Impact Modification of PA-6 and PBT by Epoxy-Functionalized Rubbers

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Summary: Glycidylmethacrylate (GMA) grafted apolar (ethylene/propylene/diene - EPDM) and polar (acrylonitrile/butadiene - NBR) rubbers were melt blended with polyamide–6 (PA-6) and polybutylene terephthalate (PBT). The toughness of the blends containing 5, 10 and 50 wt.% epoxy functionalized rubbers was assessed by various methods (notched Charpy, perforation impact) as a function of temperature (T=23 and –40 °C). The notched Charpy tests served to deduce the fracture toughness (K_c) and energy (G_c) data. It was established that EPDM-g-GMA is a slightly better impact modifier than is NBR-g-GMA albeit the latter polar rubber is more compatible with both matrices than the less polar EPDM-g-GMA. This finding was traced to the difference in the glass transition temperature (T_g of NBR is higher than that of EPDM) and to the dispersion of the epoxy funtionalized rubbers.

Keywords: EPDM; epoxy functionalization; grafting; NBR; PA-6; PBT; toughness

Introduction

Funtionalized rubbers are widely used for the impact modification of thermoplastic polycondensates, such as polyamides (PA) and polyesters. Maleated (maleic anhydride grafted) polymers work as efficient tougheners in PAs,[1-4] which is mostly due to the high reactivity between the related functional groups. Maleated polymers are, however, far less efficient in linear polyesters, such as polyethylene (PET) and polybutylene terephthalate (PBT).[5] To improve the interfacial compatibility of polar polyesters and apolar additives during reactive blending most straightforward is to exploit the reactivity of epoxy groups towards the –OH and –COOH functions of the polyesters. This concept has been approved recently by several researchers.[5-9] It is worth of noting that the epoxy group is highly reactive also with the functional groups of PAs (i.e., $-NH_2$, -COOH, -NH-CO-). So, epoxy functionalized rubbers may improve the toughness of PAs, as well. It was recently demonstrated that the initial polarity of the grafted rubbers strongly affects the blend compatibility with thermoplastic polyesters.[5,7] This work was aimed at studying the toughness response of PA-6- and PBT-based blends

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containing epoxy funtionalized apolar (ethylene/propylene/diene - EPDM) and polar (acrylonitrile/butadiene - NBR) rubbers. The related rubbers, denoted further on as EPDM-g-GMA and NBR-g-GMA, were home made by melt grafting with glycidylmethacrylate (GMA).

Experimental

Materials and Blending

The EPDM (component ratio: 71/24/5 wt.%, Type: Buna® EPG 6470) and NBR (acrylonitrile content: 40 wt.%, Type: Perbunan® NT 3946) rubbers of Bayer were melt grafted by GMA in the presence of peroxide. The grafted GMA content of EPDM-g-GMA and NBR-g-GMA was 8.7 and 5 wt % respectively. EPDM-g-GMA contained also 0.7 wt% homopolymerized GMA according to the analytics used.[7,10] PA-6 and PBT were Ultramid® B3 and Ultradur® B 4520 grades of BASF. Blends were produced on twin-screw extruders: the PA-6 based one on Brabender DSE 25, whereas the PBT-based blends on Werner-Pfleiderer ZSE II. The maximum melt temperature was set for both blends at 250°C.

Specimens Preparation and Testing

The granulated blends were injection molded on an Arburg Allrounder following the recommendations of the polymer producer. Film-gated plaques (80x80 mm^2) in 1 mm thickness along with dumbbells (according to ISO 3167) were produced.

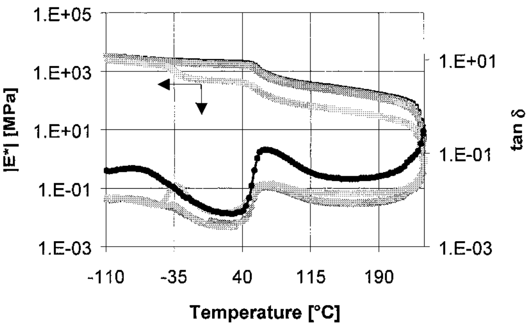
Specimens for dynamic mechanical thermal analysis (DMTA) and for instrumented notched Charpy tests were taken from the gauge section of the dumbbells. This sampling along with the determination of the fracture toughness (K_c) and fracture energy (G_c) at 1.2 m/s deformation rate are described in our former paper.[11]

Plaques of 1 mm thickness were used for instrumented falling weight impact (IFWI) performed on Ceast Dartvis® at v = 3.2 m/s. Further details to this technique are disclosed in Ref. [12]. Both instrumented impact tests (viz. Charpy high-speed flexural and falling dart) were performed at T=23 and –40 °C, respectively.

Results and Discussion

Phase Structure

Figure 1 compares the DMTA spectra of the PBT blends with EPDM-g-GMA and NBR-g-GMA.



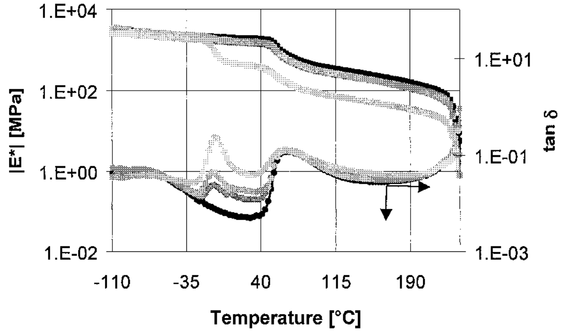


Fig. 1. DMTA spectra of PBT blends with different amounts of EPDM-g-GMA (top) and NBR-g-GMA (bottom). Designations: • 0 %, ● 5%, ● 10%, ● 50% rubber (i.e. with increasing rubber content the related lines become less black).

As expected, the complex moduli decrease with increasing amount of funcionalized rubber. Based on the fact that the glass transition temperatures (T_g) of the blend constituents are well discernible and their position did no change in the blends one can presume the presence of a two-phase structure. Note that the T_g of the EPDM-g-GMA is far less pronounced compared to the NBR-g-GMA. This is related to the T_g peak position of the related rubber. NBR-g-GMA has a higher T_g (–5 °C) than EPDM-g-GMA (T_g ~ -30 °C) and thus there is no overlapping with the β-relaxation transition of the PBT matrix. The |E*| vs T curves (cf. Figure 1) of the blends with 50 wt.% rubbers suggest the onset of a co-continuous structure.[5,7] On the other hand, the blends with ≤ 10 wt% rubber blend show a disperse-type morphology. Similar results, as discussed above, were received also for the PA-based blends.

Tensile Mechanical Results

Results listed in Table 1 demonstrate that with increasing rubber content stiffness, strength and ductility of the blends decrease. Based on the ultimate elongation one can claim that EPDM-g-GMA is a more suitable toughener than NBR-g-GMA. Attention should be paid to the fact that the ethylene/GMA (E/GMA) copolymer outperforms both epoxy functionalized rubbers in respect with the 'wet' tensile performance. The property retention with the PBT blends was similar: EPDM-g-GMA yielded higher values than NBR-g-GMA both at T=23 and -40 °C. It is noteworthy that the blends with 50 wt.% rubber showed ultimate elongations (≥ 130 % except the NBR-g-GMA containing blend at T= -40°C) which are characteristics for thermoplastic elastomers. This is a further hint for the formation of a co-continuous structure in the related blends.

Table 1. Tensile mechanical properties of the PA-based blends after conditioning. Notes: for comparison purpose results achieved on blends with ethylene/GMA (Lotader® AX 8840 of Atofina) are also indicated.

Blend Composition	E-Modulus [MPa]	Tensile Strength [MPa]	Elongation at Break [%]
PA-6	892 ± 23	42 ± 0.6	200 ± 5
PA-6 + EPDM-g-GMA			
5 wt%	640 ± 18	36 ± 1.0	120 ± 5
10 wt%	545 ± 10	32 ± 0.7	110 ± 10
PA-6 + NBR-g-GMA			
5 wt%	659 ± 21	35 ± 0.7	59 ± 8
10 wt%	566 ± 17	32 ± 0.2	54 ± 5
PA-6 + E/GMA			
5 wt%	680 ± 16	44 ± 3.3	230 ± 26
10 wt%	605 ± 20	41 ± 2.2	240 ± 15

Fracture Toughness and Energy

Table 2 shows that both functionalized rubbers toughen the PBT. Their efficency is comparable at both testing temperatures. One can also notice that incorporation of more than 5 wt.% grafted rubber has no effect on the linear elastic fracture mechanical parameters. Contrary to the predictions based on the DMTA and tensile mechanical results NBR-g-GMA yields slightly better values than EPDM-g-GMA. Note that similar fracture results as given in Table 2 were reported for the neat PBT in earlier works.[13-14] Similar tendency, as deduced for the PBT-blends, was observed also for the PA-6 blends. However, in this case E/GMA outperformed both EPDM-g-GMA and NBR-g-GMA which was in line with the prediction based on the tensile mechanical performance (cf. Table 1).

Table 2. Fracture toughness (K_c) and energy (G_c) as a function of blend composition and testing temperature. Notes: K_c was determined by the method described in Ref. [15]. G_c was computed via $G_c = K_c^2/E$, where E was taken from the DMTA spectra.

Blend Composition	K_c [MPa.m$^{1/2}$]		G_c [kJ/m^2]	
	23 °C	- 40°C	23 °C	-40 °C
PBT	5.5	5.3	15.6	12.5
PBT + EPDM-g-GMA				
5 wt%	6.3	5.9	22.1	16.0
10 wt%	6.1	5.9	23.1	16.6
PBT + NBR-g-GMA				
5 wt%	6.1	5.9	24.6	18.1
10 wt%	5.7	6.8	20.0	19.6

Scanning electron microscopic (SEM) pictures taken on the fracture surface of PBT blends containing 5 wt.% grafted rubber are depicted in Figure 2.

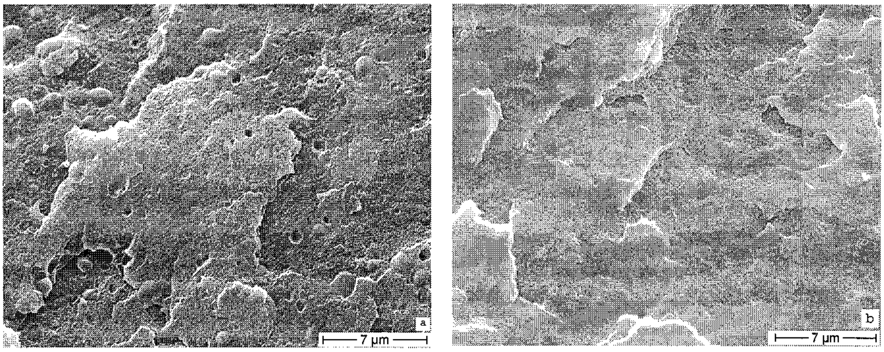


Fig. 2. SEM pictures taken on the fracture surface (T= -40°C) of PBT blends with 5 wt% EPDM-g-GMA (a) and NBR-g-GMA (b), respectively.

According to Figure 2a EPDM-g-GMA is present in a coarse dispersion (particle size <2 µm). On the other hand, NBR-g-GMA produced likely a much finer dispersion (particle size <0.5 µm). This is, however, an artifact. Etching the particle surface by xylene a bimodal, coarse dispersion became visible - cf. Figure 3.

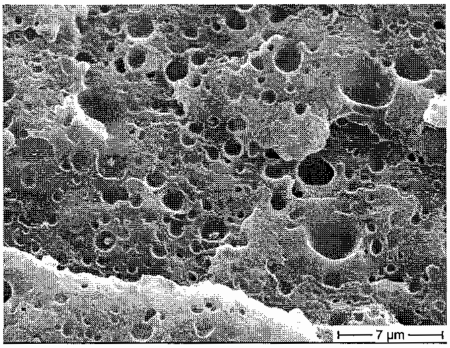


Fig. 3. SEM picture taken on the xylene etched fracture surface (T=23 °C) of PBT blended with 10 wt.% NBR-g-GMA.

In case of the blends with 50 wt.% functionalized rubbers a co-continuous morphology was found as shown on the example of PBT+50 wt.% EPDM-g-GMA (cf. Figure 4).

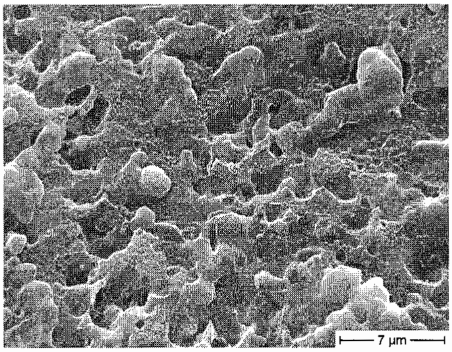


Fig. 4. Co-continuous phase structure in PBT with 50 wt.% EPDM-g-GMA (Note: SEM picture was taken from the fracture surface).

Instrumented Falling weight Impact (IFWI)

The effects of type and amount of the epoxy functionalized rubbers, as well as that of the testing temperature, are summarized in Figure 5. Figure 5 shows that the specific (i.e. thickness related) perforation energy of the blends with both rubbers is similar at least at ambient temperature. However, EPDM-g-GMA outperforms NBR-g-GMA, when tested at T = - 40°C. This behavior should be linked with the T_g of the corresponding rubber.

The fact that the specific perforation impact of PBT blended with EPDM-g-GMA does not depend on the testing temperature should be traced to the co-continuous phase structure.

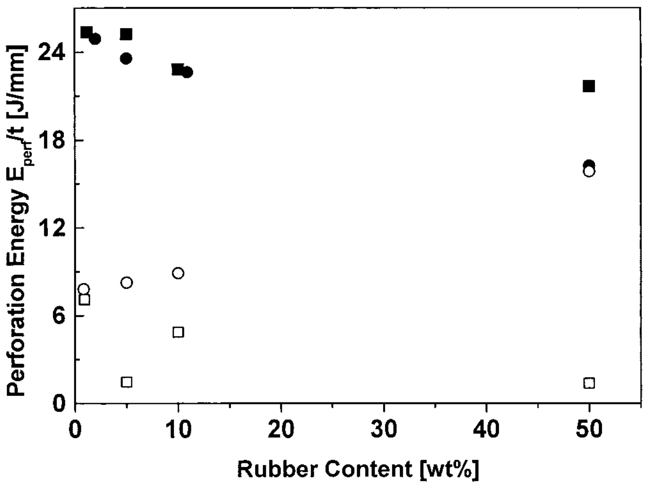


Fig. 5. Specific perforation impact energy as a function of rubber content and type when tested at T=23 and =-40 °C, respectively. ■NBR-g-GMA, T=23°C; • EPDM-g-GMA, T=23 °C; o EPDM-g-GMA, T= -40°C; □ NBR-g-GMA, T= -40°C.

Conclusions

Based on this work devoted to study the toughening efficiency of the epoxy functionalized apolar (EPDM-g-GMA) and polar (NBR-g-GMA) rubbers blended with PA-6 and PBT, respectively, the following conclusions can be drawn:

- The rubbers are dispersed at low (≤ 10 wt.%), whereas form a co-continuous structure at high (~ 50 wt.%) concentrations.
- The enhancement in the fracture toughness and energy is similar for both rubbers in the tested temperature range. Adding more than 5 wt.% epoxy functionalized rubber does not improve the linear elastic fracture mechanical response.
- The perforation impact (biaxial loading) of the blends were similar for both rubber at ambient temperature. At T= -40°C, however, EPDM-g-GMA was superior to NBR-g-GMA, which reflected the difference in the T_g of the rubbers.

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