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The role of various modifiers in the compatibilisation of PP/PET blends — rheological and structural properties

Summary — The present paper deals with structural and flow properties of polypropylene (PP) and poly(ethylene terephthalate) (PET) blends compatibilized by maleic anhydride (MA) in combination with two modifiers — epoxidized thermoplastic elastomer and silicone/acrylic-based rubber. Rheological experiments were performed at both steady and dynamic (oscillating) shear regimes at temperature 245 $^{\circ}$C and 265 $^{\circ}$C, *i.e.* below (when PET particles are not completely molten acting as soft filler) and above melting temperature of PET. Increased rheological functions are generally observed for PP/PET/MA (due to enhanced interfacial interactions), which is further improved by elastomeric modifiers. These also bring satisfactory phase structure resulting from possible reactions between functional groups of the modifier and blend components, particularly for epoxy-modified thermoplastic elastomer. From the application viewpoint, the addition of elastomeric modifiers leads to a significant increase in viscosity of PP/PET blends, which can be useful in their processing, for example in extrusion of mixed plastics wastes.
Key words: polypropylene, poly(ethylene terephthalate), blends, elastomeric compatibilizer, rheological properties, structure.

Polymer blends play an important role in obtaining new high-performance materials with required properties [1]. However, blending of polymers is often complicated by the immiscibility of the majority of polymer pairs caused by unfavourable thermodynamics of the interactions between the blend components, which reflects their physical and chemical structures. As a result, phase separation of the matrix and minor phase, large interfacial tension, and poor mechanical properties are typical features of immiscible polymer blends.

To eliminate undesirable consequences of immiscibility, various compatibilizing methods have been applied, especially reactive *in situ* techniques. In this case, the compatibilizer, which main role is to reduce an interfacial tension and to prevent coalescence and enhance interfacial adhesion, is created during blending.

From the application point of view, the main objective of compatibilization is to prepare material showing enhanced mechanical properties, most often impact strength. To achieve such improvement, the adhesion between two phases must be strengthened, which enables an efficient stress transfer. This way, the brittleness typical for immiscible blends is eliminated [2—4].

In many cases A-B-A type block copolymers have been successfully used as impact modifiers. They consist of styrene endblocks (A) and butylene, isoprene, or ethylene/butylene midblocks (B) thus combining hard polystyrene microdomains, which act as physical cross-linking agents between the elastomeric sequences providing high strengths and elasticity similar to conventional vulcanized rubbers. Therefore, their advantages can be seen in physical properties typical for rubbers, and on the other hand, melt processability analogous to conventional thermoplastics. In addition, these additives have been tested as compatibilizers of different polymer blends, especially polystyrene or polyesters with polyolefins, where they bridge the blended polymers *via* physical or chemical interactions. For this purpose, functionalities like maleic anhydride or epoxy groups are grafted onto the midblocks of the copolymer to allow to go the reactions with the end groups of polyamides or polyesters [5].

Similarly to our previous works [6, 7], the present paper deals with the blends consisting of polypropylene (PP) and poly(ethylene terephthalate) (PET). Generally, blends of polyolefins and PET attract considerable attention since both of them belong to significant waste materials, and in addition, they are often used in the same applications (soft drink bottles, carpets). Therefore, their blending represents a promising alternative to current recycling procedures, which in principle include the

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separation of both material classes. Processing them together, on the other hand, offers advantageous properties of the final product, such as good barrier properties, however, it requires compatibilization. It is often based on the functionalization of the polyolefinic component by reactive monomers (*e.g.* maleic anhydride [8—12], glycidyl methacrylate [13, 14] or oxazoline [15—18]) leading to the increase in polarity and affinity to other polymers, which subsequently allows the reactions with the other blend component to go.

In the present paper, the rheological behavior of polypropylene/poly(ethylene terephthalate) blends is studied, focusing on the influence of modification. Besides the use of maleic anhydride, which compatibilizing effect was evaluated in our previous research [6, 7], two other modifiers were employed. The first one (Epofriend) consists of hard polystyrene and soft diene segments and has some of double bonds epoxidized. This way, also compatibilizing effect is expected *via* the interactions between functionalized modifier and blend components. The other modifier (Metablen) has core-shell structure with silicone/acrylic-rubber in its core. Both are used in several applications, including impact resistance and processability enhancement.

EXPERIMENTAL

Materials

The basic components of blends were polypropylene (PP, Chisso Co. Ltd. Japan, density 0.901 g/cm^3, melt flow rate 50 g/10 min) and poly(ethylene terephthalate) (PET, Unitika Co. Ltd. Japan, density 1.390 g/cm^3, intrinsic viscosity 0.68 dl/g).

As modifiers the following substances were used:
— maleic anhydride (MA, Yoneyama Chemicals Co. Ltd., Japan),
— thermoplastic elastomer (Epofriend A1020, density 0.985 g/cm^3, Daicel Co. Ltd., Japan),
— silicone/acrylic-rubber (Metablen S-2001, density 1.080 g/cm^3, Mitsubishi Rayon Co. Ltd., Japan).

Blend preparation

All blend components were melt mixed using an elastic extruder (developed in the laboratory of National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan) at 267 ±2 ^{o}C and rotation speed 250 rpm. PET was dried at 120 ^{o}C in the air oven before melting. After mixing, sheets of 3 mm thickness were compression molded in a heat press under 50 MPa at 265 ^{o}C, and cut into circular specimens.

PP and PET contents were always set to 80 and 20 wt. parts respectively.

Elastomeric modifiers were added in amount 5.6 or 13.6 wt. parts, and maleic anhydride in the respective samples 1 wt. parts. The codes and compositions of the blends are given in Table 1.

T a b l e 1. Compositions (in weight parts) of the blends and respective codes used

Code	PP	PET	Modifier		
			MA	Epo-friend	Meta-blen
PP/PET	80	20	—	—	—
PP/PET/MA	80	20	1	—	—
PP/PET/MA/Epofriend 5.6	80	20	1	5.6	—
PP/PET/MA/Epofriend 13.6	80	20	1	13.6	—
PP/PET/MA/Metablen 5.6	80	20	1	—	5.6
PP/PET/MA/Metablen 13.6	80	20	1	—	13.6

Methods of testing

Scanning electron microscope (SEM — Vega TS 5130, Tescan) was used to study blend morphology of the samples cryogenically fractured in liquid nitrogen and covered with platinum by vacuum sputter coater (SCD 050, Balzers).

Rheological properties were measured using rotational rheometer (cone-plate type, RGM 151-S, Nippon Rheology Kiki Co., Ltd.). The cone-plate radius was ($R = 21.5$ mm, the gap between the cone and plate $H = 1$ 75 μm, and cone angle θ = 4°). The experiments were carried out under nitrogen atmosphere.

The steady shear flow properties — shear viscosity (η), shear stress (σ) and the first normal stress difference (N_1) — were evaluated at shear rates ($\dot{\gamma}$) ranging from 10^{-2} to 10^1 s^{-1}.

Dynamic functions — storage and loss moduli, dynamic and complex viscosities and complex modulus (G', G'', η′, η*, $G*$, respectively) were determined with an oscillatory angle ±2° in the range of angular frequencies (ω) from 10^{-2} to 10^1 rad/s, and were obtained from Lissajous figures.

Rheological experiments at both steady and dynamic shear regimes were performed at 265 ^{o}C (above melting temperature of PET) and at 245 ^{o}C (below it). In the latter case, PET particles are not completely molten, acting as soft filler.

RESULTS AND DISCUSSION

Morphology

As generally known, for multiphase systems such as polymer blends, there exists strong interrelationship between rheological and morphological aspects. Therefore, in order to support the rheological investigation of PP/PET blends, the study of the phase structure was provided. Presented work follows our previous papers that dealt with rheological behavior of PP/PET blends
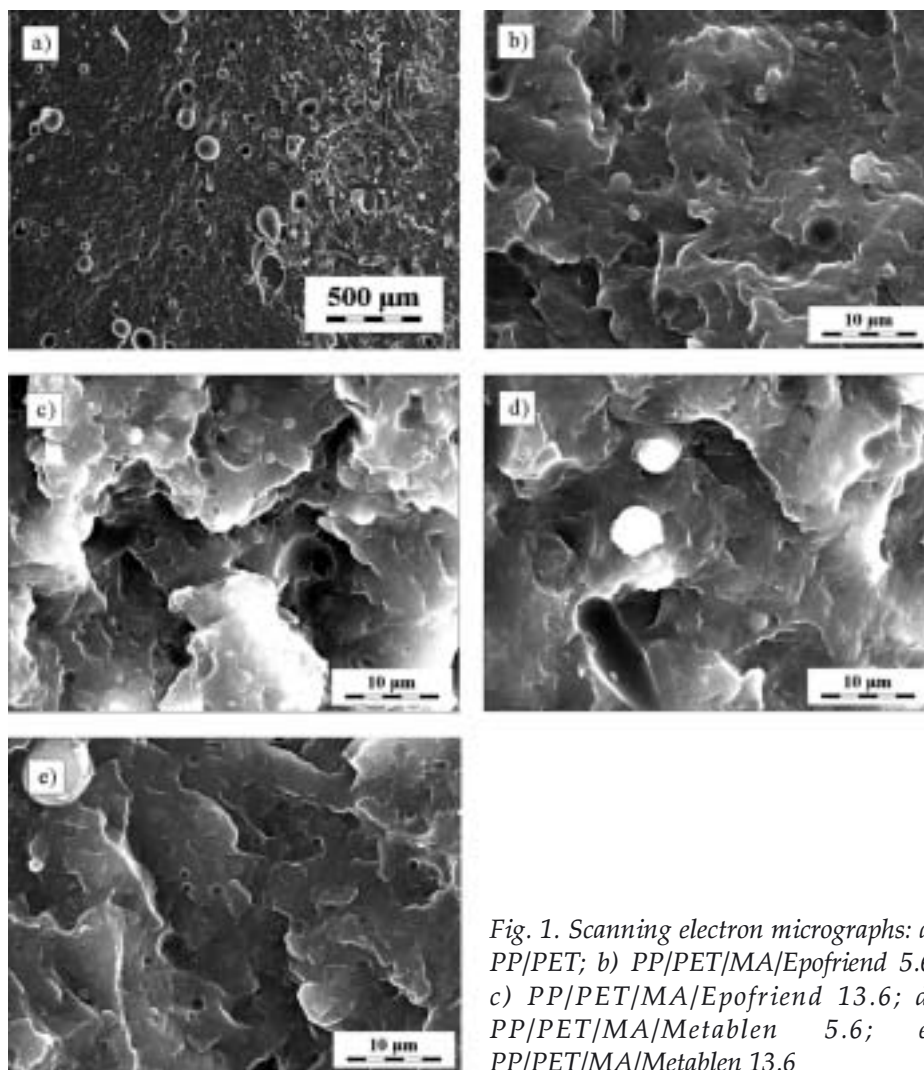
Fig. 1. Scanning electron micrographs: a) PP/PET; b) PP/PET/MA/Epofriend 5.6; c) PP/PET/MA/Epofriend 13.6; d) PP/PET/MA/Metablen 5.6; e) PP/PET/MA/Metablen 13.6

before and after compatibilization by maleic anhydride and contained also the information about morphology of these systems [6, 7]. Nevertheless, for a comparative purpose, the example of unmodified sample can be also seen in Fig. 1a, where the typical morphology of immiscible systems can be observed including large PET particles immersed inside PP matrix, and weak interfacial adhesion between the two phases. On the other hand, the addition of MA in combination with elastomeric agents covered by this study brings both the reduction of particle size of the dispersed droplets, and enhancement of the adhesion between the phases, which is depicted in Figs. 1b—e.

It is supposed that these improvements, in particular for samples containing Epofriend as modifier, can be attributed to the presence of functionalized sites (epoxidized), facilitating strong interactions or chemical reaction with the remaining blend components.

Steady shear flow properties

To simplify the discussion of the results, collective figures were prepared containing all samples covered by the experiment.

Firstly, the attention will be paid to viscous properties. Figure 2 depicts steady shear η as a function of $\dot{\gamma}$ at 245 and 265 $^{\circ}$C. As can be seen, at the higher temperature η of unmodified PP/PET blends is very low, what, from the application viewpoint, can be unfavourable (*e.g.* for possible extrusion). The desirable viscosity increase is partly reached by the addition of maleic anhydride, where the increment is attributed to enhanced interactions between functionalized PP and PET. Nevertheless, much more significant viscosity rise, mainly at low $\dot{\gamma}$ region, is obtained when using Metablen, and especially Epofriend. Consequently, clear non-Newtonian manner occurs compared to nearly Newtonian of PP/PET blends without elastomers. The amount of modifier also plays an important role — the higher the content, the higher the viscosity growth. Particularly in the case of Epofriend, reactions between the epoxy groups present in the modifier and the end groups of PET are supposed.

A similar situation after addition of elastomers can be observed at the lower temperature (245 $^{\circ}$C). As compared with the previous case, the viscosity reaches almost an order of magnitude higher values, which can be attributed to unmolten PET particles acting as a filler in the system.
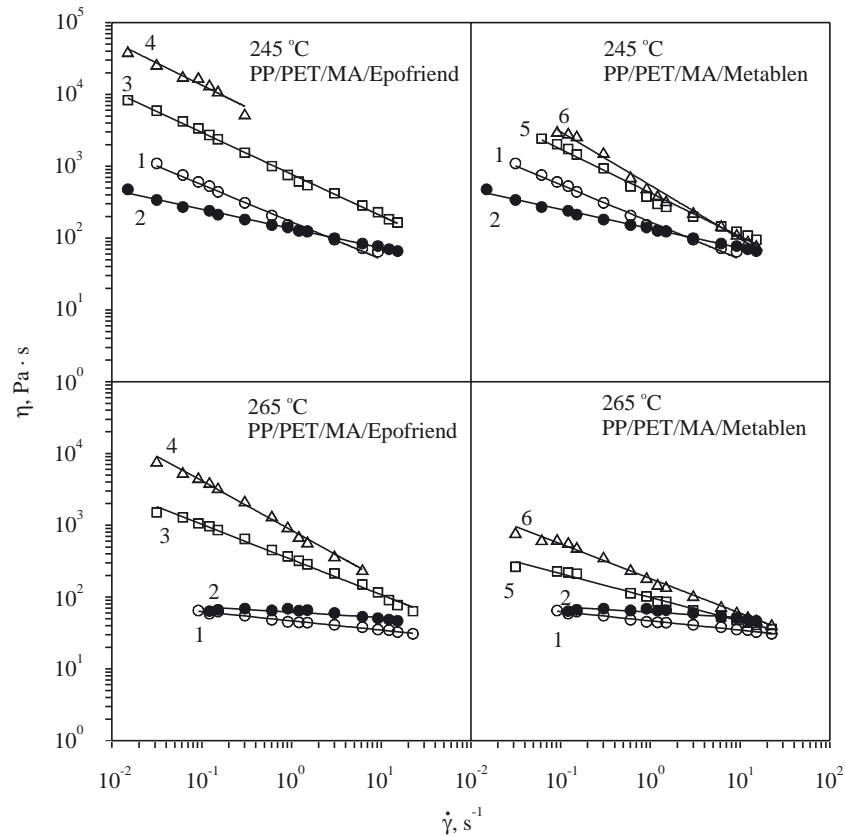
Fig. 2. Shear viscosity (η) versus shear rate ($\dot{\gamma}$) at 245 ^{o}C (upper figures) and 265 ^{o}C (lower figures). For all plots, particular blends are represented by the following lines: 1 – PP/PET; 2 – PP/PET/MA; 3 — PP/PET/MA/Epofriend 5.6; 4 — PP/PET/MA/Epofriend 13.6; 5 — PP/PET/MA/Metablen 5.6; 6 — PP/PET/MA/Metablen 13.6
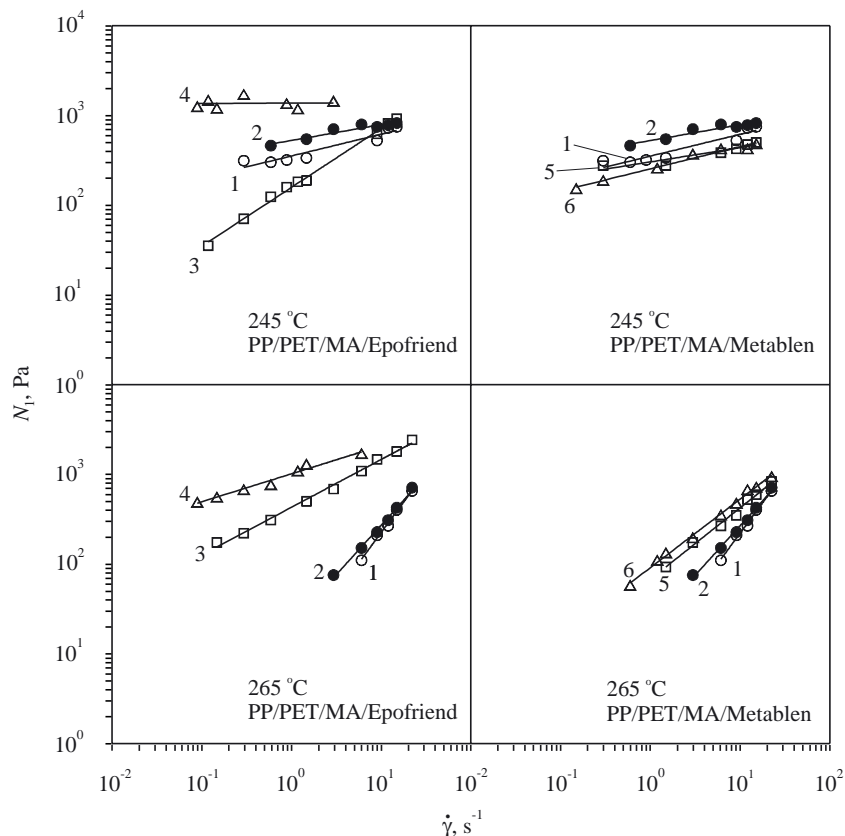

Fig. 3. The first normal stress difference (N_1) versus shear rate ($\dot{\gamma}$) at 245 ^{o}C (upper figures) and 265 ^{o}C (lower figures); denotations — see Fig. 2

Elastic properties represented by the first normal stress difference are shown in Figure 3. At 265 °C, similarly to shear viscosity behavior, N_1 increases with modification by maleic anhydride alone, and much more markedly for its combination with two other additives (more for Epofriend). Although such observation can be expected because of elastomeric nature of both modifiers, more complex outcomes have been found at the lower temperature. In this case, the situation differs for PP/PET/MA/Epofriend and PP/PET/MA/Met-

Oscillatory shear flow properties

Storage moduli (G') are depicted in Figure 4. With respect to PP/PET/MA blends, G' reaches higher values than of their noncompatibilized counterparts at 265 °C, as explained by the contribution of the interphase created due to enhanced interactions between PP and PET phases after MA addition. At 245 °C, this does not happen, contrary to N_1. Therefore, different behavior at different flow conditions is demonstrated. For elastomer
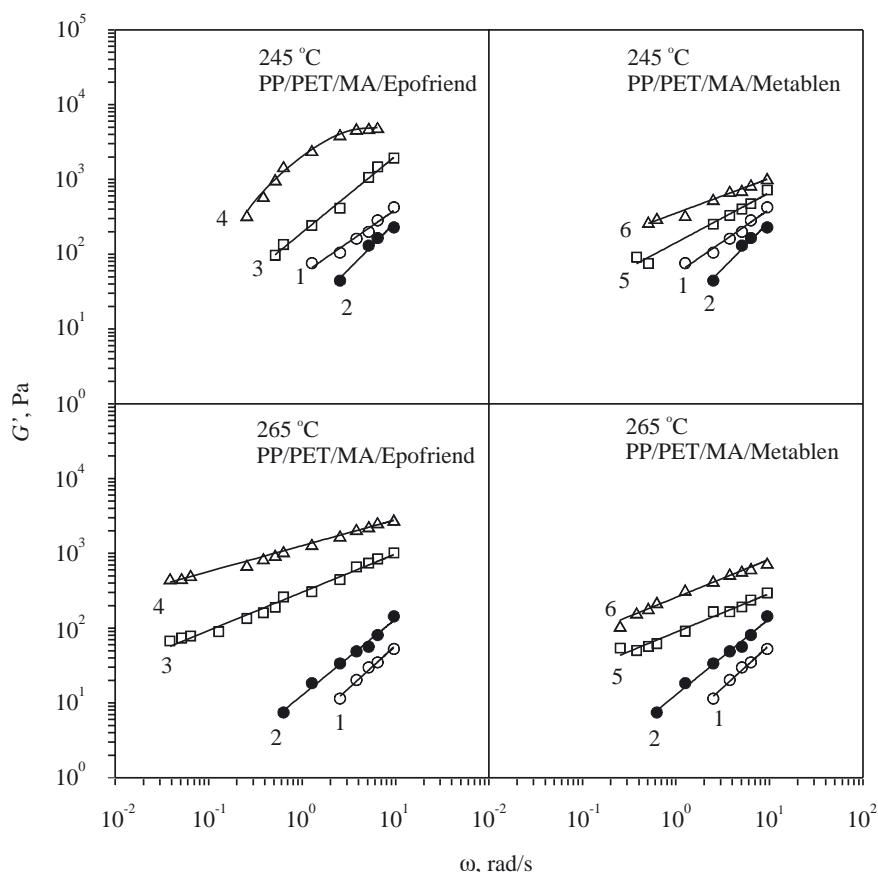
Fig. 4. Storage modulus (G') versus angular frequency (ω) at 245 °C (upper figures) and 265 °C (lower figures); denotations — see Fig. 2

ablen. Regarding the latter, the first normal stress difference of modified samples is lower than that of PP/PET or PP/PET/MA despite the presence of silicone/acrylic-based rubber. Similarly, N_1 values of blends with Epofriend (thermoplastic elastomer) at its lower concentration are rather lower than supposed ones. Only for the sample containing 13.6 wt. parts of Epofriend, the first N_1 increases over those for PP/PET and MA-modified blends. Such peculiar behavior presumably arises from the complex structure containing unmolten PET particles, which strongly influences the rheological behavior under large scale deformation applied during steady state shear measurements. It seems that only high concentration of Epofriend (13.6 wt. parts) is able to suppress the effect of PET and manifest itself.

modified blends (by both Epofriend and Metablen), in contrast to rather complex results shown for the first normal stress difference, G' exhibits more transparent behavior. At both temperatures, it increases with elastomers' addition and their concentration regularly, thus following the predictions. Samples containing Epofriend again reach the higher values.

To compare the findings from both shear flows, different extent of deformation of PET particles under different conditions must be considered. Most probably, at steady shear regime, PET particles pass through large deformation or even fracture to smaller ones. In the oscillatory shear flow, on the other hand, they are deformed to a lesser extent (periodical deformation), so the structure of samples is not violated in such a detrimental way, as reflected in the peculiar results of N_1.
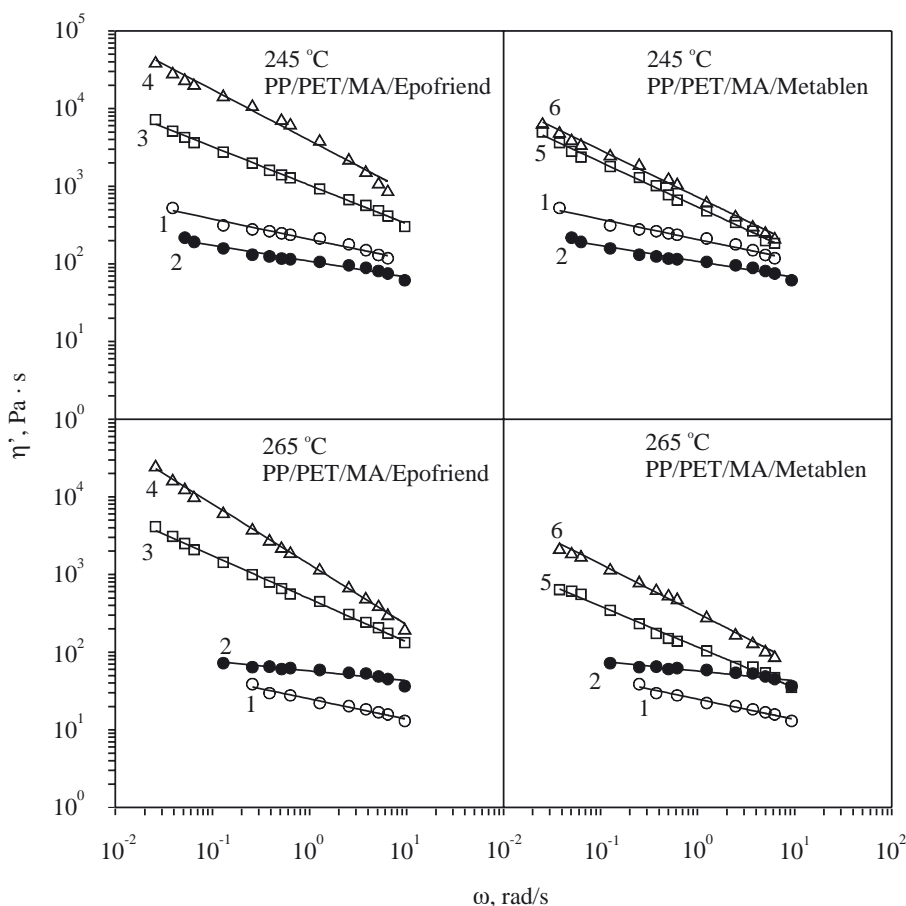
Fig. 5. Dynamic viscosity (η') versus angular frequency (ω) at 245 °C (upper figures) and 265 °C (lower figures); denotations — see Fig. 2

Figure 5 presents the plots of dynamic viscosity (η') versus angular frequency (ω) for all samples at both temperatures tested. Generally, similar tendencies are recorded as for η and G'. At higher temperature (265 °C), dynamic viscosity increases after addition of MA, and even more significantly with elastomers (the higher the modifier content, the more visible influence on the viscosity). At 245 °C, Epofriend and Metablen act the same way, whereas PP/PET/MA samples reach lower viscosity than pure PP/PET.

Yield behavior

Complex viscosity is plotted against complex modulus in Figure 6 and, together with the dependence of steady shear viscosity (η) on shear stress (σ) (Fig. 7), it is used to indicate the yield behavior. As can be seen from the plots curvature and from Table 2 summarising yield values calculated by Casson's method [19], this yield behavior is apparent especially at 245 °C, most probably due to the effect of unmolten PET particles. Elastomer modified specimens, however, exhibit yield behavior also at the higher temperature, which is rather surprising. In these cases, relatively high yield values of shear stress and complex modulus are attributed to marked modifiers elasticity. Comparing the results from both

flow conditions, higher values are observed for the oscillatory regime. Regarding the effect of modifier content, the yield values of both rheological functions are superior for the greater content (13.6 wt. parts).

T a b l e 2. Yield values of shear stress (σ_y) and complex modulus (G_y*) at 245 °C and 265 °C

Yield values		PP/PET/MA	PP/PET/MA/Epofriend		PP/PET/MA/Metablen	
			5.6	13.6	5.6	13.6
245 °C	σ_y	1.5	50.8	196.0	17.5	28.1
	$|G_y*|$	1.6	98.5	583.8	59.6	89.0
265 °C	σ_y	0	19.8	126.4	0	4.2
	$|G_y*|$	0	73.9	577.3	14.4	28.2

Comparison between both types of flow conditions

To compare steady state with oscillatory shear results, well-known methods have been applied. Firstly, shear and complex viscosities can be confronted quantitatively in terms of the validity of Cox-Merz rule [20] expressed as

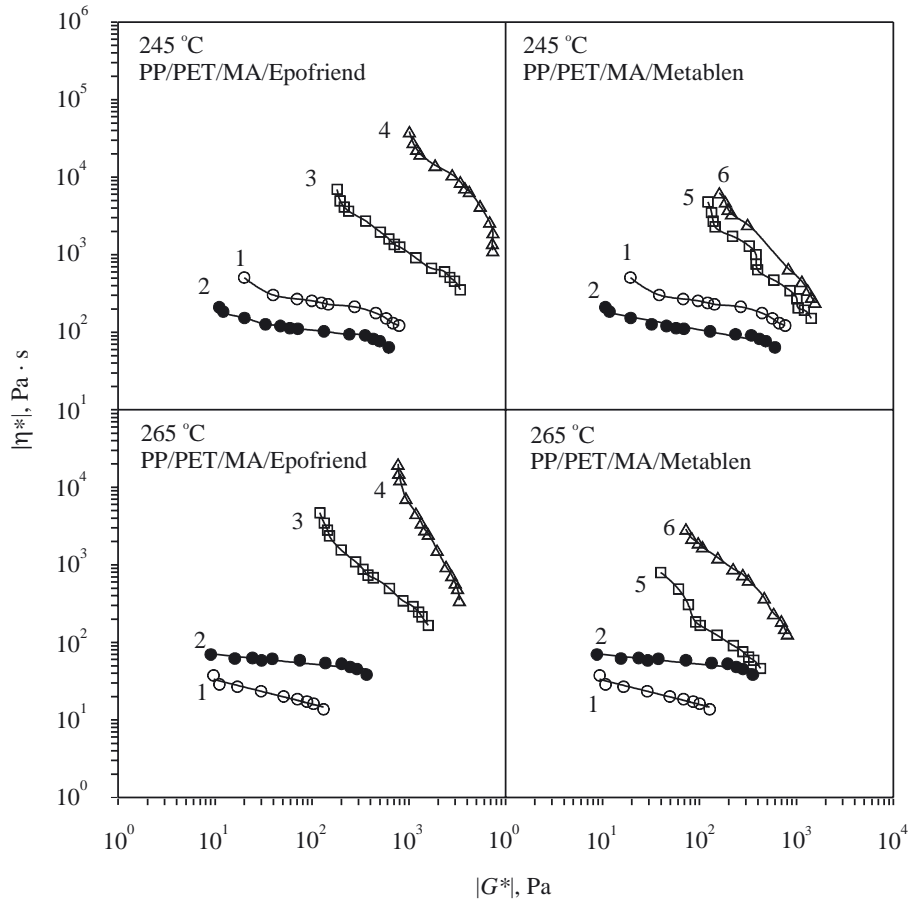$$\eta(\dot{\gamma}) = |\eta*(\omega)| \quad \text{with} \quad \dot{\gamma} = \omega \qquad (1)$$

Fig. 6. Complex viscosity ($|\eta^*|$) versus complex modulus ($|G^*|$) at 245 ^oC (upper figures) and 265 ^oC (lower figures); denotations — see Fig. 2
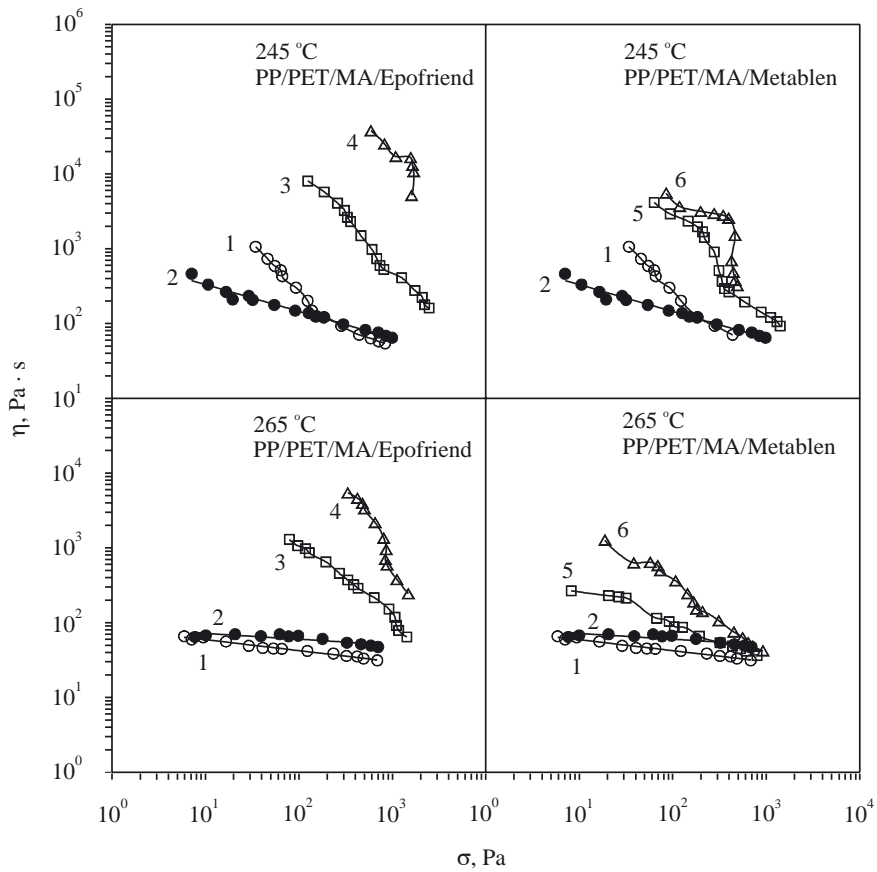

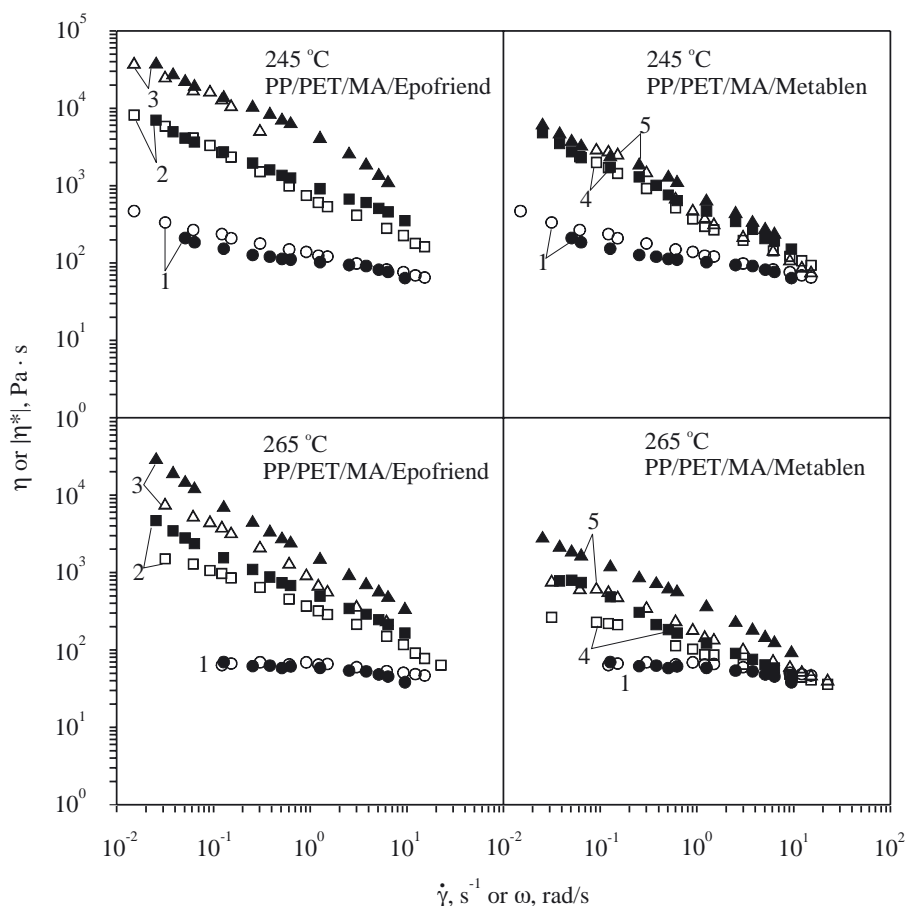Fig. 7. Shear viscosity (η) versus shear stress (σ) at 245 ^oC (upper figures) and 265 ^oC (lower figures); denotations — see Fig. 2

*Fig. 8. Cox-Merz rule: comparison between shear viscosity (η) versus shear rate (γ̇) (open symbols) and complex viscosity (Iη*I) versus angular frequency (ω) (solid symbols) at 245 °C (upper figures) and 265 °C (lower figures). For all plots, particular blend are represented by the following lines: 1 — PP/PET/MA; 2 — PP/PET/MA/Epofriend 5.6; 3 — PP/PET/MA/Epofriend 13.6; 4 — PP/PET/MA/Metablen 5.6; 5 — PP/PET/MA/Metablen 13.6*

As illustrated in Figure 8, good correspondence of both viscosities of the blends modified by elastomers is shown at 245 °C at low shear rates, or angular frequencies, respectively. The steady shear viscosity of PP/PET/MA samples, on the other hand, slightly exceeds complex viscosity values; both functions approach each other at higher shear rate/angular frequency. Regarding the situation recorded at the higher temperature (265 °C), very good agreement is found for PP/PET/MA, while samples modified by Epofriend and Metablen exhibit higher complex viscosity.

Similarly, quantitative comparison of elastic characteristics can be provided using Roscoe's rule [21] developed by Coleman and Markovitz [22] as the limiting relationship when the shear rates approach zero

$$\Psi_1 = \frac{N_1}{\dot{\gamma}^2} = \frac{2G'}{\varpi^2} \text{ with } \dot{\gamma} = \omega \qquad (2)$$

where: Ψ_1 — *normal stress coefficient.*

As can be seen from Figure 9, an analogy to viscosities comparison is observed at 265 °C, *i.e.* the rule holds well for PP/PET/MA blend, while storage modulus is superior to the first normal stress difference of PP/PET/MA/elastomers. The situation at 245 °C is more complicated and no agreement between both

rheological functions has been found. Nevertheless, the failure of the Roscoe rule is not much surprising in this case when considering quite complex structure created by unmolten but soft and easily deformable PET particles, and its crucial influence on the elastic properties.

CONCLUSIONS

The flow properties of PP/PET blends modified by MA and elastomeric additives were studied at both steady and oscillatory shear regimes at 245 °C and 265 °C. At higher temperature, both viscous and elastic characteristics of PP/PET/MA blends reach higher values than for PP/PET presumably due to enhanced interactions between the components. Even more visible increase at both temperatures is observed after addition of elastomers — the higher content, the more marked increase. At 245 °C, the unmolten PET particles complicate especially elastic behavior at the steady shear flow, and contribute to significant yield behavior. To compare the two modifiers, the influence of thermoplastic elastomer is more expressed, which is attributed to the presence of epoxy groups and their strong interactions with the other blend components. Such effect is also indicated by SEM analysis revealing quite satisfactory phase struc-
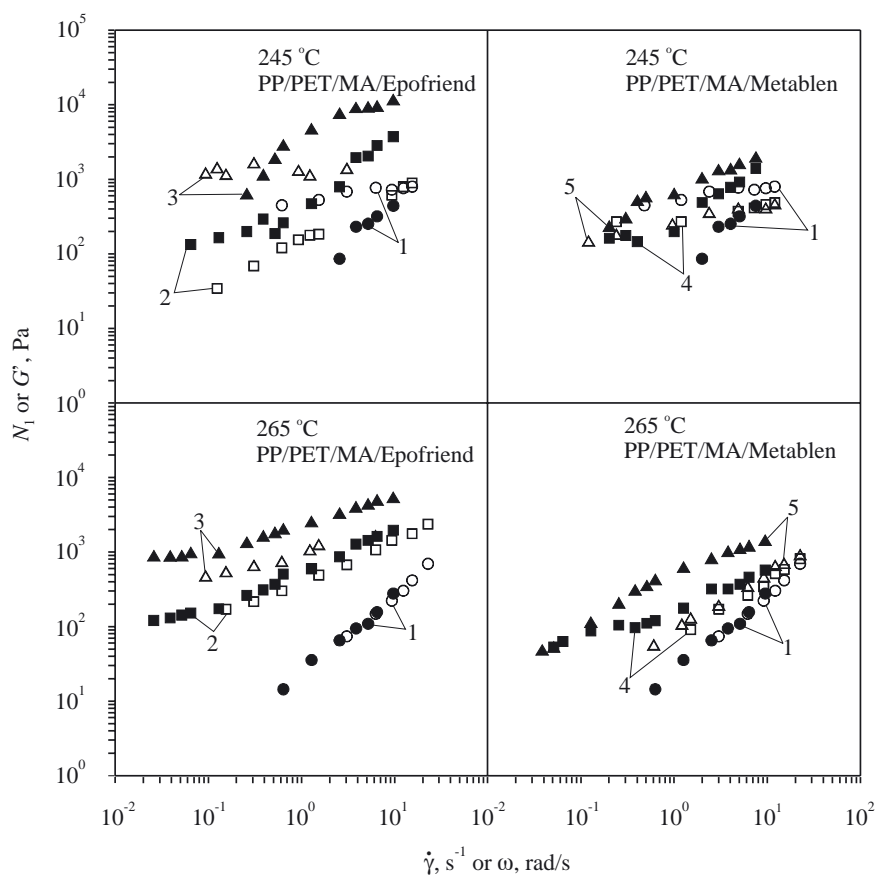
*Fig. 9. Comparison between the first normal stress difference (N_1) versus shear rate ($\dot{\gamma}$) (open symbols) and storage modulus (G')
versus angular frequency (ω) (solid symbols) at 245 °C (upper figures) and 265 °C (lower figures); denotations — see Fig. 8*

ture of all modified blends. In comparison with binary
PP/PET materials, improved interfacial adhesion and
great reduction in the particle size of the dispersed do-
mains is observed.

Comparing both steady and oscillatory shear data at
265 °C, *i.e.* when systems are completely melted, very
good accordance is recorded for PP/PET/MA blends.
For elastomer-added blends, on the other hand, the dy-
namic viscoelastic properties exceed the steady shear
ones. With respect to the lower temperature, the complex
structure caused by unmolten PET has to be considered
as a critical parameter influencing samples' morphology
and resulting in rather complicated elastic response. To
conclude, the addition of the elastomeric modifiers leads
to a significant increase in viscosity of PP/PET blends,
which can be beneficial in their processing *via* extrusion.

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