBS-GMA particles are finely dispersed (domains of 200 nm), indicating that the epoxy group of the GMA is chemically bonded to the polyamide matrix. The reactive groups at the surface of the particle provide a high extent of interfacial adhesion to the polyamide matrix.

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



Figure 5 TEM micrograph of PA-6/MBS-GMA blend (no.10). The butadiene is stained with OsO_4

copolymers, but also by a variety of other (co)polymers. Some examples of these copolymers contain small amounts of GMA^{28,29}. Too high a GMA content results in a less effective compatibilization of PPE/PBT blends, as mentioned previously for styrene-GMA compatibilizers²⁸. 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

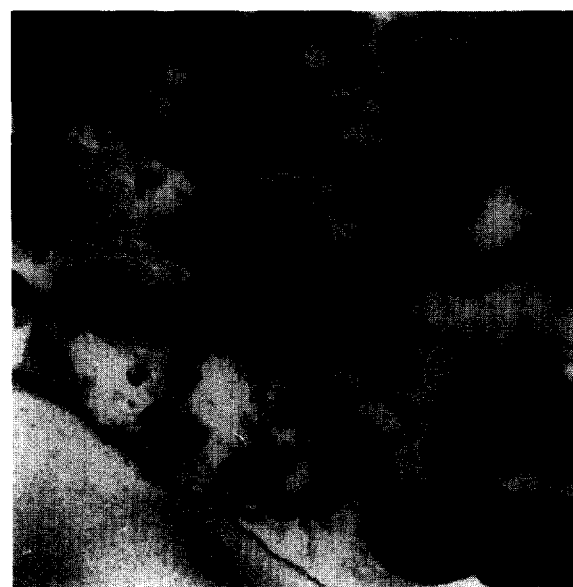


Figure 6 TEM micrographs of 40 wt% PPE 803/60 wt% PBT315 blends: (a) without compatibilizer; (b) with 5 wt% MBS-GMA

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.

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