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Thermoplastic elastomers based on compatibilized poly(ethylene terephthalate) blends: effect of rubber type and dynamic curing

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Abstract

Thermoplastic elastomers containing poly(ethylene terephthalate) (PET) in 50 wt%, compatibilizer (glycidyl methacrylate grafted rubber or glycidyl methacrylate containing copolymer) in 30 wt% and various rubbers (20 wt%) were produced by melt blending with and without dynamic curing (dicumyl peroxide initiated). The static tensile (stress–strain behaviour) and dynamic mechanical thermal properties (DMTA) of the systems along with their phase morphology (scanning electron microscopy of cryofractured and etched surfaces) were determined. It was found that the blend compatibility with PET is strongly improved when a high acrylonitrile-containing nitrile rubber (NBR) and an ethylene-glycidyl methacrylate copolymer (EGMA) or a GMA grafted ethylene/propylene rubber (EPR-*g*-GMA) are used as rubber and/or compatibilizer in the blend recipes. The effect of dynamic curing on the tensile and DMTA properties of the blends was negligible. Fractographic inspection of the fractured surface showed the development of a co-continuous phase structure which was in accordance with learnings from the DMTA spectra. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate); Thermoplastic elastomer; Glycidyl methacrylate functionalization

1. Introduction

Poly(ethylene terephthalate) (PET) is a widely used engineering plastic [1]. Especially in the field of soft drink bottle applications a steep PET consumption occurred in the recent years [2]. Weight saving and breakage security are the major reasons behind this success. As a result, fast-growing quantities of used, secondary PET material became available [2]. Various recycling options are worked out for PET since the most straightforward reuse viz. ”bottles from bottles“ implies some difficulties. Note that polycondensates undergo hygrothermal chain degradation when melt processed in the presence of moisture [3]. Research and development trials based on blending and alloying techniques to produce commercially relevant materials are nowadays in progress. The commercial success of polypropylene/polyamid (PP/PA) alloys can possibly be repeated with PET-based ones. Blends of plastics and rubbers offer alternatives to conventional thermoplastic elastomers such as those based on block copolymers composed of hard and soft block segments. Coran et al. have conducted excessive studies on such blends [4]. The customary applied elastomers (ethylene/propylene copolymer (EPR), ethylene/propylene/diene terpolymer (EPDM), styrene/butadiene rubber (SBR)) are highly immiscible with PET or poly(butylene terephthalate) (PBT) and thus the related blends show unfavourable mechanical properties. Therefore compatibilization in order to obtain good interfacial adhesion and to reduce the interfacial tension between the components is necessary. The compatibility can be improved by addition of suitable block or graft copolymers [5]. This subject has been studied by various researchers. Binary blends with PBT/PP applying various in situ compatibilizing agents are reported by Sun et al. [6–8] and Holsti-Miettinen et al. [9]. PBT/EPDM blends with and without glycidyl methacrylate (GMA) functionalization were reported in Ref. [10], while PBT/poly(ethylene-*co*-glycidyl methacrylate) (PBT/EGMA) blends were described by Okamoto et al. [11]. In the literature, the number of articles dealing with PBT blends exceeds those with

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Abbreviations: DCP, dicumylperoxide; EPDM, ethylene/propylene/diene rubber; EPR, ethylene/propylene rubber; EPR-*g*-GMA, ethylene/propylene rubber grafted with glycidyl methacrylate; GMA, glycidyl methacrylate; IMIX, rubber + peroxide premixture prepared at low temperatures; IPN, interpenetrating network (cf. co-continuous phase structure); NBR, nitrile/butadiene rubber; PET-TDV, blend prepared of PRE-BLEND-TDV and PET; PRE-BLEND-TDV, dynamic vulcanisate prepared of IMIX and EPR-*g*-GMA; TDV, thermoplastic dynamic vulcanisate.

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PET by far. PET/polyethylene (PET/PE) blends compatibilized by ozonization or copolymerization with various monomers, namely methyl methacrylate, hydroxyethyl methycrylate, GMA, maleic acid anhydride and ethyl acrylate are described by Boutevin et al. [12]. Results on the compatibilizer effectiveness in PET/PE blends were reported by Kalfoglou et al. [13–15] and Pietrasanta et al. [16]. Besides these, Akkapeddi et al. [17] studied PET/PE blends with commercial ethylene/glycidyl methacrylate copolymers (EGMA) compatibilizers. In comparative compatibilization studies [13,18] EGMA copolymers were found to be more effective than maleated PE, EPR and styrene/ethylene/butadiene/styrene copolymers (SEBS). The same finding was stated for PET/PP blends applying GMA functionalized PP by Champagne et al. [19]. Patents also teach the efficiency of GMA (EPDM-*g*-GMA) or glycidyl acrylate grafted EPDM as impact modifiers [20,21]. For cost reduction reasons commercial compatibilizers should be substituted by home-made products. The learning from the above literature survey is that GMA functionalization is the key. Therefore this study focuses on the use of GMA grafted EPR (EPR-*g*-GMA).

A typical method to improve the rubber performance and to stabilize the morphology of blends of thermoplastics with elastomers is dynamic curing. Dynamic curing or vulcanization has been extensively reviewed [22–27]. It describes the process of vulcanizing the elastomer during melt-mixing with a non-curable thermoplastic. Typical property improvements achieved by dynamic curing are reduced permanent set, improved ultimate mechanical properties, improved fatigue resistance and resistance to aggressive mediums. In most cases small dispersed ideally fully cross-linked droplets of 0.1–2.0 μm diameter are dispersed in a thermoplastic matrix. Besides these, another class of blended compounds, consisting of interpenetrating co-continous polymer phases (IPN), first proposed in 1971 by Klempner et al. [28] exists. Numerous patents are also claiming the production of thermoplastic elastomers of IPN structure [29–33]. The benefit of the IPN morphology is that the properties of the blend components are fully exploited. It was recently reported that even thermoplastic dynamic vulcanisates (TDV) may have IPN domains in microscale [34].

Note that PET is prone to physical aging, the outcome of which is material embrittlement [35]. In order to avoid this undesirable side-effect, our strategy was to produce PET-based blends of elastomeric character with IPN morphology. So, the aim of this work was to produce thermoplastic elastomers consisting of PET, compatibilizer (EPR-*g*-GMA) and various rubbers and thermoplastics by keeping the PET content at 50 wt%. A further aim of this study was to check whether or not the mechanical performance can be upgraded by dynamic curing. Recall that this study was directed to check an upcycling option for secondary PET from discarded multi-way or one-way bottles.

2. Experimental

2.1. Materials

The applied rubber materials along with their basic characteristics are listed in Table 1. The dicumylperoxide (DCP, Perkadox BC-40B-pd, DCP content: 40 wt%) used for dynamic curing was purchased from Akzo Nobel (Germany). A commercial bottle grade PET (Eastapak 9921W, clear, $M_n = 26$ kg/mol, $M_w = 52$ kg/mol, Eastman Chemical Co., UK) was used as raw material for the melt blending trials.

2.2. Elastomer functionalization

GMA was grafted onto the EPR using an internal batch mixer (Brabender® Plasticorder). Torque and temperature were recorded online. The required amount of EPR was charged into the preheated mixing chamber. The liquid GMA was mixed with liquid peroxide (Trigonox 29 B90, Akzo Nobel) and introduced into the mixing chamber after 2-min mastication of the EPR at ∽120°C with 20 rpm. The mixing chamber was kept closed by a ram. The melt temperature was increased in order to initiate the free radical grafting reaction by increasing the mixing speed to 55 rpm. After the reaction had ended (assessed by the torque) the samples were discharged from the mixing chamber and cooled to room temperature. The amount of grafted and homopolymerized GMA was determined by applying the purification method of Al-Malaika [36]. The GMA content of the functionalized EPR was determined by Fourier transformed infrared spectroscopy (FTIR)

Table 1
Sample coding, supplier and specifications of the applied elastomers. Abbreviations used: E, ethylene; P, propylene, ENB, ethylidenenorbornene

Sample	Material	Specifications (composition in wt%)
EPR	Tafmer-P 0480; Mitsui Chemicals, Japan	E:P = 80:20; MFI: 1.1 dg/min (190°C, 2.16 kg weight)
EPDM	Buna AP 447 (EP G 6470); Bayer AG, Leverkusen, Germany	E:P:ENB = 71:24.5:4.5; Mooney viscosity ML (1 + 4) 100°C: 59
NBR-1	Perbunan NT 2831; Bayer AG, Leverkusen, Germany	Acrylonitrile content: 28.6 ± 1; Mooney viscosity ML (1 + 4) 100°C: 30 ± 5
NBR-2	Perbunan NT 3946; Bayer AG, Leverkusen, Germany	Acrylonitrile content: 40.0 ± 1; Mooney viscosity ML (1 + 4) 100°C: 37 ± 5
E/αO-1	Engage 8200; DuPont Dow Elastomers GmbH, Germany	E:alpha-olefin = 90.5:9.5; Mooney viscosity ML (1 + 4) 100°C: 8; MFI: 5.0 dg/min, (190°C, 2.16 kg weight)
E/αO-2	Engage 8445; DuPont Dow Elastomers GmbH, Germany	E:alpha-olefin = 76:24; Mooney viscosity ML (1 + 4) 100°C: 8.0; MFI: 3.5 dg/min, (190°C, 2.16 kg weight)
EGMA	Lotader AX 8840 Elf Atochem GmbH, Germany	Ethylene-*co*-GMA; 8 wt% GMA

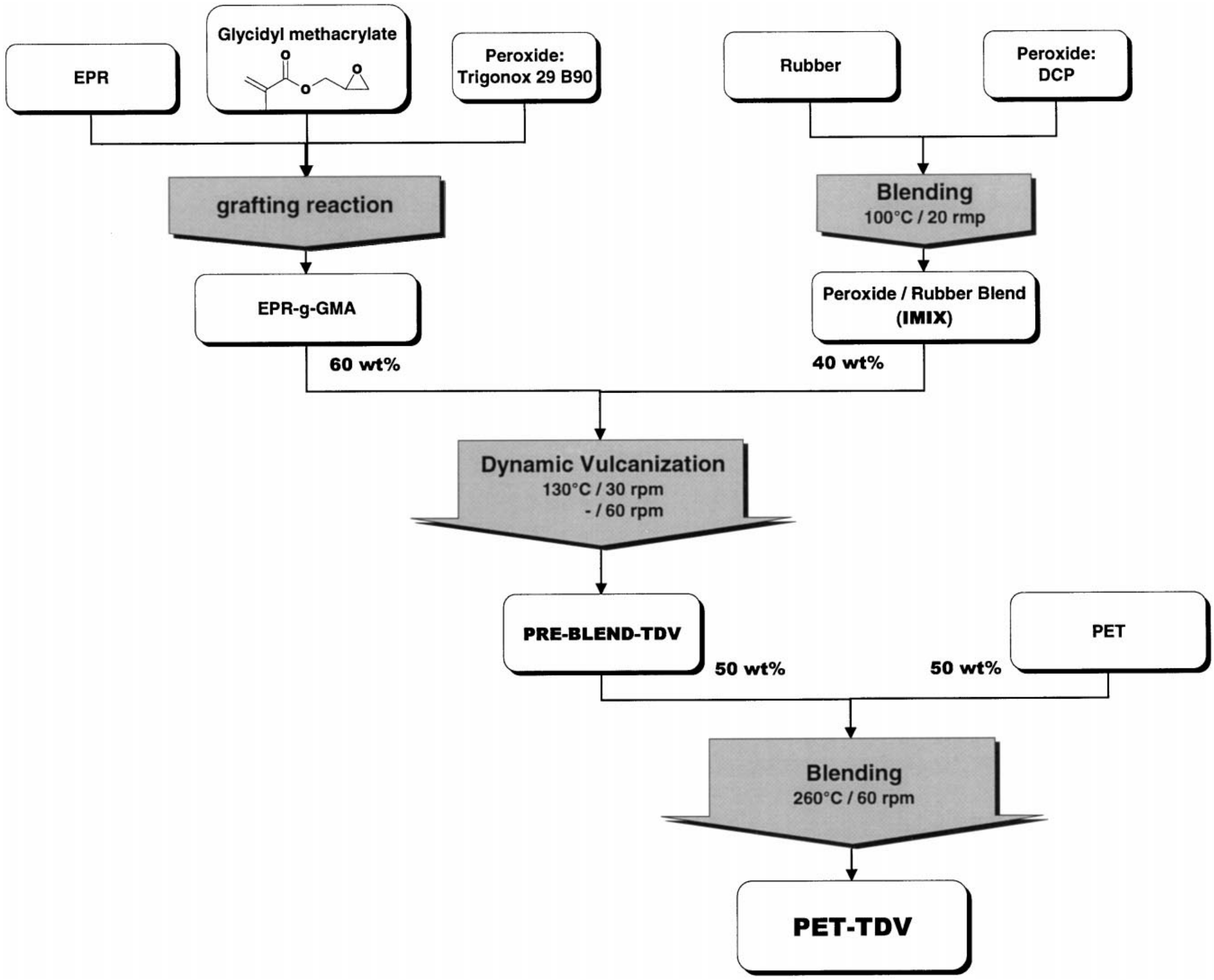

Fig. 1. Flow chart of the production of PET-based thermoplastic elastomers.

according to the calibration method of the authors [37]. Accordingly, the EPR-*g*-GMA contained 11.1 wt% grafted GMA and 0.6 wt% homopolymerized GMA.

2.3. Melt blending, compounding, specimen preparation

The flow chart on the functionalization, blending and dynamic curing is outlined in Fig. 1. All described blending and compounding processes were performed in the Brabender® batch mixer.

Preliminary experiments have shown that the dynamic curing process cannot be performed at elevated temperatures needed to process the PET. Therefore an *indirect, two-step* masterbatch process was chosen. *Indirect* means that the peroxide was premixed and dispersed in the rubber, which ought to be dynamically cured. *Two-step* masterbatch means that the dynamic vulanisate is prepared first and then blended with the PET in the next step (Fig. 1).

The major advantage of this procedure is that the peroxide does not interfere with the PET. The dynamic vulcanisate is produced as follows: first a rubber/peroxide premixture (IMIX) was prepared (3.75 phr peroxide, 100°C, 20 rpm) at temperatures lower than the decomposition temperature of the peroxide. Note, 3.75 phr in the IMIX corresponds to 1.5 phr in the PET-TDV.

In a second step the blend (PRE-BLEND-TDV) of 60 wt% GMA functionalized EPR rubber (EPR-*g*-GMA) with 40 wt% IMIX was prepared (130°C, 30 rpm) and dynamically cured. For this reason the mixing speed was increased to 60 rpm for 5 min. The stronger internal friction in combination with the dissipating heat energy initiated the peroxide decomposition as evidenced by the torque/time curves.

The final thermoplastic dynamic vulcanisates with PET (PET-TDV) were prepared by blending the PRE-BLEND-TDVs with PET at 260°C, 60 rpm for 6 min. The

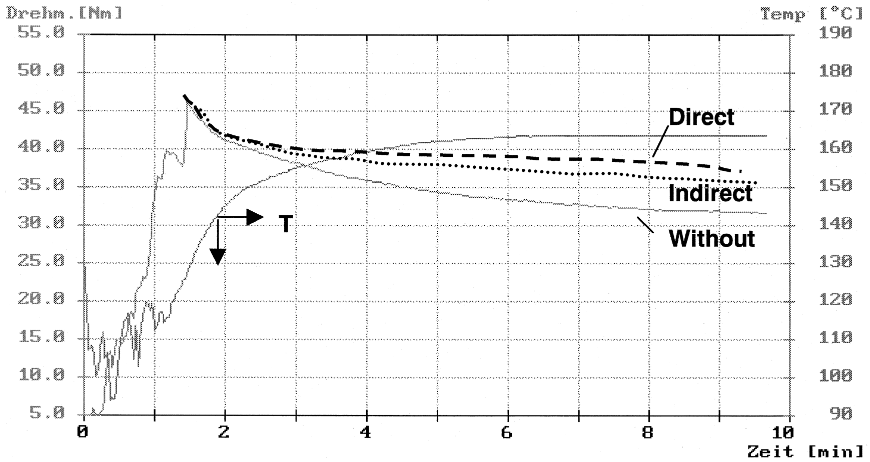

Fig. 2. Mixing torque vs. time traces for variants of the dynamic curing (without peroxide, direct and indirect methods, respectively).

PET-TDVs were cryogenically crushed to small pellets. The pellets were dried at 120°C for about 12 h before plates (2 mm thickness) were compression moulded at 300°C (3 min). The required specimens were punched out of these plates.

2.4. Blend characterization

2.4.1. Tensile testing

Tensile tests under static conditions were carried out on a Zwick 1474 100 kN (Ulm, Germany) universal testing

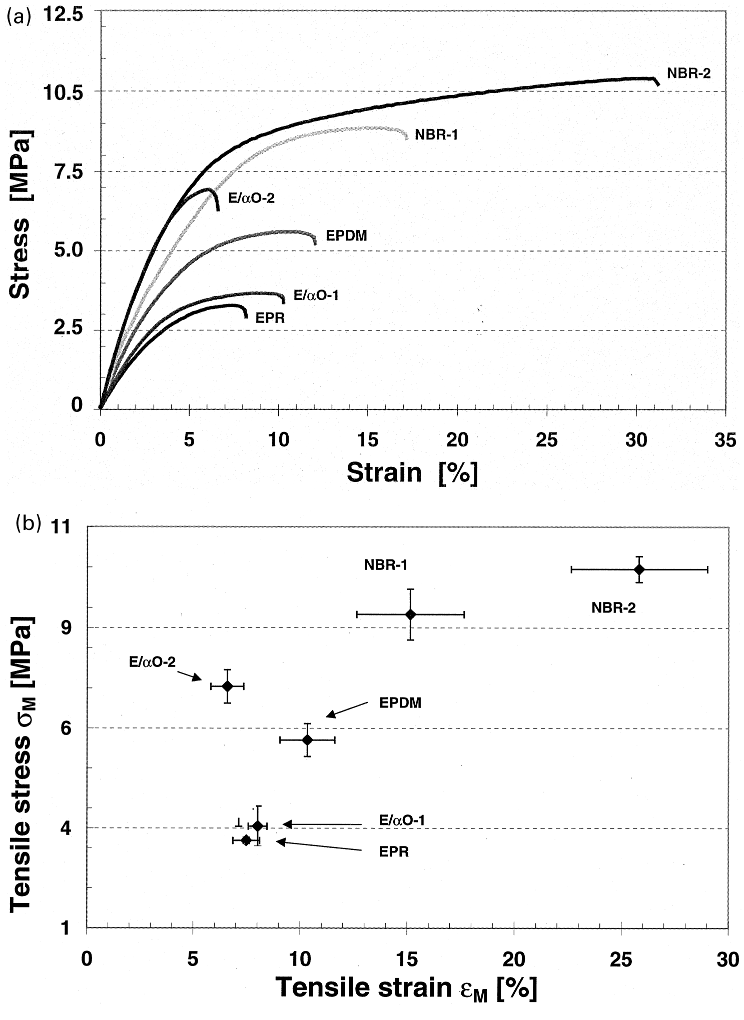

Fig. 3. Stress–strain behaviour of PET-TDVs with various elastomers: (a) primary curves, and (b) ultimate properties.

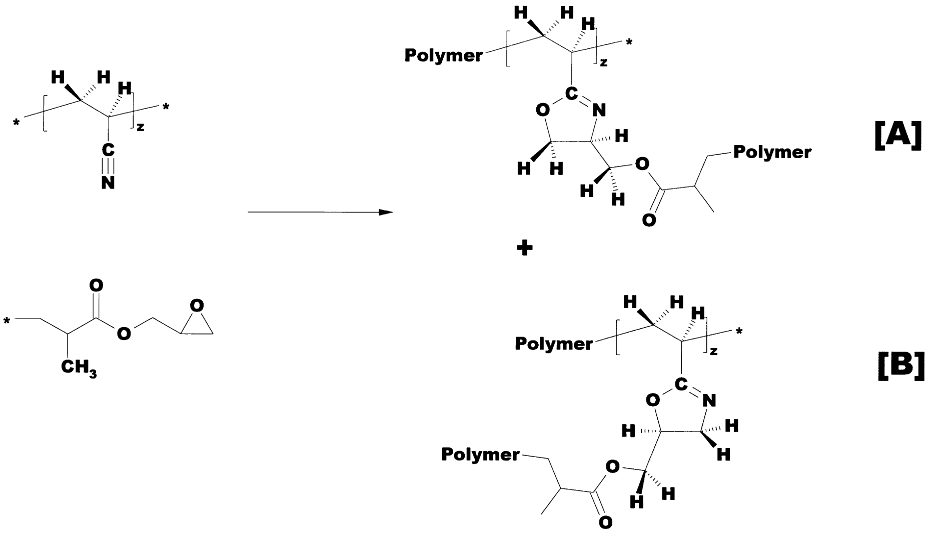

Fig. 4. Chemical reaction pathways of epoxide and nitrile functions to oxazoline. A and B are two structure variations.

machine. Crosshead speed was set at 20 mm/min. Tensile yield strength σ_M and strain ϵ_M were determined according to DIN EN ISO 527-1 and 527-2 using specimen 1B, but with 2.0 mm thickness. At least four specimens for each blend were used to get the mean values.

2.4.2. Thermomechanical evaluation

The viscoelastic response of the PET-TDV blends was studied by dynamic mechanical thermoanalysis (DMTA) using an Eplexor® 150 N (Gabo Qualimeter, Germany) DMTA device. Rectangular specimen of $60 \times 10 \times 2$ mm^3 (length × width × thickness) were subjected to oscillating tensile loading. The selected static preload was 3.0 ± 0.5 N on which a oscillating load of 1.5 ± 0.3 N (sinusoidal wave) at 10 Hz frequency was superimposed. Heating occurred at a rate of 1°C/min in a temperature range between −100 and +280°C.

2.4.3. Blend morphology

The morphology of the blends was studied in a scanning electron microscope (Jeol® JSM 5400, 25 kV acceleration voltage) after cryofracture and subsequent etching. Etching was performed in boiling xylene or 1,1,2,2-tetrachloroethane, respectively. The fracture surfaces of the samples were sputtered with Pd/Pt alloy in a Balzers® SCD 050 device.

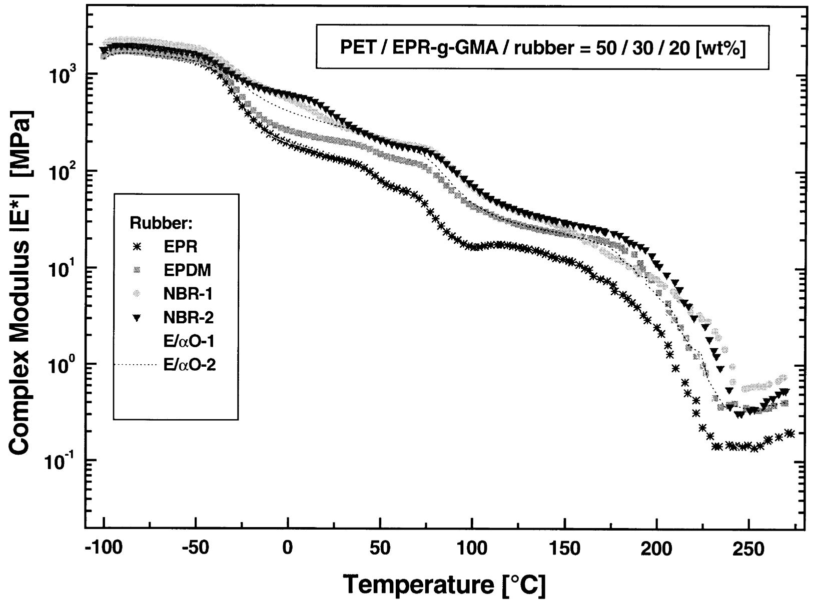

Fig. 5. $|E^*|$ vs. T traces for the PET-TDVs with various elastomers.

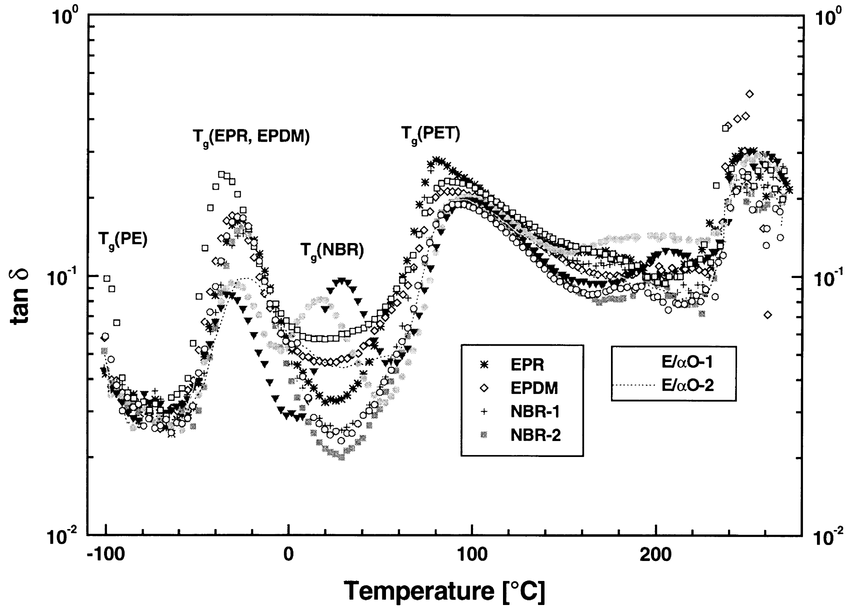

Fig. 6. tan δ vs. *T* traces for the PET-TDVs with various elastomers (for their compositions cf. Fig. 5).

3. Results and discussion

For the dynamic curing, direct and indirect methods to introduce the peroxide were checked. In this context, direct means that peroxide and both elastomers were added into the mixing chamber without any premixing. In this case the peroxide is likely to disperse in both phases according to its thermodynamic solubility. For the indirect method, the peroxide was premixed at a temperature below its decomposition with that rubber which was supposed to cure. This premixture is later added to the second elastomer (EPR-*g*-GMA) and subsequently cured dynamically. The plastograms in Fig. 2 (torque/time plots) show that there is a slight difference in torque for each method. For the indirect method 36 N m, and for the direct 38.5 N m were determined after 8 min of blending. Accordingly, the degree of crosslinking of the EPR-*g*-GMA present (in 60 wt% in the PRE-BLEND-TDV of Fig. 1) is likely to be lower by following the indirect path. Therefore the functionalized elastomer can still act as efficient compatibilizer in the

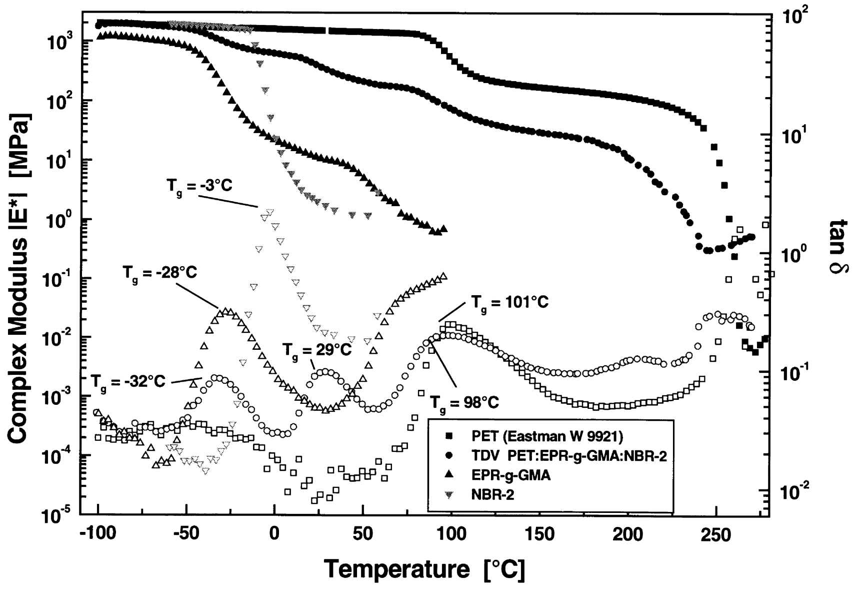

Fig. 7. $|E^*|$ vs. *T* and tan δ vs. *T* traces for the PET-TDV with NBR-2 and its components (PET, EPR-*g*-GMA, NBR-2). Note: open symbols are related to the tan δ values.

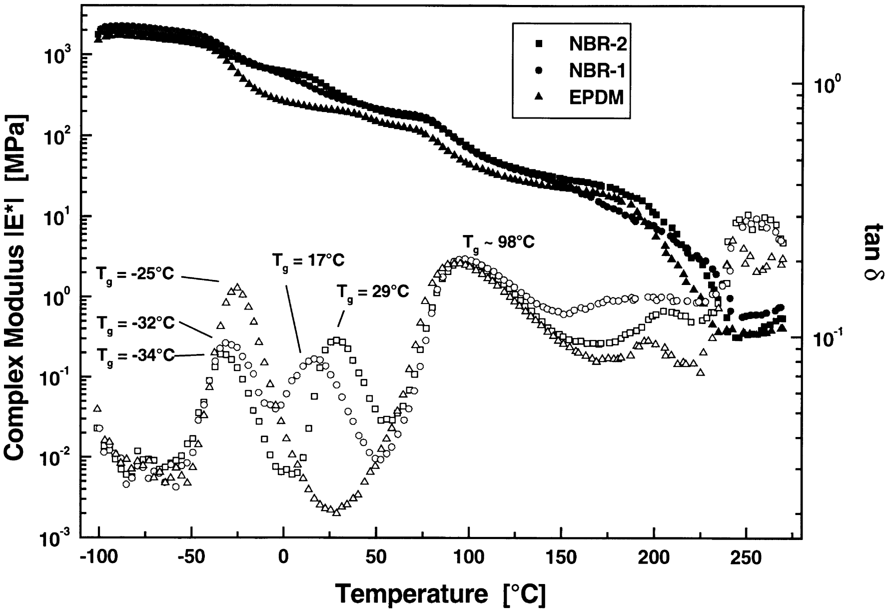

Fig. 8. $|E^*|$ vs. T and tan δ traces for TDV compositions PET:EPR-*g*-GMA:(NBR-1, NBR-2, EPDM) = 50:(30:20). Note: open symbols are related to the tan δ values.

later PET compound (PET-TDV). Hence, for all later experiments the indirect route of peroxide addition was chosen.

3.1. Effect of the rubber type

3.1.1. Tensile testing

One of the key properties of thermoplastic elastomers is their stress–strain behaviour, which also yields the first information on the compatibility of blends. The tensile stress (σ_M) versus tensile strain (ϵ_M) values with the standard deviations of all PET-BLEND-TDV are shown in Fig. 3. The highest elongations in combination with the highest tensile stress values are found for the blends with nitrile rubbers (NBR). The blend with NBR-2 rubber yielded $\epsilon_M = 25.8\%$ and $\sigma_M = 10.0$ MPa, whereas for the NBR-1-containing one $\epsilon_M = 15.2\%$ and $\sigma_M = 8.8$ MPa were determined. Note that both NBR-1 and NBR-2 rubbers exhibit a very high acrylonitrile content (~40 wt% for NBR-2 and ~29 wt% for NBR-1, Table 1). The stress–strain data showed that the compatibility of the PET blend increases with increasing acrylonitrile content of the NBR.

There is, however, another possible explanation for this finding. The nitrile functions (–C≡N) in the NBR can react with the epoxide functions of the GMA to form an oxazoline intermediate (Fig. 4). The resulting intermediate has a higher reactivity [38–40] towards the carboxylic acid group (–COOH) as well as the hydroxyl groups (–OH) of the PET and thus acts as an in situ compatibilizer. The intramolecular formation of an oxazoline by a reaction of

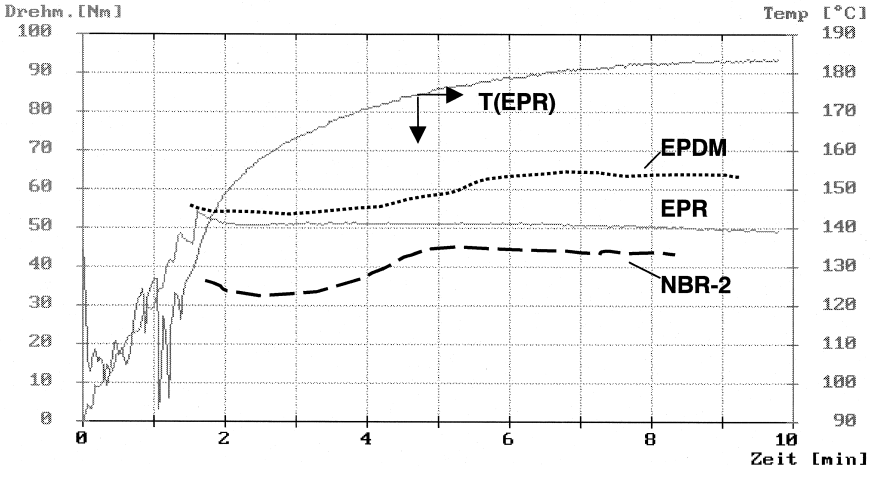

Fig. 9. Torque vs. time and T vs. time traces of PET-BLEND-TDV with NBR-2, EPDM and EPR.

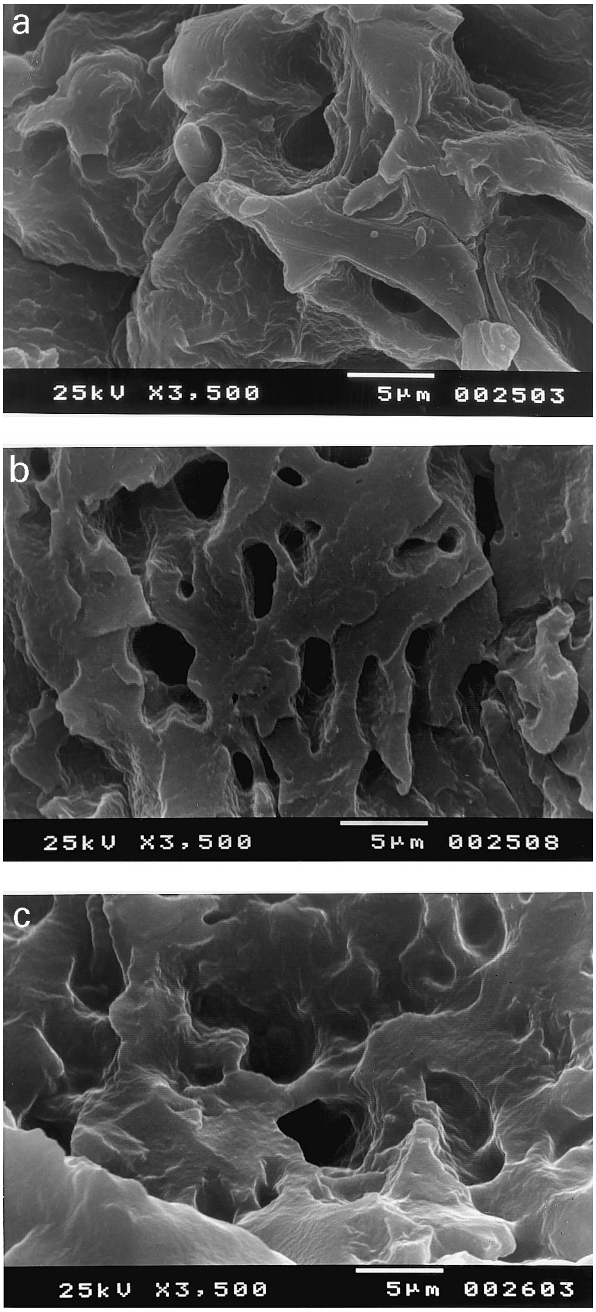

Fig. 10. SEM pictures of cryofractured and etched PET-TDVs with various elastomers. (a) PET/EPR-*g*-GMA/EPR TDV = 50:(30:20). (b) PET/EPR-*g*-GMA/EPDM TDV = 50:(30:20). (c) PET/EPR-*g*-GMA/NBR-2 TDV = 50:(30:20).

the nitrile function in an NBR with the epoxide groups of a GMA grafted NBR was recently demonstrated by Papke and Karger-Kocsis [41].

Though blends with EPR and EPDM resulted in similar ultimate tensile stress and strain data, the EPDM (Buna AP 447) proved to be one of the best rubber candidates. Both E/αO polymers show medium strain values. E/αO-2 with the higher α-olefin content in the polymer and with higher initial stiffness yields a higher ϵ_M in the later TDV.

3.1.2. DMTA properties

The DMTA results of all PET-BLEND-TDV are presented in Figs. 5 and 6 in terms of temperature dependence of the absolute complex modulus value ($|E^*|$) and the loss factor tan δ, respectively. Both NBR containing TDV showed the highest complex modulus over the entire temperature range. The $|E^*|$ of all TDVs begin to drop sharply at temperatures higher than ~180°C. This is an effect of the melting rubber rather than of the PET according to the morphology discussed later. Each TDV is clearly phase separated as suggested by the multiple glass transition temperatures (T_g) in the tan δ vs. T traces (Fig. 6). All TDVs containing EP(D)M or E/αO show two major loss factor maxima indicating the T_g of the respective phases (PET and EPR). On the other hand, three relaxation peaks can be resolved for the NBR-containing blends.

The most interesting PET-BLEND-TDV, with respect to the mechanical performance, contain NBR-1, NBR-2 and EPDM. The related relaxation peaks are: T(PET-BLEND-TDV-NBR-1) = −34, 29, 98°C; T(PET-BLEND-TDV-NBR-2) = −32, 17, 98°C; and T(PET-BLEND-TDV-EPDM) = −25, 97°C. Both NBR-containing TDVs showed three T_g values indicating a three-phase system (Fig. 7). An interesting feature is the shift in the T_gs for the PET-BLEND-TDV-NBR-2 compared to its plain components (Fig. 7). The T_g deriving from the EPR-*g*-GMA is shifted towards lower temperatures from −28 to −32°C. The effect on the T_g deriving from the PET is quite similar, hence it is shifted from 101 to 98°C. On the other hand, the T_g deriving from the NBR-2 is shifted extremely ($\Delta T =$ 26°C) towards higher temperatures from −3 to 29°C. This finding will be discussed in a later section. The DMTA results of PET-BLEND-TDVs with both NBRs and EPDM are presented in Fig. 8 in terms of temperature dependence of the $|E^*|$ and tan δ, respectively.

3.1.3. Blend morphology

Torque versus time and temperature versus time plastograms of some EPR-*g*-GMA/rubber/peroxide (60:40:3.75) PRE-BLEND-TDVs are shown in Fig. 9. A horizontal torque line with a slight decrease was found with EPR as elastomer. With no dynamic curing typically a steeper torque decline with increasing temperature would be expected. In contrast to this, EPDM and the NBR showed a clear torque increase. A possible explanation for this finding is that both elastomers (EPDM and NBR-2) contain unsaturated sites in the polymer chain. In the EPDM the ENB and in NBR the butadiene and nitrile structural units are likely the preferred crosslinking sites for the peroxide. The nitrile functions are curable sites, too. Comparing NBR-1 and NBR-2 (effect of acrylonitrile content), a stronger torque increase was noticed for the NBR-2. The crosslinking presumably occurred in the NBR phase causing the observed viscosity rise.

Fig. 10 presents SEM pictures taken of the cryofractured and etched surfaces of four PET-BLEND-TDV with EPR, EPDM, and NBR-2 as elastomers. In all TDV a co-continuous

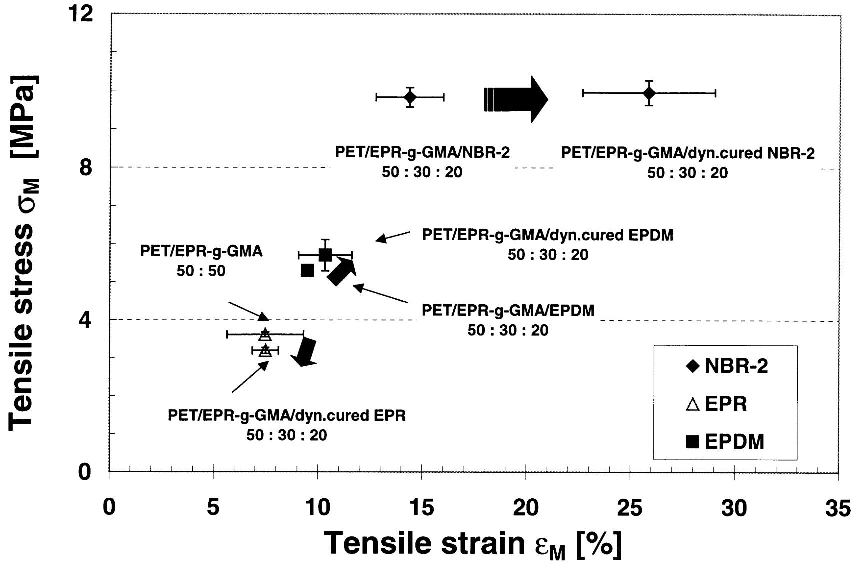

Fig. 11. Comparison of the ultimate stress and strain behaviour between dynamically cured and non-cured compositions containing PET/EPR-*g*-GMA/elastomer (50:30:20). Designation: arrow shows the effect of dynamic curing.

PET and elastomer phase can be resolved or suspected. So an interpenetrating network structure [29–33]) is formed. This finding explains the high stiffness ($|E^*|$) in the DMTA tests over a large temperature interval: the continuous PET phase guarantees the mechanical stiffness. In most cases there are no unequivocal proofs for a three-phase morphology, i.e. PET, uncured and cured elastomers. Thus the cured elastomer is presumably dispersed in the EPR-*g*-GMA phase. Unfortunately, etching experiments using boiling xylene did not result in selective removal of the EPR-*g*-GMA. Instead, the entire elastomer phase has been removed — see SEM picture in Fig. 10.

3.2. Effect of dynamic curing

Recall that the flow chart in Fig. 1 is rather complex. The production of the thermoplastic elastomer contains a four-step grafting–blending–curing–blending sequence, which is hardly economical. Therefore, blends without dynamic curing were prepared by blending PET and EPR-*g*-GMA with selected elastomers (EPR, EPDM, NBR-2).

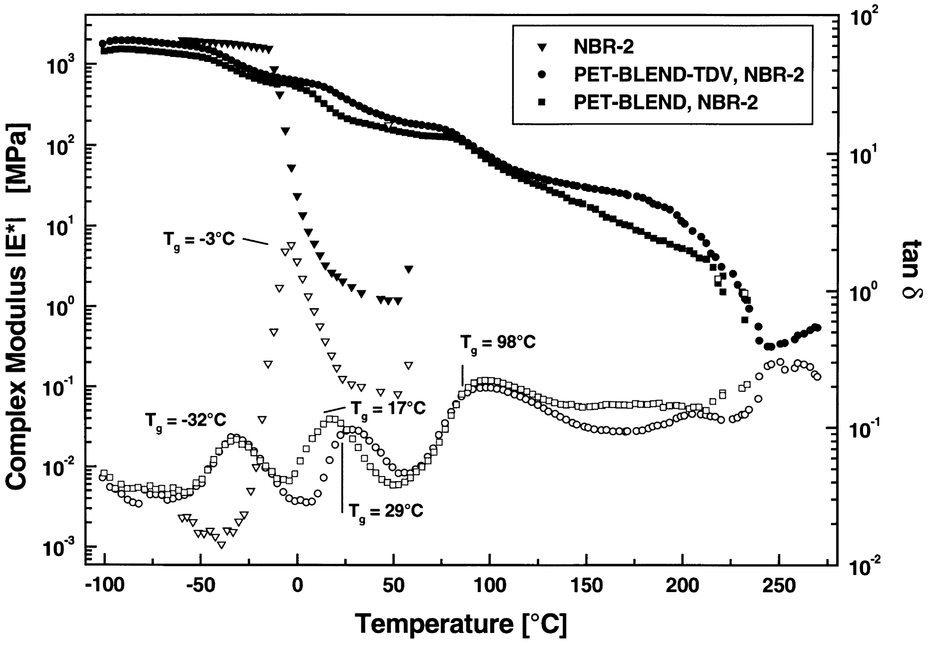

Fig. 12. $|E^*|$ vs. T and tan δ vs. T traces for PET-TDV and PET-BLEND with NBR-2. Note: open symbols are related to the tan δ values.

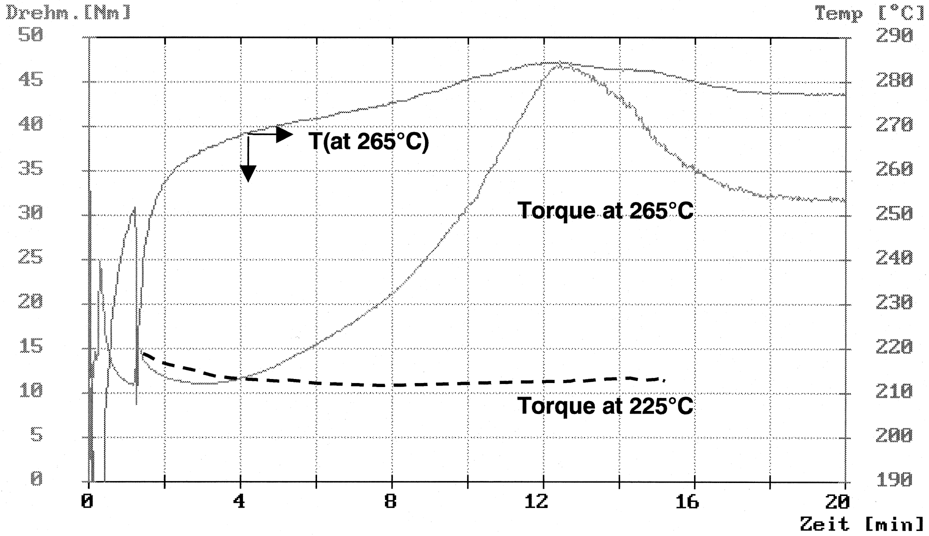

Fig. 13. NBR-2 processing plastograms at two different temperature conditions: 225°C, 40 rpm and 265°C, 40 rpm.

Melt-mixing of these components occurred at 260°C in a Brabender internal mixer (~5 min at 60 rpm mixing speed) and their properties compared with those produced by dynamic curing (discussed above).

3.2.1. Tensile testing

Fig. 11 compares the stress–strain behaviour of the blends and TDVs are presented. Note that the influence of the dynamic curing is affected by the applied elastomer. On the other hand, no general improvement can be assigned to the dynamic curing. For the NBR-2-containing blend the tensile strain increase was noticeable. The corresponding stress values rise by $\Delta = 7\%$ (9.3–10.0 MPa). For the EPDM-containing blend, the influence on the stress–stain data was less distinct. For the blends with EPDM or EPR, the effect of dynamic curing is negligible. One can thus state that dynamic curing is superfluous in most of the cases.

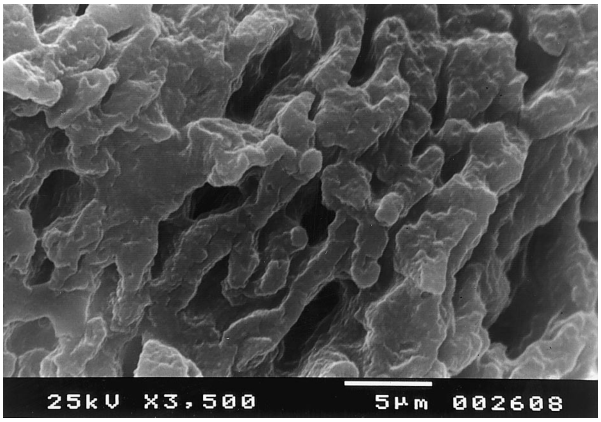

Fig. 14. Scanning electron micrographs of cryofractured and etched PET/(EPR-*g*-GMA/NBR-2) BLEND = 50:(30:20).

3.2.2. DMTA properties

Fig. 12 shows the DMTA behaviour of PET-BLEND and PET-TDV containing NBR-2. $|E^*|$ of the TDV was found on a higher level over the entire temperature interval compared to the blend. This is in agreement with the observed mechanical behaviour. While $|E^*|$ decreased almost linearly for the blend at temperatures above 100°C (T_g of PET), $|E^*|$ of the TDV remained on a higher level until it started to drop at around 200°C. tan δ revealed two identical glass transition temperatures for the TDV and the blend at −32 and 98°C, respectively. The third T_g deriving from NBR-2 was found at 17°C ($\Delta = 20$°C) in the blend and 29°C ($\Delta = 32$°C) in the TDV. The difference in this relaxation peak between the blend and the TDV is $\Delta(\Delta) = 12$°C. A possible explanation is that the NBR component experienced pronounced crosslinking in the TDV. Even though NBR-2 is not known as self-curing rubber according to a torque testing method [42], it crosslinks at temperatures which are necessary to process PET (Fig. 13). The degree of crosslinking of NBR-2 in the cured TDV exceeds that of the blend resulting in higher T_g. Recall that the observed change in the T_g may be related also to the oxazolin formation (Fig. 4). If this is so, the T_g shift should be smaller for the system with NBR-1 than with NBR-2, as NBR-1 has a lower acrylonitrile content. DMTA spectra confirmed this expectation, in fact.

3.2.3. Blend morphology

As expected according to the DMTA results, a co-continuous phase structure (IPN) was also found for the blend. The SEM micrograph in Fig. 14 shows no clear evidence, however, for a three-phase structure of the blend. Based on a less coarse IPN morphology of the blend compared to the TDV (Fig. 10c), one expects higher strength and elongations for the blend. On the other hand, the mechanical performance of the TDV was better (cf. Fig. 11).

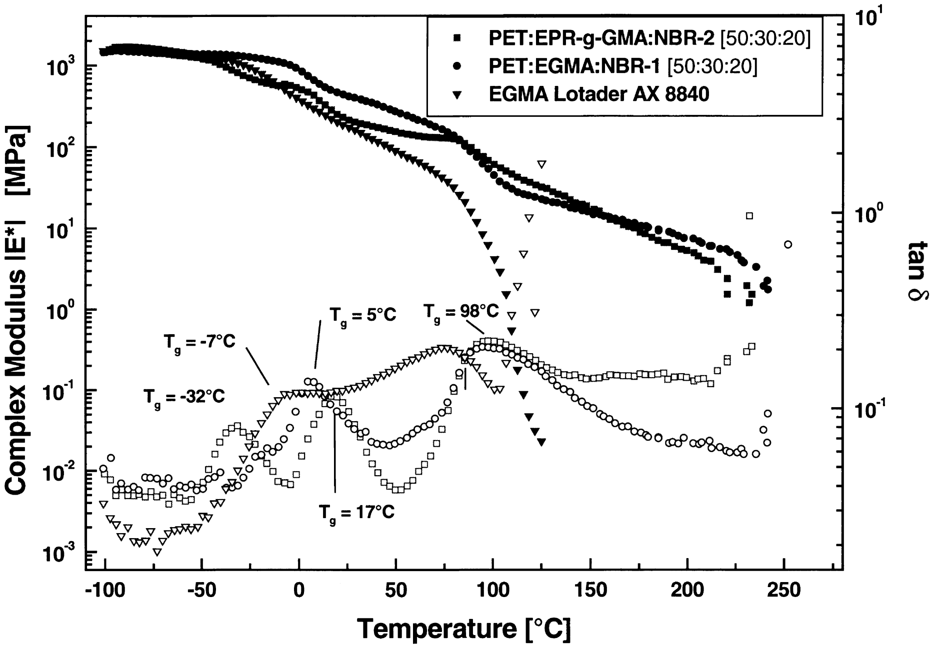

Fig. 15. $|E^*|$ vs. T and tan δ vs. T traces for PET-BLEND with EPR-*g*-GMA and commercial EGMA copolymer. Note: open symbols are related to the tan δ values.

3.3. Compatibilizer effect

The above results support that the type and even the grade of the applied elastomer have a pronounced effect on the performance of the PET/elastomer blends. Therefore, it is reasonable to check the efficiency of the state of the art compatibilizing elastomers. EPR-*g*-GMA was substituted by a commercially available ethylene/glycidyl methacrylate (EGMA) copolymer (Lotader A × 8840, ca. 8 wt% GMA comonomer content). Recall that this EGMA copolymer is widely used as compatibilizing agent in the literature [6,11,13,17,18].

3.3.1. Tensile testing

The mechanical performance of the blend containing a commercial EGMA performed significantly better. The ultimate tensile strain rose by about 100% from 14.4 to 28.7%. At the same time, the tensile stress increased by about 60% from 9.8 to 15.3 MPa.

3.3.2. DMTA properties

The DMTA results are presented in Fig. 15. Comparing the $|E^*|$ vs. T traces, the two blends have similar stiffness. In the region between ca. -50 to $+100$°C and above ~150°C, the blend with commercial compatibilizer revealed somewhat higher $|E^*|$. This finding, however, is in harmony with the tensile properties found. Considering the tan δ in the EGMA-containing blend, only one peak appears at 5°C. Both original peaks from EGMA at $T_g = -7$°C and NBR-2 at $T_g = -23$°C are shifted towards higher temperatures. One can suspect that the uncured elastomer phase comes under hydrostatic compression due to the PET crystallization and related shrinkage. It is obvious that this effect is more pronounced in the blend than in the TDV compound. A further possibility is the in situ compatibilization via oxazoline formation. Additionally, an improved miscibility of the fairly polar EGMA with NBR-2 or PET may be a possible explanation, too. Below 0°C the material is, however, rather brittle, which reduces the application of products.

3.3.3. Blend morphology

The SEM pictures in Fig. 16 do not prove an IPN structure. On the other hand, this should be the case according to the DMTA response. The continuous rubber phase (arrows indicated) seems to involve both NBR-2 and EGMA. The reason for the appearance of a fine nodular morphology in the other thermoplastic phase is not yet known by the authors. Considering the fact that a similar structure (but less pronounced) appeared also in the TDV with NBR-2 and EPR-*g*-GMA, this nodular structure may be traced to the oxazoline reaction.

4. Conclusions

The selection of the elastomer type plays a crucial role by influencing the morphology and the related mechanical properties in elastomeric blends composed of PET (50 wt%), compatibilizer (30 wt%) and elastomer (20 wt%). The compatibilizing effect of EGMA was slightly better than a home-made GMA grafted EPR at comparable GMA functionality. The best mechanical performance was

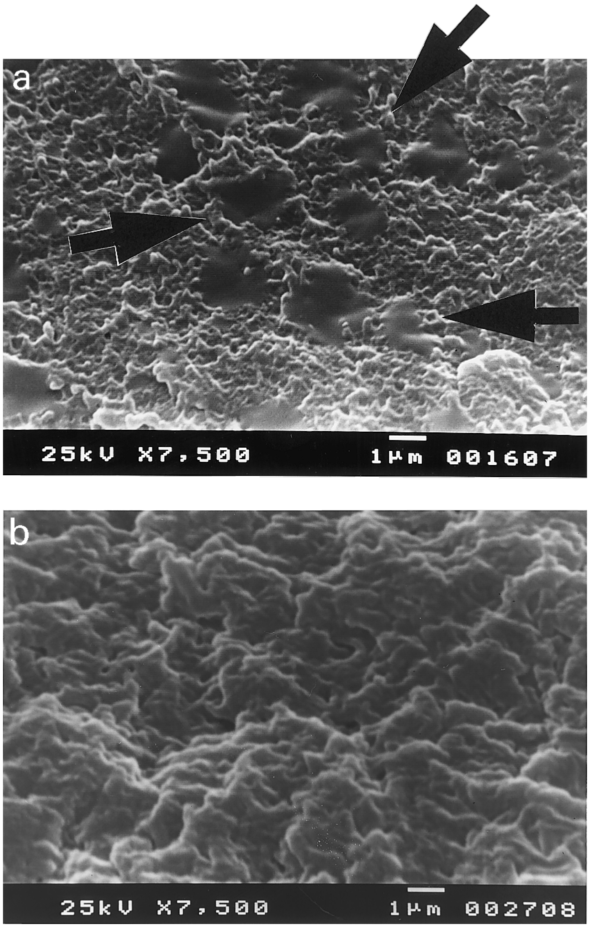

Fig. 16. Scanning electron micrographs of cryofractured PET/(EGMA/NBR-2) BLEND = 50:(30:20) (a) not etched, and (b) etched with boiling 1,1,2,2-tetrachloroethane.

established for those thermoplastic elastomers which contained NBR of high acrylonitrile content instead of polyolefin rubbers. Peroxide-assisted dynamic curing of the rubber phase did not improve the mechanical response significantly. The structure of the thermoplastic elastomers produced by melt blending or in a two-step process involving dynamic curing was of IPN type according to the DMTA and SEM results. It was established that the mechanical properties of blends containing high amounts of linear polyesters can be strongly improved when GMA functionalized NBR rubbers are used [43,44].

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