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# Rheology of compatibilized immiscible viscoelastic polymer blends

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## Abstract

Rheological behavior of a PS/PE model viscoelastic immiscible blend compatibilized by two types of inter facial modifiers was investigated. Dynamic, steady shear, and transient experiments were performed to probe the effect of the interfacial modification on the rheological behavior of the blend. While the effect was relatively small in dynamic and steady shear experiments, significant signature of the presence of the copolymer was observed in transient experiments after start up of shear flow.
The magnitude of the departure from Doi-Otha theory (worked out for non-compatibilized blends) was evaluated.

## Key words

Immiscible blends   Compatibilization Doi-Ohta model   Rheology

## Introduction

Compatibilization of polymer blends through addition of a copolymer is now a well-established route to ensure more finer and stabilized morphology and to enhance adhesion at the interface between the components of the blend Since the effect of compatibilization acts mainly in the molten state during melt blending, the rheology of molten compatibilized blends is of crucial importance. There is only limited rheological data in the literature about the effect of copolymers on the rheological properties of blends. The majority of studies were concerned with oscillatory shear measurements under small amplitude of deformation in the molten state Few others have also dealt with the steady shear behavior, but to the best of our knowledge compatibilization effects on the rheology of blends under transient shear flow have never been reported.
Various results have been reported but none of them allows drawing a general conclusion about the effect of copolymer modification The results variously refer to no effect, to an increase as well as to a decrease of melt-viscosity, and elastic modulus of the blend Utracki and Sammut (1988) examined the effect of SBS addition on steady-shear properties of PE/PS blends. No significant effect was found either on rheological or morphological properties of the blends Lyngaae-Jorgensen et al. (1988) reported an increase in viscosity after addition of a diblock copolymer to PS/PMMA blends. Such increase was also reported for compatibilized blends of PE/PA, PP/PA6 and PET/PA6 by Germain and Genelot (1991), by Nishio et al (1994), and by Higuchi et al. (1994), respectively. Other studies conducted on PS/PA6 revealed that copolymer addition resulted in a decrease in blend's viscosity at high shear rates and an increase at low shear rates (Chang and Wu 1991).
Gleinser et al (1994) found that upon compatibiliza-tion with diblock copolymer P(S-b-MMA), the blends of SAN/PS become more elastic in the terminal region. The same trend was reported by Riemann et al. (1997) for compatibilized blends of PS and PMMA with P(S-b-MMA), by Guo et al (1998) for LDPE/PS blend compatibilized by poly(styrene-*b*-ethylene) block copolymer and by Astahana and Jayaranama (1999) for reactively compatibilized blends of PA and PP. Mekhilef et al. (1997) have studied PS/HDPE blend compatibilized with polystyrene-hydrogenated polybut-adiene-polystyrene triblock copolymer (SEBS). They reported that at content of SEBS allowing presumed complete saturation of the interface, the dynamic viscosity as well as the elastic modulus in low frequencies region were much higher than those of unmodified blend Shi-Ai Xu and Chi-Ming Chan (1998) studied the same blend using the same compatibilizing agent and found that the steady shear viscosity increased only after addition of 2% of compatibilizer. When SEBS content exceeded 4%, saturation of the interface was presumed to be reached and the viscosity did not increase any more Hong and Jo (2000) reported an increase in

dynamic viscosity of syndiotactic PS/EPR blends compatibilized with SEBS triblock copolymer of various molecular weights.

Dynamic mechanical properties of HDPE/HIPS blends compatibilized by two types of diblock copolymers — a pure diblock and a tapered one — were performed by Brahimi et al. (1991a, b) Their studies included temperature dependence as well as the frequency dependence of the dynamic viscosity and the elastic modulus The results showed a strong dependence of the modulus on the structure and the amount of the added compatibilizer and also on the composition of the unmodified blend. In the low frequency region, the addition of pure diblock copolymer resulted in an increase of dynamic viscosity, while addition of tapered diblock copolymer induced a first decrease at 1% and then an increase after further addition. Kim et al (1993) reported some results on blends of poly(2,6-dimethyl-1,4-phenylene ether) and poly(hydroxy ether of bisphenol A) compatibilized by styrene-methyl methacrylate block copolymer The dynamic viscosity of 30/70 blend was found to be increased even with 10% content of the compatibilizer, For blends of 50/50, addition of compatibilizer up 5% decreased the dynamic viscosity in respect to the original blend, while a further increase of compatibilizer content resulted in an increase of dynamic shear viscosity Bousmina et al. (1995) reported a significant decrease in the dynamic moduli at low frequencies when adding 1% of SEBS to a 70/30 mixture of PS/PE blend. Identical result was obtained by Lacroix et al (1996) for compatibilized blends of PETG and EVA.

These rather contradictory results show the complexity of these systems of which the rheology is strongly affected by several parameters (structure of copolymer and nature of interfacial interactions, composition, state of dispersion, and distribution, etc.) and indicate that the rheology of compatibilized blends is still an open problem.

In this work we report some results on the effect of copolymer addition on the rheological behavior of a model blend in three situations of flow: (i) linear oscillatory shear measurements, (ii) steady shear flow, and (iii) transient experiments. The model system consists of a binary mixture of (50/50) commercial polystyrene (PS) and high-density polyethylene (HDPE) Two types of interfacial modifiers expected to have different interfacial activities were selected: (i) a triblock commercial copolymer and (ii) a synthesized tapered diblock copolymer The results obtained were then compared to the non-linear transient viscoelasticity model of Doi and Ohta (1991) that was developed for completely immiscible blends with sharp interface (without copolymer), The objective here was only to evaluate the magnitude of the departure from the scaling laws and not to apply the model for compatibilized blends To the best of our knowledge this is the first time that such a study is reported in the literature.

## Experimental

### *Materials*

The immiscible blends investigated ate made of polystyrene (PS) supplied by Novacor Chemical Co, and a high-density polyethylene homopolymei (Fortiflex HDPE) obtained from Solvay Polymers, Inc. (density = 0.962 g/cc, M F.I = 0 7) The interfacial agents selected for compatibilization were a commercial copolymer (Kraton G-1701) from Shell Chemical Co and a laboratory-synthesized copolymer (coded MCL) Kraton copolymer is a triblock copolymer of styrene-ethylene/propylene-styrene (SEBS), whereas MCL is a tapered symmetric diblock copolymer consisting of a random copolymer sequence between pure hydrogenated polybutadiene and polystyrene blocks [$M_n$ (PS) = 21,000] synthesized at University of Liege by anionic-copolymerization following the procedure described in Fayt et al. (1982).. The copolymer has a number-average molecular weight of 62,000 with a polymolecularity index of 1 05 and the styrene block represents 50 wt % of the total weight.

### *Preparation of blends*

50/50 (wt/wt) PS/HDPE blends were prepared by melt blending in a Haake batch mixer at 180 °C and a rotor speed of 50 rpm for 10 min (time to reach a constant torque) In order to evaluate the effect of compatibilizer, 1 wt % or 4 wt % (relative to the total weight of the blend) was added to the blend during the melt blending.

Samples in the form of discs of 25 mm in diameter and 1 5 mm thick suited for rheological testing were prepared by compression molding at 180 °C for 5 min.

### *Morphological analysis*

Blend morphologies were examined by scanning electron microscopy using a leol model ISM-840A microscope. Specimens used for morphological characterization were submitted to thermal and shearing histories as the rheological samples. Thereafter, they were frozen in liquid nitrogen between the two parallel plates of the rheometer., After extraction from the rheometer, the samples were cryofractured in liquid nitrogen and the resulting fracture surfaces were coated with gold/palladium prior to observations.

### *Rheological measurements*

Two rheometers — a controlled stress rheometer CVO (Bohlin) and a controlled strain rheometer ARES (rheometrics) - were used to carry out the experiments in parallel plate geometry with a 1-mm gap. After loading and removal of excess sample, a predetermined
time (generally 20 min) was allowed to achieve complete thetmal equilibrium and relaxation of eventual residual stresses. This time determined from preliminary experiments was found to be necessary to ensure reliable and reproducible results.
All measurements were carried out at 180 ± 0 1 °C under continuous purge of nitrogen Under these conditions, no significant thermal degradation was detected as was verified by previous time sweep experiments for a period of 4 h For the steady shear measurements, no correction was made to account for the variation of shear rate along the radial position.

## Results

The results are presented in two sections  In the first section, the morphological and theological results are qualitatively presented and the quantitative discussion is left to the second section.

### *Morphologies*

The typical morphologies of the unmodified and com-patibilized PS/HDPE blends are shown in Fig. la-d. The micrographs correspond to samples that have been submitted to. identical loading and heating between the two parallel plates of the rheometer (but without shear) as the samples used for theological experiments. Figure la shows a typical morphology of immiscible blends composed of it tegular and coarse domains. It is a mix of elongated particles and droplets; with visibly a somewhat interconnected phase structure. After addition of Kraton triblock copolymer, the PS/HDPE blend shows more regular and finer dispersion of particles (Fig. lb, c). The particle size significantly decreases with increasing the amounts of Kraton, which indicates an efficient activity of the Kraton compatibilizer.
When 1 wt % of MCL tapered diblock copolymer is added (Fig. Id), a breakdown of interconnected structure is observed Moreover, less irregular and less elongated droplets with respect to the uncompatibilized blend are obtained However, when compared with corresponding PS/HDPE/Kraton blends, MCL diblock copolymer seems to be less efficient in reducing the droplet size and in refining the coarsening of the morphology. Nevertheless, the adhesion between phases seems to be enhanced (voids between the phases seem to be disappeared through addition of MCL copolymer).

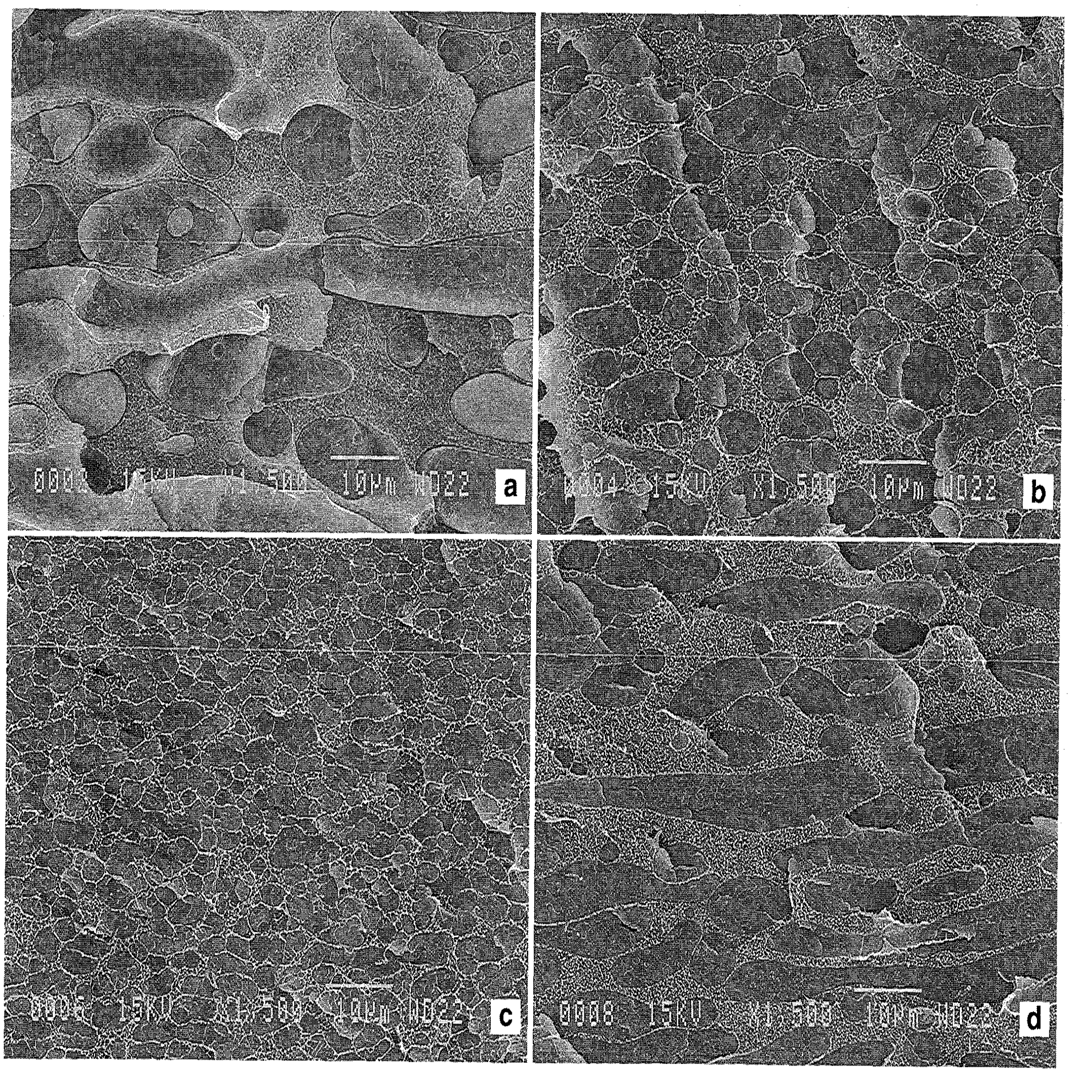


*Fig. la-d SEM micrographs of the fracture surfaces of (50/50) PS/ HDPE blends with: a 0% copolymer; b 1% Kraton; c 4% Kraton; d 1% MCL. T = 180 °C. magnification 1500x.*

### *Dynamic measurements*

Linear viscoelastic modulus, G', for the pure components, the unmodified, and the modified blends with the two copolymers are reported in Fig. 2a, b. As can be expected for immiscible blends, an increase in the elastic modulus in the low frequency range is observed (Palierne 1990; Bousmina 1999). While the pure components seem to reach their terminal zone (G' x $\omega^2$, G" x $\omega$), the blends do not. The addition of the copolymers does not seem to greatly affect the dynamic moduli of the blend (Fig. 2b) However, when representing the phase lag instead of G', a slight effect of compatibilization can be detected especially at low frequencies (Fig. 3). Addition of tapered diblock copolymer leads to a slight increase of the original blend phase angle, while the presence of triblock copolymer results in a decrease of the phase angle at low frequencies and an increase at high frequencies. The most significant effect was observed with 4% addition of Kraton. In the high frequencies range, the concentration and the nature of compatibilizer have a little effect compared to the effect observed at low frequencies.
It is also worth mentioning that at high frequencies (>100 rad/s) the inertial effects of the instrument may be important and consequently the accuracy of the results could be affected.

### *Steady shear flow experiment*

Steady-state shear results for the pure components, the unmodified and modified blends are shown in Figs. 4 and 5 In the shear rate range explored, the copolymers exhibit only a shear-thinning behavior while the pure components and the blends show a shear-thinning behavior at high shear rates and Newtonian plateau at low shear rates (typically for shear rates lower than 0.1 $s^{-1}$).. By increasing the shear rate, the viscosity ratio between PS and HDPE decreases from 3 to about 2. In the shear-thinning region, addition of the interfacial modifiers makes the blend more resistant to flow (modified blends are less shear thinning) suggesting interactions brought by the interfacial modification.

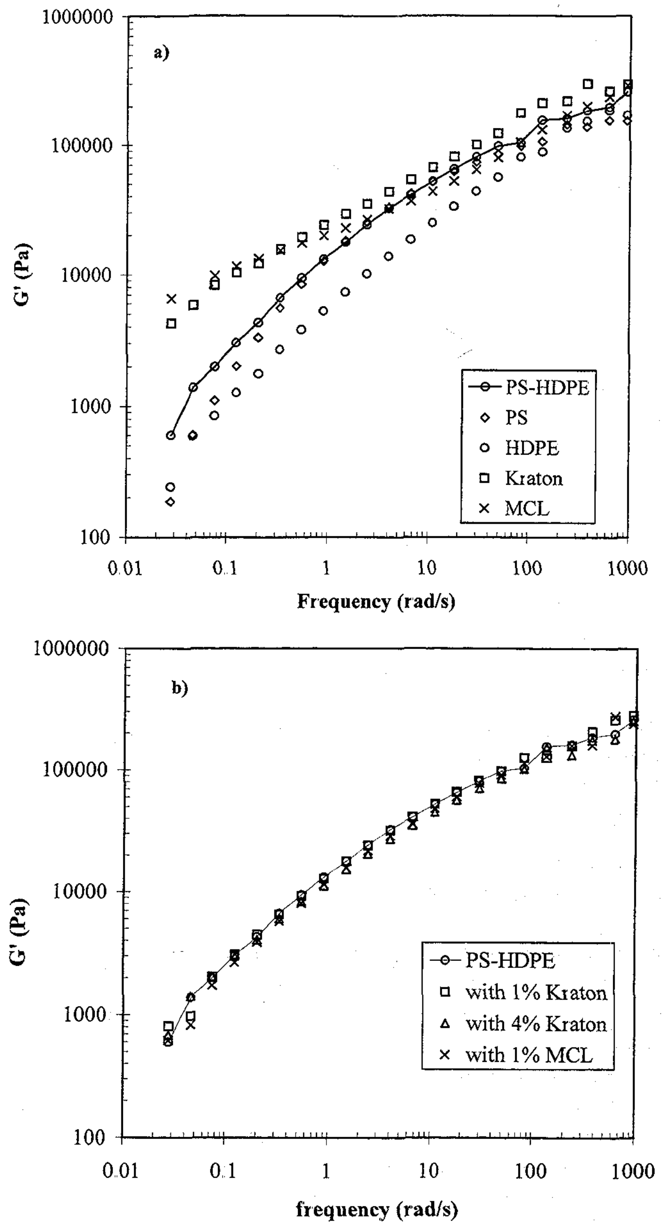


*Fig. 2a, b G' vs frequency for: a (50/50) PS-HDPE blend and pure components; b the modified blends T = 180 °C. (Lines are drawn to guide the eye)*

Over' the overall shear rate range explored, the viscosity of compatibilized blends lies between that of PS and HDPE. The addition of compatibilizer does not affect the extent of the Newtonian region of the original blend (Fig 4b). Only the magnitude of viscosity was found to be slightly affected by the interfacial modification. Upon addition of copolymer a systematic decrease of viscosity is observed in the low shear rate region. The most significant decrease is obtained after 1 wt% addition of the tapered copolymer.

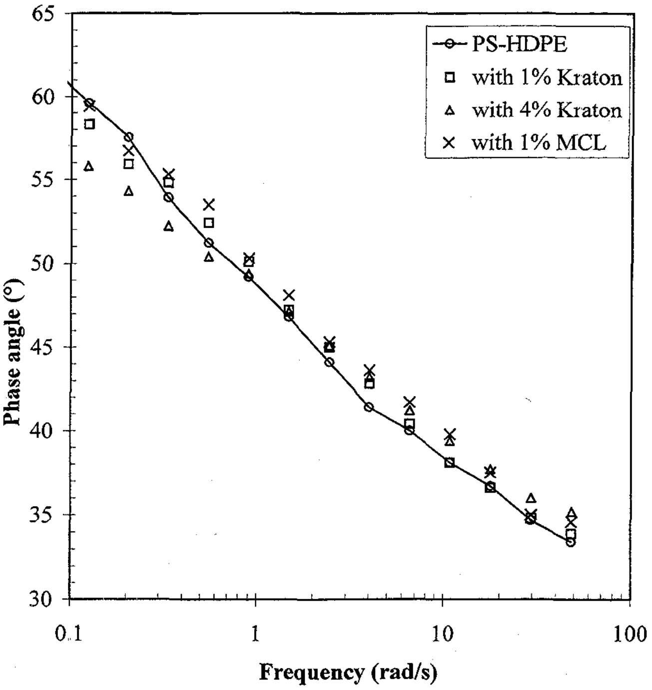


*Fig. 3 Phase angle vs frequency for (50-50) PS-HDPE blend, pure components and the modified blends T= 180 °C. (Lines are dtawn to guide the eye)*

Figure 5 shows the shear rate dependence of the first normal stress difference ($N_1$) for the blends and the pure components. Reliable values of $N_1$ were detected for shear rates higher than 0.1 $s^{-1}$.. As expected, the copolymers show higher viscosity function and first normal stress difference. At low shear rates, $N_1$ of the pure components increases monotonically on log-log scale with a slope of approximately 2($N_1$ x $\gamma^2$), which indicates that the terminal zone is achieved. In contrast, $N_1$, for the interfacial modifier (Kraton) varies as $\gamma^{06}$, whereas the $N_1$ variation of the blends depends on the shear rates region At low shear rates, $N_1$ of the blend is comparable in magnitude to that of individual components Upon increase of the shear rate, similarly to the viscosity, $N_1$ of PS becomes higher than that of PE, whereas $N_1$ of the blends lies in between.

Figure 5 also shows the variation of the first normal stress difference with shear rate after addition of compatibilizer, A slight dependence can be observed after copolymer addition, mainly at low shear rates. The most significant effect is obtained for 4% addition of triblock copolymer and 1 % of diblock copolymer,

Figures 4 and 5 show that the theological properties (dynamic and steady) of the blends were not significantly affected by the compatibilization The slight observed effect could be due to the mutual reduction of interfacia ltension and the characteristic domain size of blends which cancel each other, hence masking the effect on the G' or $N_1$.

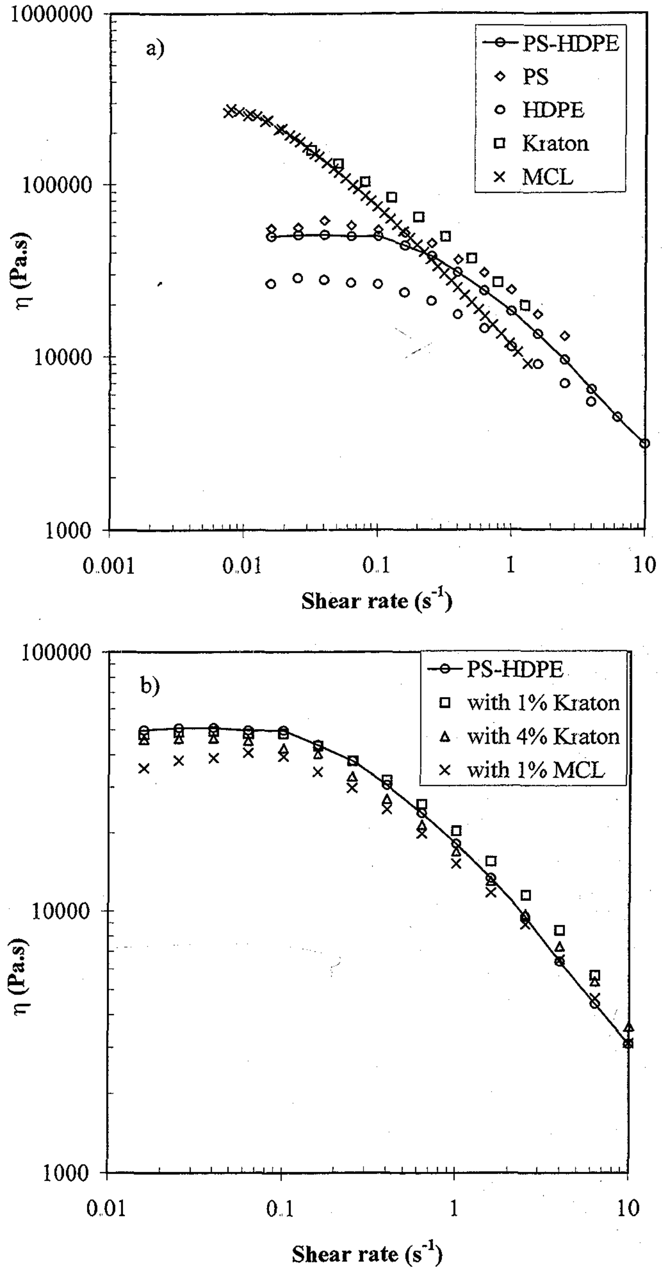


*Fig. 4a, b Steady state viscosity of: a neat components and the uncompatibilized blend; b compatibilized (50/50) blend of PS/HDPE T = 180°C*

A quantitative comparison between the dynamic viscosity, $\eta^*(\omega)$, and the steady-state shear viscosity, $\eta(\dot{\gamma})$, at the corresponding values of shear rate and frequency revealed that the Cox-Merz rule $[\eta(\dot{\gamma}) \approx \eta^*(\omega = \dot{\gamma})]$ holds, within the experimental errors, for the pure components. Figure 6a, b shows that, in the case of the blends (unmodified and 1% Kraton modified blends), the principle was also fulfilled at low shear rates and curiously also for intermediate shear rates, between 0.1 $s^{-1}$ and 1 $s^{-1}$.

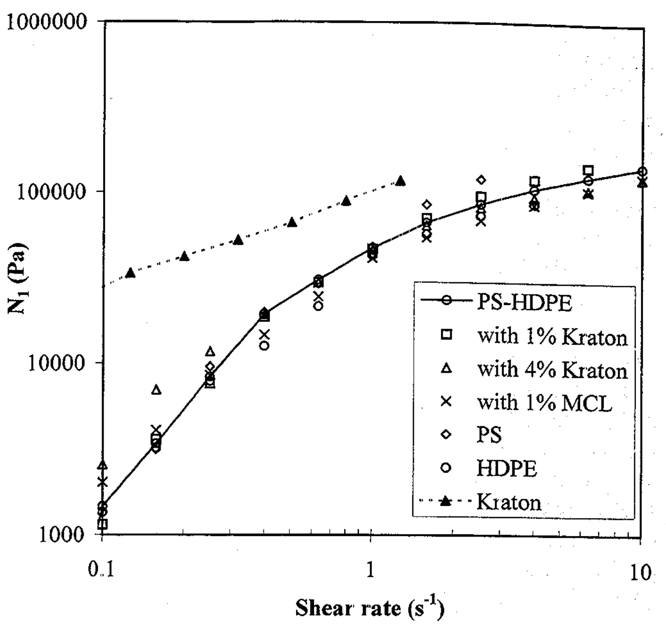


*Fig. 5 $N_1$ vs shear rate for neat components, the uncompatibilized and compatibilized (50/50) blend of PS/HDPE T = 180 °C. (Lines are drawn to guide the eye)*

This unusual behavior suggests that the blend's morphology was not significantly perturbed by the flow field up to 1 $s^{-1}$ At high shear rates, the steady shear viscosity becomes lower than the dynamic viscosity and approaches the real part, $\eta'$, of the dynamic complex viscosity, $\eta^*$. Several authors such as Germain et al (1994) for PP/PA blends and Huitric et al. (1998) for PE/PA blends have reported similar behavior.

The morphologies extracted from SEM of sheared samples at low and intermediate shear rates (frequencies) are quite similar, while at high shear rate the morphology undergoes significant changes (rupture of interconnected domains), which results in the failure of the Cox-Merz rule.

### *Steady and transient shear start-up flow*

The flow history reported in this section consists of a start up flow experiment followed by a stress relaxation for various shearing times. In the first part, the results are relative to experiments after shearing till a steady state is reached

The shear stress growth function, $\sigma^+(t, \dot{\gamma})$, and the first normal stress difference, $N^+(t,\dot{\gamma})$, after shear start up of 0.1 $s^{-1}$ are shown in Figs. 7 and 8. In contrast to the dynamic and steady shear experiments, transient flow experiments show an obvious sensitivity to the addition of the copolymers.

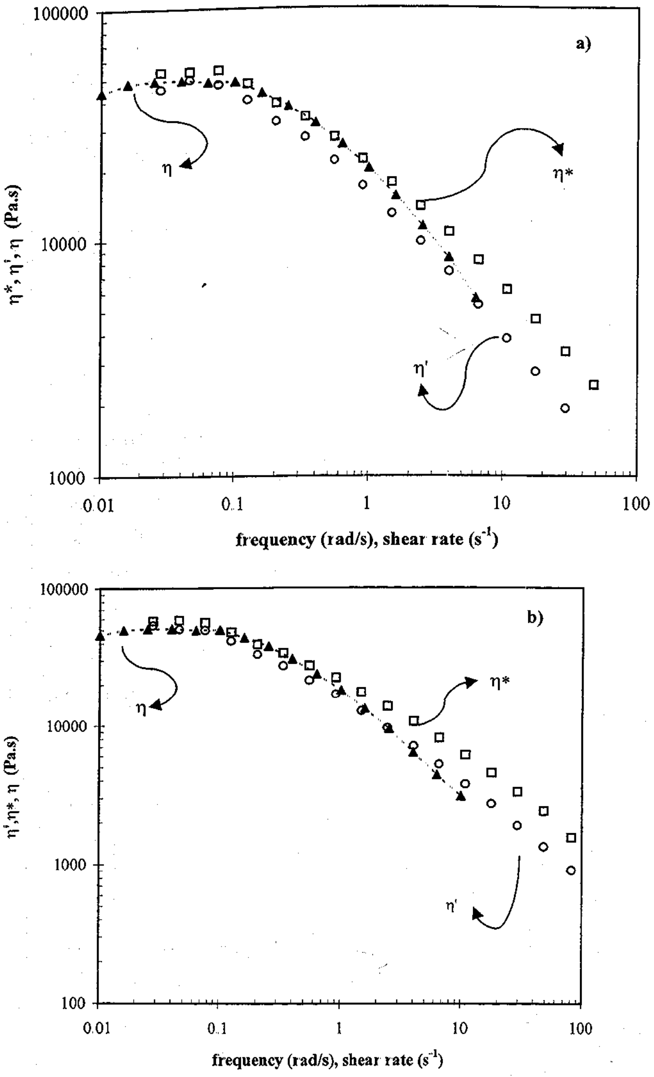


*Fig. 6a, b Viscosity curves of: a PS/HDPE blend; b PS/HDPE blend containing 1% of Kraton*

The transient shear stress at the start up of steady shear flow for both modified and unmodified blends display a large overshoot at approximately 30 s after inception of shear It is followed by a monotonic decrease to a steady state value Polystyrene stress growth curve displays narrower overshoot occurring earlier, while HDPE does not show any evidence of a maximum Instead, it increases monotonically towards the steady state shear stress. This feature could be originated from the shorter relaxation time of HDPE. It is also not to be excluded that overshoot could be observed at higher shear rates The rather large overshoot for the blends may be associated with two-phase morphology. It appears from Fig 7 that the maximum in $\sigma^{+}(t, \dot{\gamma})$ occurs at shear strain ($\gamma_{max} = \dot{\gamma}\ t_{max}$) of about 2 to 3 and it is insensitive to the interfacial modification brought by the copolymers Surprisingly, this value is similar to that found experimentally for polymer melts and predicted by Doi-Edwards theory (Graessly 1974).

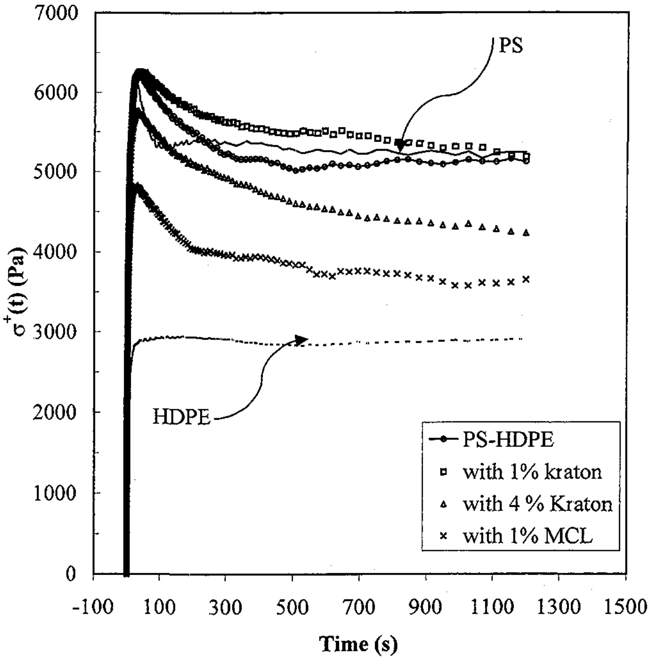


*Fig. 7 Shear stress growth function for the PS, HDPE, modified, and unmodified blends Test shear rate of 0. 1 $s^{-1}$*

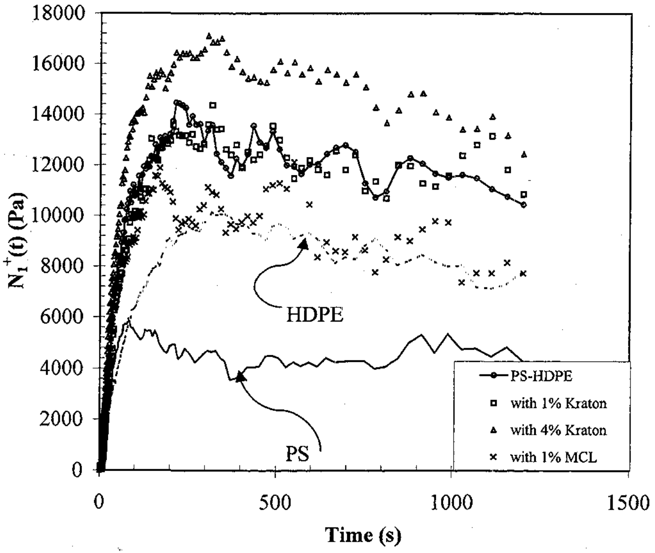


*Fig. 8 First normal stress growth function for the PS, HDPE, modified, and unmodified blends Test shear rate of 0.1 $s^{-1}$*

The addition of compatibilizer affects the magnitude of the stress overshoot but does not change its position significantly.

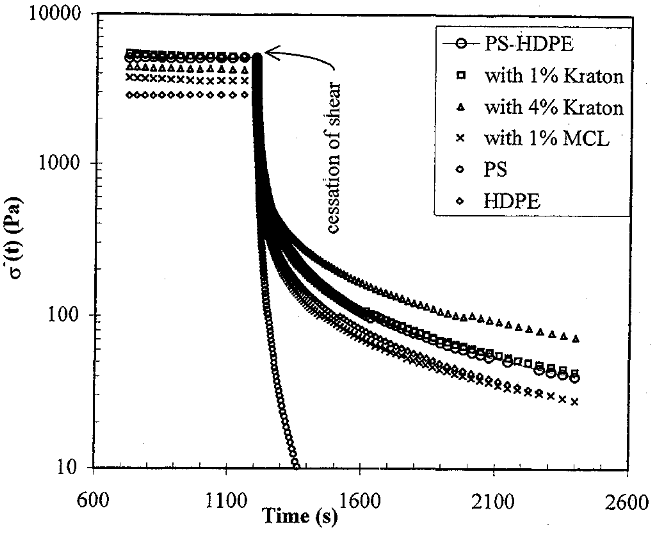
Except in the case of blends containing 1% of Kraton, the addition of compatibilizer decreases the magnitude of $\sigma^+(t,\dot{\gamma})$ Upon addition of 1% of Kraton, $\sigma^+ (t, \dot{\gamma})$ increases at large strains but does not show any significant effect for strains lower than the strain corresponding to the stress growth maximum. The drastic effect of inter facial modification on transient shear stress growth is observed for blends modified by 1 % of MCL tapered diblock copolymer.

The growing first normal stress difference (Fig. 8) also shows the effect of compatibilizers addition. First, the figure shows that HDPE is mote elastic than PS and the normal stresses of the blends increase due to the interfacial tension contribution, especially at low deformation. All the $N^+(t,\dot{\gamma})$ curves go through a maximum and then approach a steady state value. Despite the slight evidences of the maximum (compared to that observed for shear stress growth function curves) its position and magnitude depend on the type and amount of the added compatibilizer It also occurs for larger strain than shear stress. Thus, when 1% of MCL is added to the blend, the maximum of $N_1^+(t,\dot{\gamma})$ occurs earlier and its magnitude decreases as compared to the original blend. A decrease in magnitude in $N_1^+(t,\dot{\gamma})$ is observed by addition of MCL while the addition of Kraton at 1% does not show any significant variation. At 4% content of Kraton, the blend exhibits a remarkable increase

### *Stress relaxation following steady shear*

After cessation of steady start-up flow experiments at 0.1 $s^{-1}$, the shear stress and the first normal stress difference data were collected and displayed in Figs 9 and 10. After steady shear flow, the data indicate that the shear stress relaxes monotonically. Except for polystyrene that relaxes instantaneously, all the materials behave like viscoelastic solids An instantaneous relaxation is followed by a slower one with a plateau for long periods of time It is not excluded that for very long times the stress may vanish. However, due to problems of thermal stability, long time experiments could not be undertaken

As for the normal stress growth, the unmodified and the 1% Kraton modified blends and the 1% MCL modified blend and HDPE relax in the same way, respectively. The slower relaxation and the higher pseudo-plateau magnitude are obtained for the blend with 4% Kraton addition. Addition of 1% MCL yields to a faster relaxation. For the first normal stress difference relaxation (Fig. 10), the addition of 1% of compatibilizer does not significantly affect the normal stress decay function $N_1^-(t,\dot{\gamma})$ of the blend. A significant effect on the normal stress relaxation is only obtained with 4% compatibilizer composition Transient stress relaxation The relaxation mechanisms after cessation of different transient shear histories of 0.1 $s^{-1}$ were examined by measurements of shear stress and normal stress decay functions.



*Fig,, 9 Sheat stress relaxation function, $\sigma^-(t,\dot{\gamma})$, for the components, unmodified blend and compatibilized blends. Experiments after cessation of a steady shear flow of 0,1 $s^{-1}$*

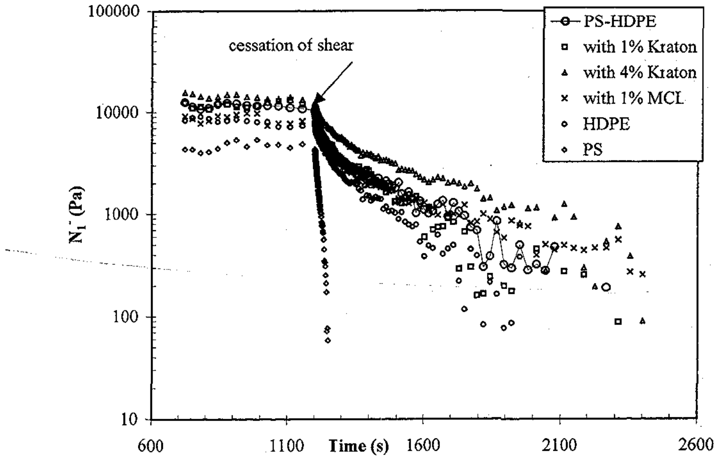


*Fig. 10 First normal stress decay function, $N_1^-(t,\dot{\gamma})$, for the components, unmodified blend and compatibilized blends. Experiments after cessation of a steady shear flow of 0.1 $s^{-1}$*

The relaxation starting times were chosen before and after the maximum of the shear stress overshoot was achieved (i.e., before steady state was reached). Relaxation experiments with starting times around the peak in the stress overshoot were also performed. Results of such measurements are displayed in Figs 11 and 12, For comparison, shear stress and first normal stress difference relaxation after steady shear were added. As in the case of relaxation after steady shear flow, the shear stresses relax in two steps - fast relaxation followed by a slower one. The profile of relaxation curves does not depend on the shear histories (even at small deformation); only the magnitude of relaxation stress seems to depend on the total deformation before cessation of shear.

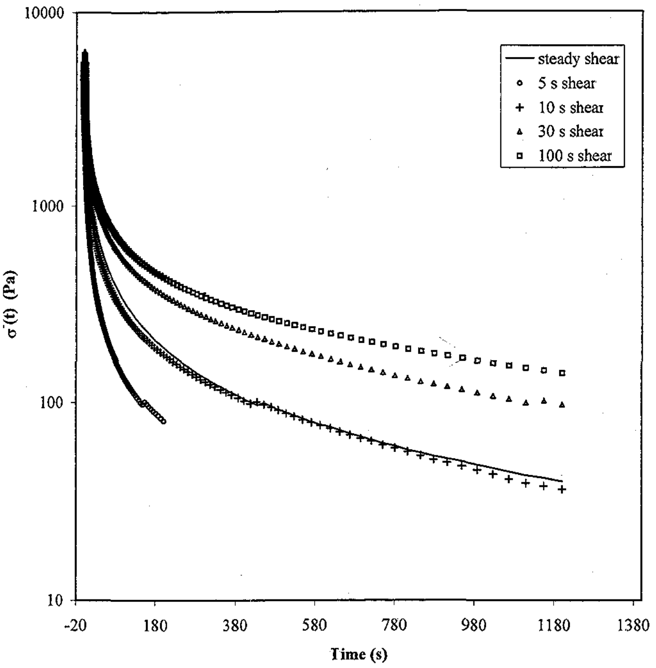


*Fig. 11 Shear stress relaxation function, $\sigma^-(t,\dot{\gamma})$, for unmodified blend Experiment after cessation of different shear flow histories of 0.1 $s^{-1}$*

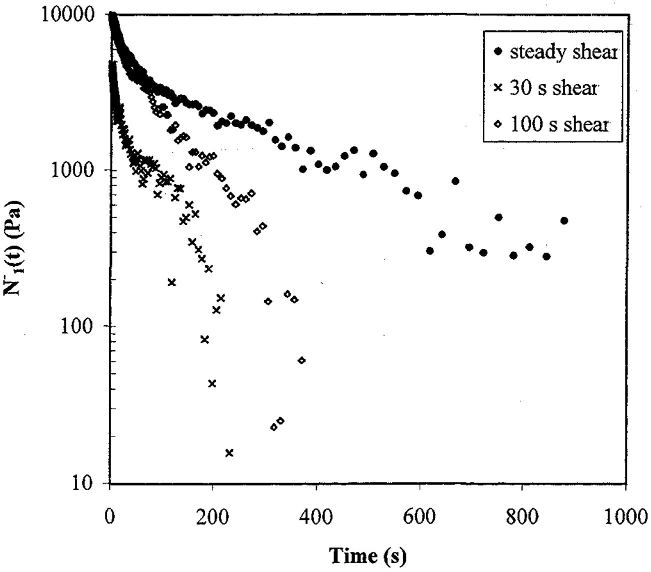


*Fig. 12 Normal stress relaxation function, $N_1^{-}(t, \dot{\gamma})$, for unmodified blend. Experiments after cessation of shear flow of 0.1 $s^{-1}$ at different moment*

Noting that the level of relaxation after a steady shear (at $\gamma = 120$) is equivalent to the relaxation after 10 s of shear at 0,1 $s^{-1}$ ($\gamma = 1$). In fact, the stress level just before cessation of shear is the same after a steady shear and after 10 s of shear. In Fig. 12, relaxation of $N_1$ after different shear histories is displayed. Due to the scattered measurements of $N_1$ after .5 s and 10 s of shear, the corresponding relaxation curves are not shown In this case, the profile of relaxation is shear history dependent and a shoulder in $N_1$ curves is observed after unsteady shear.

Addition of compatibilizer does not significantly affect the relaxation profile. The only effect detected was for short times of shearing (below the time for which the overshoot has occurred). In this range, the rate of relaxation depends on compatibilizer and on its amount.

## Discussion

Steady shear and dynamic experiments showed that the effect of compatibilizer is mainly located in the low frequency (shear rate) region. As this terminal zone was not completely reached for PS/HDPE blends at 180 °C, the effect of interfacial modification on dynamic moduli could not be accurately detected Only the phase shift data have provided some sensitivity to the copolymer addition in oscillatory shear experiments. As most of the effects of compatibilization were mainly observed during transient experiments, the discussion is essentially focused on results obtained after start up shear flow. The different theological behavior induced by the copolymer addition suggests an interfacial activity that strongly depends on the copolymer structure. The results show that the compatibilization differently affects the shear stresses and normal stresses. The different rheological behaviors observed on normal and shear stresses reflect the difference in interfacial activity of both copolymers. While $N_1$ and $\sigma$ undergo the same effect by addition of MCL diblock copolymer, Kraton triblock copolymer addition acts differently on $N_1$ and $\sigma$. For instance, addition of 1% of Kraton increases the steady shear stress (Fig. 7) but does not affect the steady first normal stress (Fig. 8). By adding 4% of Kraton, $N_1$ undergoes a drastic increase (Fig. 8), while the shear stress decreases (Fig. 7).

Addition of 1% of MCL induces a drop of the rheological material functions, which may indicate that the interface was saturated at MCL content lower than 1% Similar trends were reported by Brahimi et al. (1991a) for the same system. Their results indicated that for low content of copolymer the tapered copolymer was a more efficient compatibilizer than the corresponding pure diblock copolymer. Upon saturation of the interface, the contribution of individual components to the rheological properties becomes important. Fayt et al (1982) showed that tapered diblock copolymer after saturation of the interface disperses preferentially in the polyethylene phase of PE/PS blends This could explain why the blends containing 1% of MCL exhibits rheological properties that tends towards polyethylene

This is valid for $N_1^+(t,\ddot{\gamma})$, $\sigma^-(t,\ddot{\gamma})$, $N_1^-(t,\ddot{\gamma})$ (Figs 8-10), and to a certain extent for $\sigma^+(t, \ddot{\gamma})$ (Fig. 7). Generally speaking, addition of Kraton at 1% did not change significantly any macroscopic rheological material function, even though 1 % addition of Kraton has revealed some morphological changes on unsheared samples (Fig. lb). This suggests that the two effects of a compatibilizer are not necessary linked, i.e., the particle size reduction and enhancement of adhesion at the interface. Two different morphologies with different interactions at the interface can in fact generate similar macroscopic rheological behaviors The most pertinent effect is that the domains deform in different fashion upon compatibilization.

With increasing Kraton content, the blend morphology becomes finer and the relaxation of normal and shear stresses is retarded while the viscosity decreases. Before closing this discussion, we have to mention that a phase inversion could be expected for these systems. The SEM micrographs of PS/HDPE samples after steady and step rate shear and after selective extraction of PS (in THF) did not show a clear phase inversion. Instead, they showed that PS forms a well-dispersed phase (Fig. 13a, b), whereas after steady shear' experiments, PS phase exhibits a somewhat interconnected structure (Fig. 13c).

### *Departure from Doi-Ohta model*

Doi and Ohta (1991) treated the behavior of an immiscible blend (1:1 blend of equidensity and equiviscous Newtonian fluids without compatibilizer) in flow field and characterized the structure by one tensor, the anisotropic interfacial tensor, q, and one scalar, the total inter/facial Area, Q, defined in terms of a single conformation tensor, c, by

$$Q = [\mathrm{tr}(\mathbf{c})]^{1/2} \qquad (1)$$

$$\mathbf{q} = \frac{\mathbf{c}}{Q} - \frac{1}{3} Q\boldsymbol{\delta} \qquad \mathbf{(2)}$$

where $\delta$ is the tensor unity and tr refers to the trace of the tensor between parenthesis.

The time evolution equations of these two quantities were obtained by decoupling the effect of the flow and the effect of the interfacial tension:

$$\frac{dA}{dt} = \left.\frac{dA}{dt}\right|_{\mathrm{flow}} + \left.\frac{dA}{dt}\right|_{\mathrm{relaxation}} \qquad \mathbf{(3)}$$

where A stands for q or Q The total stress is given by

$$\boldsymbol{\sigma} = \eta\mathbf{D} - \alpha\mathbf{q} - p\boldsymbol{\delta}$$

where $D = \kappa^T + \kappa$, $\kappa$ being the macroscopic velocity gradient tensor with components $\kappa_{ij} = (\partial\vartheta_i/\partial r_j)$ and $\kappa^T$ its transpose, $\alpha$ the interfacial tension and p the isotropic pressure.

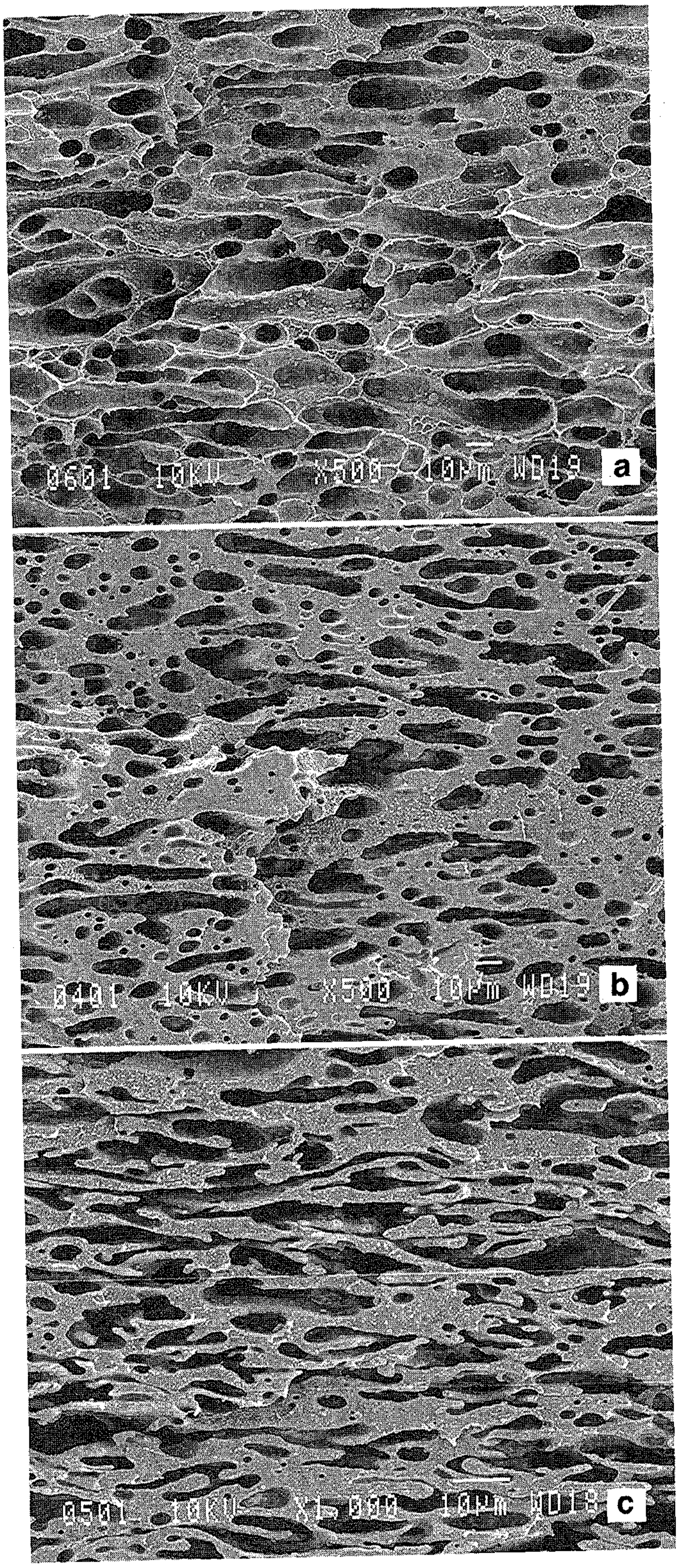


*Fig 13a-c Micrographs of (50/50) PS/HDPE samples after extraction of PS phase by THF: a unsheared sample; b after steady step rate experiment; c after steady shear*

Some interesting scaling relations were predicted:

1 For a steady shear flow, both shear stress, $\sigma$, and the primary normal stress difference, $N_1$, scale proportionally to the shear rate $\dot{\gamma}$.

$$\sigma \propto \dot{\gamma} \quad \mathbf{(5)}$$

$$N_1 \propto |\dot{\gamma}| \quad \mathbf{(6)}$$

2 In transient shear flow, when the shear rate is changed from an initial value $\dot{\gamma}_i$ to a final one $\dot{\gamma}_f$ at time t = 0, the resulting transient stress $\sigma(t, \dot{\gamma}_i, \dot{\gamma}_f)$ divided by the initial steady stress $\sigma(\dot{\gamma}_i)$ (tescaled stress) superimpose onto a single master curve in terms of strain $\dot{\gamma}_f t$, regardless of shear rate, providing that the shear rate ratio $(\dot{\gamma}_f/\dot{\gamma}_i)$ is kept constant:

$$\frac{\sigma(t, \dot{\gamma}_i, \dot{\gamma}_f)}{\sigma(\dot{\gamma}_i)} = f\left(\dot{\gamma}_f t, \frac{\dot{\gamma}_f}{\dot{\gamma}_i}\right) \quad \mathbf{(7)}$$

Experimental data were found to agree fairly well with these scaling relations as reported by several papers dealing with immiscible blends without interfacial modification. The first work on the subject was carried out by Takahashi et al. 1994a. Several other subsequent works arrived at the same conclusion (Guenther and Baird 1996; Vinckier et al 1996) Takahashi et al. (1994b) and Vinckier et al. (1996) also found that under certain specific conditions the scaling relations of Doi-Ohta hold for a mixture of viscoelastic polymers of various compositions and viscosity ratios, The slopes of $\sigma$ - $\dot{\gamma}$ and $N_1$- $\dot{\gamma}$ curves evaluated by the least-squares method (determined regression coefficient was >0.99) and determined in the low shear rate region (below critical shear rate of apparition of shear thinning behavior) are listed in Table 1 and the corresponding curves are shown in Fig.. 14. The steady shear stress results indicate that the proportionality rule as predicted by Doi-Ohta theory (Eq. 5) holds for all systems studied. Although Doi-Ohta theory was *not* worked out for compatibilized blends. The slight departure from the value unity may be caused by the non-linear effects when shear rate increases. Similar departures were observed by Takahashi et al. (1994a, b) for Newtonian and viscoelastic fluids mixtures at arbitrary composition.

*Table 1 Slopes values of $N_1$ - $\dot{\gamma}$ and $\sigma$ - $\dot{\gamma}$ curves as determined by the least-squares method*

| Sample | $N_1$ | $\sigma$ |
|---|---|---|
| PS | 1.99 | 0. 91 |
| HDPE | 2.06 | 0 .97 |
| PS-HDPE | 1.87 | 0 .95 |
| PS-HDPE (1% Kraton) | 1.97 | 0.96 |
| PS-HDPE (4% Kraton) | 1.04 | 0.97 |
| PS-HDPE (1% MCL) | 1.2 | 0;95 |

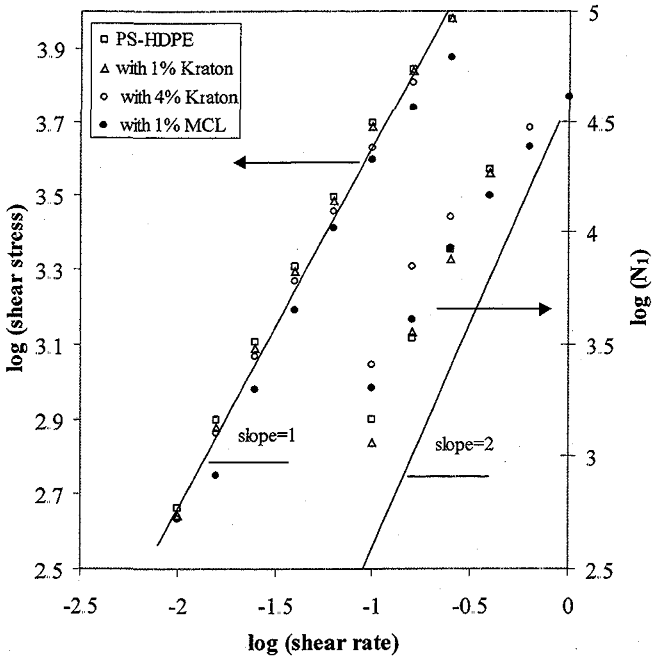


*Fig. 14 Experimental verification of scaling law (Eq 1) for the blends of PS/HDPE*

In the case of first normal stress difference, large deviation from the scaling law established by Doi and Ohta (1991) are observed. One of the curious features that can be outlined from the results is that, upon compatibilization, a priori one expects behaviors that will asymptotically tend towards the behavior of a one-phase blend This would normally lead to a scaling exponent closer to 2 for compatibilized blends than fbi unmodified blends for which the theory predicts rather an exponent of 1. Our results indeed show the reverse behavior The theoretical scaling exponent is close to 1 for compatibilized blends while for uncompatibilized blends it is rather close to 2 as for the pure components The results for 1 % of Kraton addition are coherent with the little effect observed on the first normal stress difference (see Figs. 8 and 9).

Rescaled stress and first normal stress difference vs strain are shown in Fig. 15. The ratio of the final shear rate to the initial shear rate was maintained at 2. In Fig. 15, to make things clear, the data of modified blends were vertically shifted to avoid overlapping.

For all systems, provided that the ratio $(\dot{\gamma}_f/\dot{\gamma}_i)$ is constant, the curves superimpose on a single curve as predicted by Doi-Ohta theory.

As the shear rate dependence at steady state is stronger than the first order of shear rate, the rescaled $N_1$ does not hold for the unmodified blend and for the blend modified by addition of 1 % of Kraton. Moreover, as the transient data for the shear rate explored in this experiment is scattered and inaccurate, the conclusion about the rescaled normal stress was hard to draw.

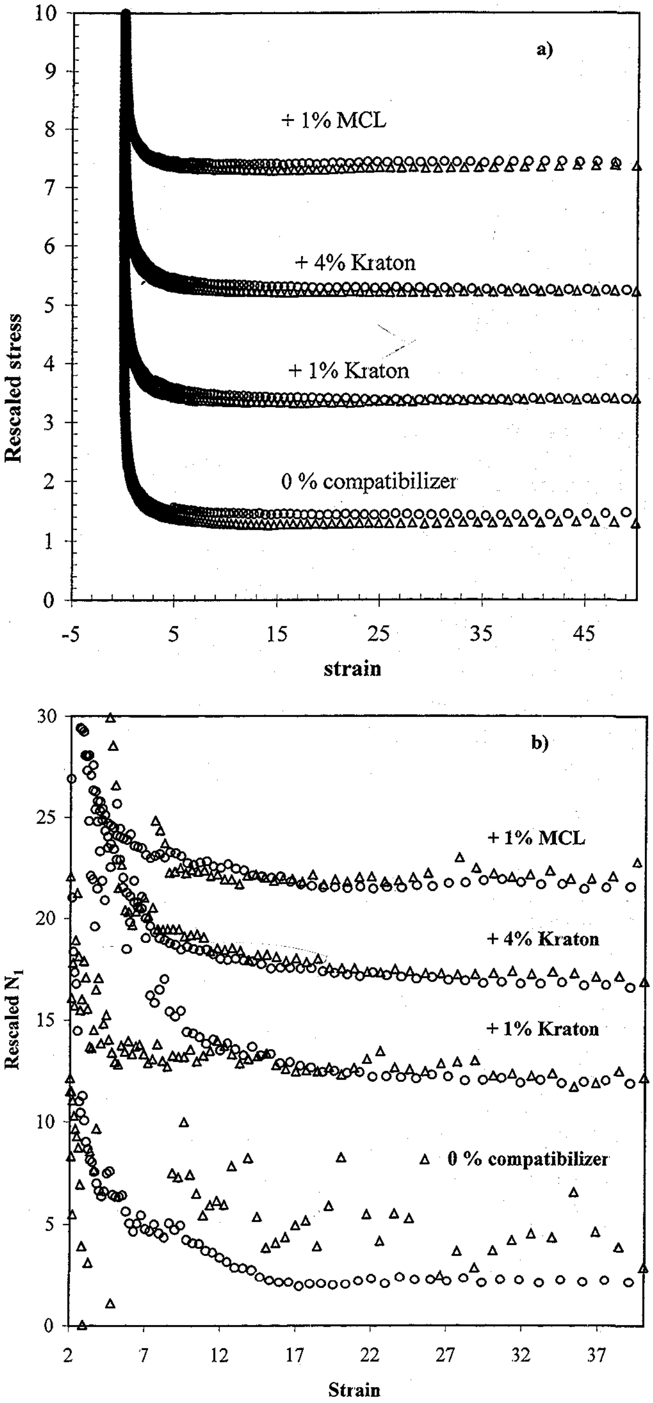


*Fig. 15 a Rescaled stress vs strain for the different blends Curves were vertically shifted to avoid overlapping (shift factors: 1% Kraton (+2), 4% Kraton (+4), and 1% MCL ( + 6)). Theratio* ($\dot{\gamma}_f/\dot{\gamma}_i$) *was set = 2. Shear rate was changed from 0.02* $s^{-1}$ *to 0 ;04* $s^{-1}$ *(Δ) and from 0.05* $s^{-1}$ *to 0 1* $s^{-1}$ *(O). b Rescaled N, vs strain for the different blends Curves were vertically shifted to avoid overlapping (shift factors: 1% Kraton (+10), 4% Kraton (+15) and 1% MCL ( + 20)) The ratio* ($\ddot{\gamma}_f/\ddot{\gamma}_i$) *was set = 2. Shear rate was changed from 0.02* $s^{-1}$ *to 0,04* $s^{-1}$ *(Δ) and from 0 .05* $s^{-1}$ *to 0.1* $s^{-1}$ *(O)*

## Conclusion

In this work the effect of compatibilization through addition of random triblock copolymer and a tapered diblock copolymer were investigated in the molten state by small amplitude oscillatory shear, steady shear, and transient measurements. The main results can be summarized as follows:

1. One of the key results of this work is that the amount of the compatibilizer as well as its structure drastically affect the theological response to a sudden imposition of a shear rate.
2 The effect of copolymer modification has little effect on dynamic and steady shear material functions of the blend. Important effects were observed through transient experiments, which suggest the large contribution of the relaxation of the modified interface This indicates that the deformation and the relaxation of the domains are completely modified by the presence of the compatibilizer at the interface
3. Triblock and tapered diblock copolymer have different interfacial activities that affect differently the normal and shear stresses.
4. Shear stress was found to obey reasonably scaling laws established by Doi-Ohta for both unmodified and copolymer modified blends Although Doi-Ohta theory was not worked out for compatibilized systems. For the normal stress, $N_1$ however the opposite results to those expected were obtained. For the virgin blend, $N_1$ was found to scale (as for the pure components) as $\dot{\gamma}^{\alpha}$·, where α is close to 2, while the theory predicts an exponent of 1 rather than 2. For copolymer modified blends, the exponent of the scaling relation was found to be close to 1, while a priori one can expect a trend that will asymptotically tend towards the behavior of the pure components (exponent 2).
5. No large effect was noticed on bulk rheological properties of the blend modified with 1% Kraton, even though some morphological modifications were observed. This suggests that there is a difference between the effect of particle size reduction and the effect of inter facial interactions between the phases and thus different morphologies can have the same macroscopic rheological properties due to the difference in interfacial properties.

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