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SHORT COMMUNICATION

A. Valenza
G. Spadaro
D. Acierno

Dynamic rheological characterization of polyamide/modified polyolefin laminates

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A. Valenza (✉)
Dipartimento di Chimica Industriale ed Ingegneria dei Materiali
Università di Messina
98166 Sant'Agata di Messina, Italy

G. Spadaro
Dipartimento di Ingegneria Chimica dei Processi e dei Materiali
Università di Palermo, viale delle Scienze
90128 Palermo, Italy

D. Acierno
Dipartimento di Ingegneria dei Materiali e della Produzione
Università di Napoli Federico II
Piazzale Tecchio 80, 80125 Naples, Italy

Abstract In this work dynamic rheological and peel strength measurements on laminates of polyamide and several modified polyolefins were made to evaluate the interfacial compatibilization phenomena. The polyolefins used were a low-density polyethylene, without any treatment and γ-ray irradiated in air, and two copolymers, an ethylene–*tert*-butyl acrylate–acrylic acid terpolymer and a partially neutralized ethylene–methacrylic acid copolymer containing sodium cations. Multilayer structures containing different amounts of both interfacial surface and volume fraction were studied. Relationships between viscoelastic functions and composition were used to analyze the effect of bulk and surface modification in the polyolefins at the interface with the polyamide. The results show that dynamic rheological measurements of stratified polymers can be used as a tool to investigate interfacial activity in multiphase systems.

Key words Polyamide · modified polyolefin · Laminate rheological behaviour

Introduction

Polyamide (PA) is often blended with some polyolefins (PO), such as polyethylene (PE) or polypropylene (PP), to overcome its disadvantages, such as brittleness, high moisture sorption and poor dimensional stability, though they are incompatible [1–3]. In fact PA is a polar molecule, whereas PE and PP are not polar; so they do not present segmental chemical similarity. One possible solution to improve the compatibility in this system is the modification of the PO phase by adding in their backbones coreactive functional groups able to interact with the terminal groups of PA [4–9]. Recently the use of γ-ray radiation to graft polar groups in the PE chains to improve the compatibility of PA 6/PE blends has also been suggested [10, 11].

Rheological characterization of polymer blends is a very useful tool especially in studying phase compatibility and structure formation [12–14]. These measurements and, in particular, the relationships between viscoelastic functions and composition can be considered as an alternative procedure to study the interfacial activity in multiphase systems [15, 16]. In fact direct study of polymer interfaces by various forms of microscopy or scattering techniques is used but the analysis is very difficult to carry out because of sample preparation, resolution and interpretation. For miscible system in the Newtonian range the log-additive rule is usually followed:

$$\log F_s = \sum_{\kappa} \phi_{\kappa} \, . \, \log F_{\kappa} \, . \tag{1}$$

A negative deviation from this rule is generally associated with system incompatibility, due to a sharp interface between the phases with either no interaction between the two phases or possible interfacial slip [16, 17].

Another type of system is the multilayer structure, which on its own is interesting in relationship to coextrusion, but when there are many layers it can also give indication of the behavior of blends.

An expression for a basic multilayer structure, consisting of a series of alternating layers of two immiscible materials, was recently proposed [18], whereby the assumption was made that every layer had the same thickness. The assumption made in developing the model handling the slippage mechanism proposed by Lin [19], who modeled the effect of interfacial slippage for immiscible polymer blends in capillary flow for a system of concentric layers, is valid up to the point where the thickness of the individual layers becomes comparable to the thickness of the interfacial region. Lin's expression is the reciprocal viscosity rule and the derivation would take the form

$$\frac{1}{\eta_s} = \beta \sum_i \frac{\phi_\kappa}{\eta_\kappa} \quad , \tag{2}$$

where β is a characteristic parameter (a slip factor).

In this work dynamic rheological and peel strength measurements on laminates of PA and several modified

Table 1 Characteristics of the used materials

Sample code	$\overline{M_w} \cdot 10^3$	$\overline{M_w}/\overline{M_n}$	Trademark	Manufacturer	Active groups
PE	108	9.8	BB2700	Enichem	
PEacr			Lupolen A2910M	BASF	*tert*-Butyl acrylate 19 wt% Acrylic acid 4%
PEion			Surlyn 8660	Du Pont	Methacrylic acid 5–20 wt% neutralization with sodium cations up to 50%
PA			Emblem 1500	SNIA Technopolimeri	

Table 2 Composition of the polymer multilayers used for the volume test

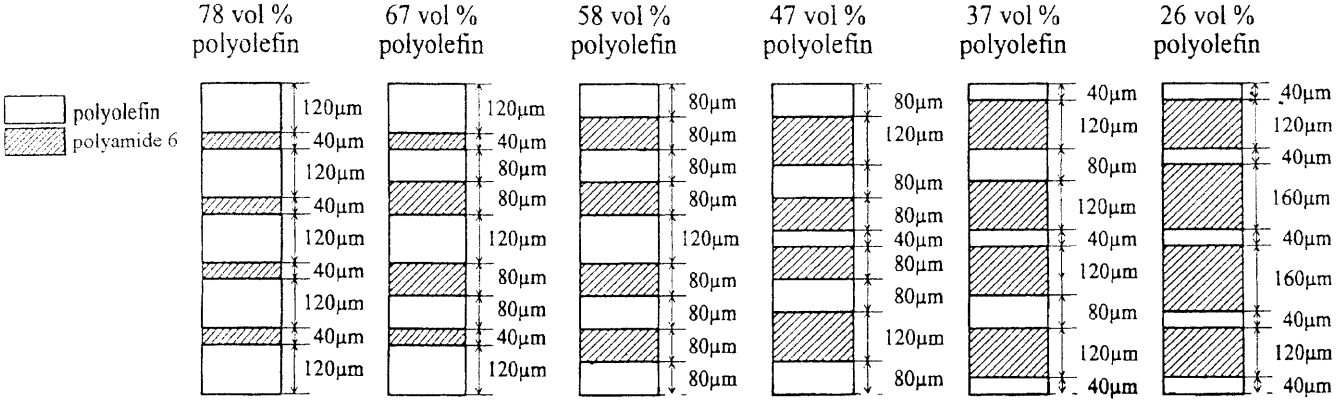
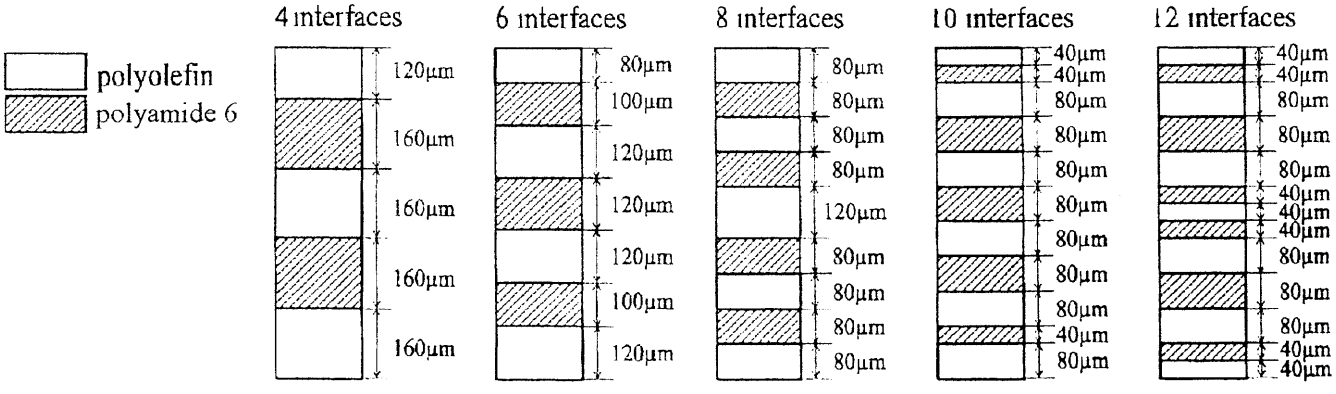


Table 3 Changes in the number of interfaces (58 vol% of the polyolefin systems)



PO were made to evaluate the interfacial compatibilization phenomena. The PO used were a low-density PE, without any treatment and γ-ray irradiated (PEirr) in air, and two copolymers, an ethylene–*tert*-butyl acrylate–acrylic acid terpolymer (PEacr) and a partially neutralized ethylene–methacrylic acid copolymer (PEion) containing sodium cations. One blend was also considered to compare the rheological results.

Experimental

The samples used in this work, whose main characteristics are reported in Table 1, were a low-density PE, a PEacr a PEion and a PA 6. All the polymers were available in the form of pellets, except for the PA, which was available in the form of a film of approximately 20 μm. Films of PE, PEacr and PEion were prepared by compression-molding in a laboratory press at 180 °C with a pressure of 300 bar. Before molding, both PEacr and PEion were dried in a vacuum oven at 80 °C for 12 h to remove additional moisture.

The irradiation of the PE films was performed in air at room temperature (about 25 °C) with a panoramic 3000 Ci ^{60}Co irradiator at 0.1 kGy/h. The total absorbed dose was 15 kGy. After irradiation the PE films were kept in air at room temperature for 3 days in order to allow further reaction of PE free radicals with atmospheric oxygen; after this treatment they were stored in a freezer at −30 °C.

Two multilayer structures were studied: one containing different amounts of interfacial surface and a constant volume fraction and the other containing different volume fractions of both components, but with a constant amount of interfacial surface between the components. To form multilayer films, individual polymeric films were placed on top of one another at room temperature. Compositions of 0, 26, 37, 47, 58, 67, 78 and 100 vol% PO were prepared, while the surface of the interface between the two materials was kept constant. A sketch of the samples is shown in Table 2. Multilayer films with a composition of 58 vol% PO but with different amounts of interfacial surface were also prepared. For these samples a sketch is reported in Table 3. Blends with 58

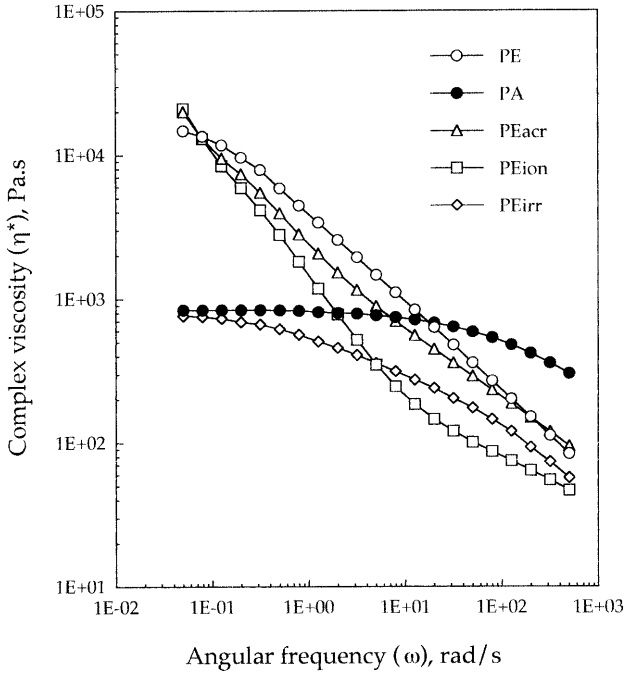


Fig. 1 Complex viscosity, η^*, versus angular frequency, ω, for all the pure polymers at 240 °C

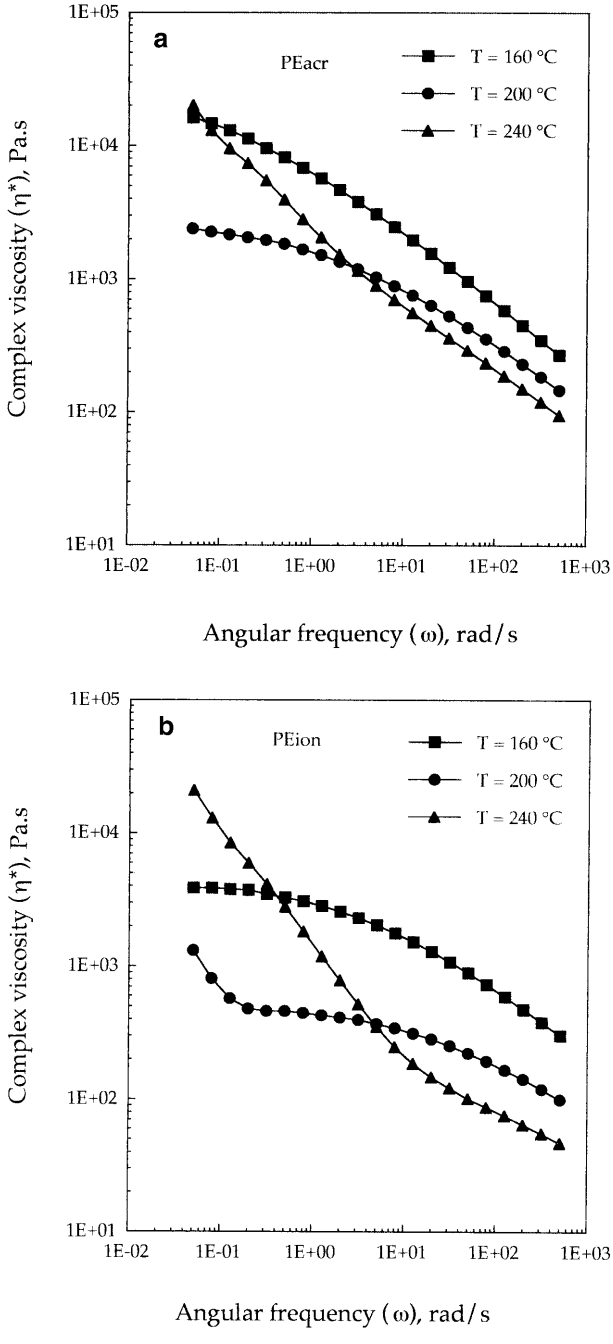


Fig. 2 η^* versus ω of **a** ethylene–*tert*-butyl acrylate–acrylic acid terpolymer (*PEacr*) and **b** partially neutralized ethylene–methacrylic acid copolymer containing sodium cations (*PEion*) at different temperatures

vol% PO were also prepared by melt-mixing with a Brabender plasticorder, model PLE 330.

Dynamic rheological measurements of pure components and two-component systems were performed with a Rheometrics RDAII dynamic analyzer using a 25-mm diameter parallel-plate fixture with a temperature of 240 °C, a maximum strain level of 5% and an angular frequency range of 0.05–500 rad/s. Sample discs of about 27-mm diameter were cut from the laminates, inserted into the plates and melted. Measurements were taken once the sample had fully relaxed, which was indicated by a normal force of less than 10%.

Peel strength specimens were prepared by laminating layers of about 250 μm PA and PO with a laboratory press, applying a bonding temperature of 240 °C and a pressure of 10 bars for 5 min. The samples were cut in strips 100-mm long and 30-mm large. The peel strength was measured using an Instrom tensile tester, model 1122, with a crosshead speed of 5 mm/min. The peel strength was the average of seven measurements.

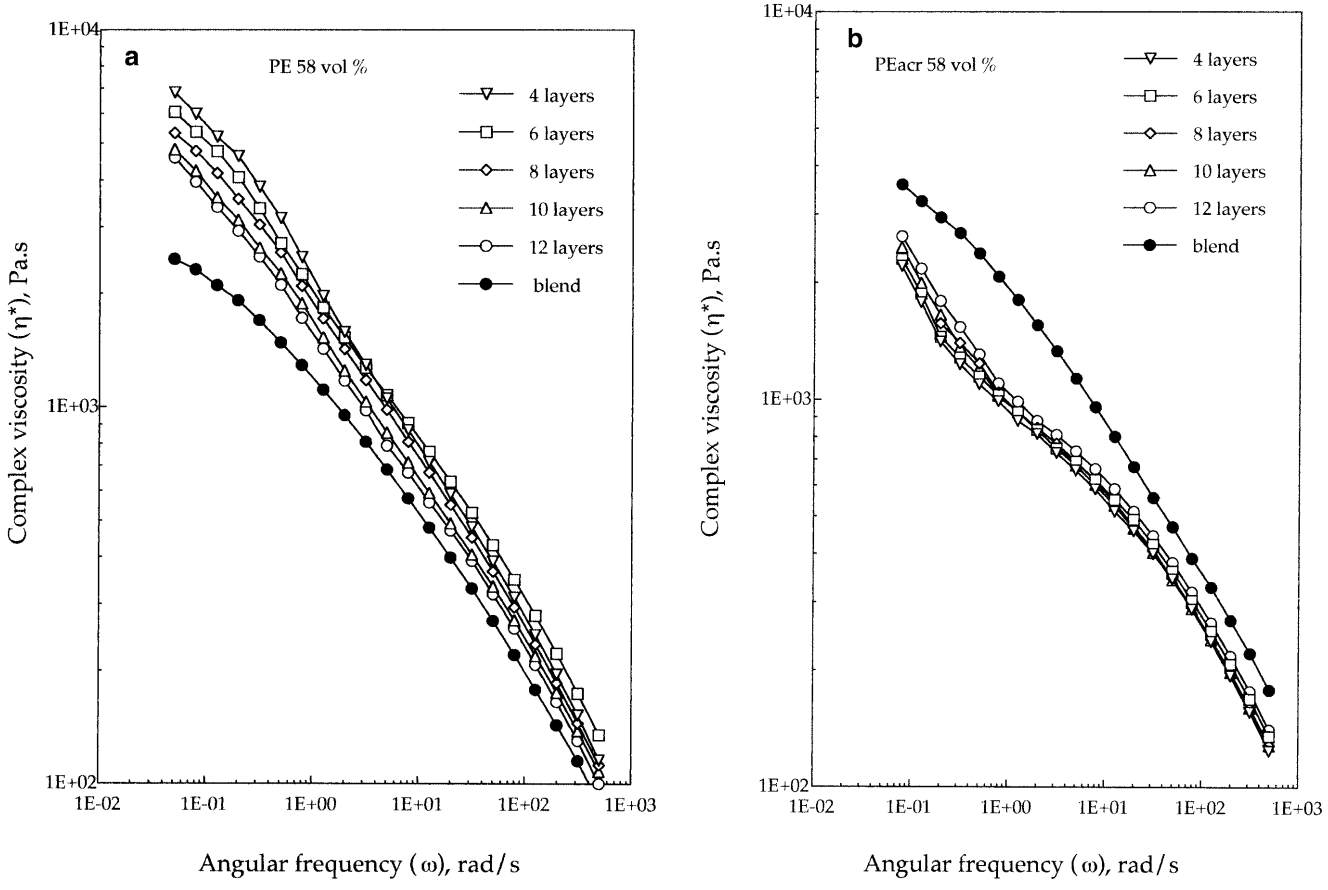
Results and discussion

The complex viscosity, η^* is reported versus the angular frequency, ω, for all the pure polymers at 240 °C in Fig. 1. The results correspond to various tests different for the number of layers superposed ranging from 1 to 12. As expected no differences are observed among the data. In the frequency range explored the PA shows typical, slightly non-Newtonian behavior, which is, in contrast, more pronounced for the PE.

The PEirr shows, with respect to the unirradiated PE, a significant decrease in viscosity and a less pronounced non-Newtonian behavior. This is due to the lowering of the molecular weight induced by the irradiation process. It is well known that irradiation of PE causes chain branching, cross-linking and oxidative degradation with the formation of polar oxidized groups grafted on the polymer chains, the extent of which depends on the irradiation conditions [20, 21]. The oxidation can be controlled by the diffusion of the atmospheric oxygen inside the bulk of the material, depending on the irradiation dose rate and the thickness of the sample. In the irradiation conditions considered in the present work oxidative degradation, with a significant increase in polar oxidized groups concentration, occurs [11]. The molecular-weight decrease is confirmed by melt viscosity behavior.

The flow curves of PEacr and PEion at this temperature show a sharp increase in the viscosity at low

Fig. 3 η^* versus ω of **a** the polyamide polyethylene (*PA*)/(*PE*) system, **b** the PA/PEacr system and **c** the PA/PEion system for different numbers of layers



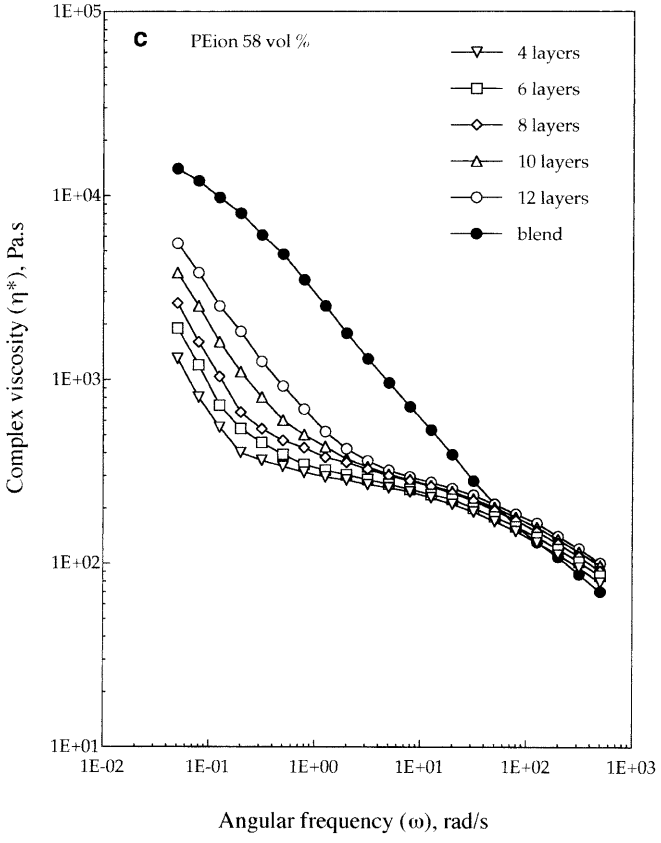


Fig. 3 (Contd.)

frequencies (yield). Such difference in the dynamic mechanical behavior in the molten state can be attributed to the presence of hindered groups grafted on the polymer chain. This phenomenon is more clearly evidenced by looking at Fig. 2, where the flow curves for PEacr and PEion are reported at different temperatures.

The dynamic mechanical behavior of the PA/PE, PA/PEacr and PA/PEion systems are represented in Fig. 3 for different numbers of layers. For comparison the data of melt blends with the same composition are also reported. A clear trend is observed: the PA/PE system (Fig. 3a) shows a decrease in viscosity with increasing number of layers, i.e. a minimum value is observed for the melt blend where the interfacial region is a maximum. The PA/PEacr (Fig. 3b) shows a slight increase in η^* with increasing interfacial area; PA/PEion (Fig. 3c) shows a significant increase in η^* with increasing interfacial area. In the last cases a different shape of the flow curves, corresponding to the layered systems and the blend, is very evident. This should be attributed to a strong interaction induced in the melt mixing.

Dynamic mechanical measurements made on laminates containing different volume fractions of PO and a constant amount of interfacial surface between the two polymers are reported in Fig. 4. The flow curves of the laminates lie between those of the pure polymers for all the compositions investigated. More particularly, at low angular frequencies the complex viscosity values are always higher than that of the PA and vice versa in the high ω region. The logarithm of the viscosity value at 500 rad/s as a function of the volume fraction of the PE phase is also reported for all the systems in Fig. 4. The frequency chosen (500 rad/s) is due to the observed yield in the ω region for the modified PO systems and, of course, the use of the corresponding viscosity values in the plot versus the composition can be considered only in a phenomenological way to fit the previously quoted Eqs. (1) and (2).

A difference in the behavior of the PA/PE, PA/PEacr and PA/PEion systems is observed. The first two show

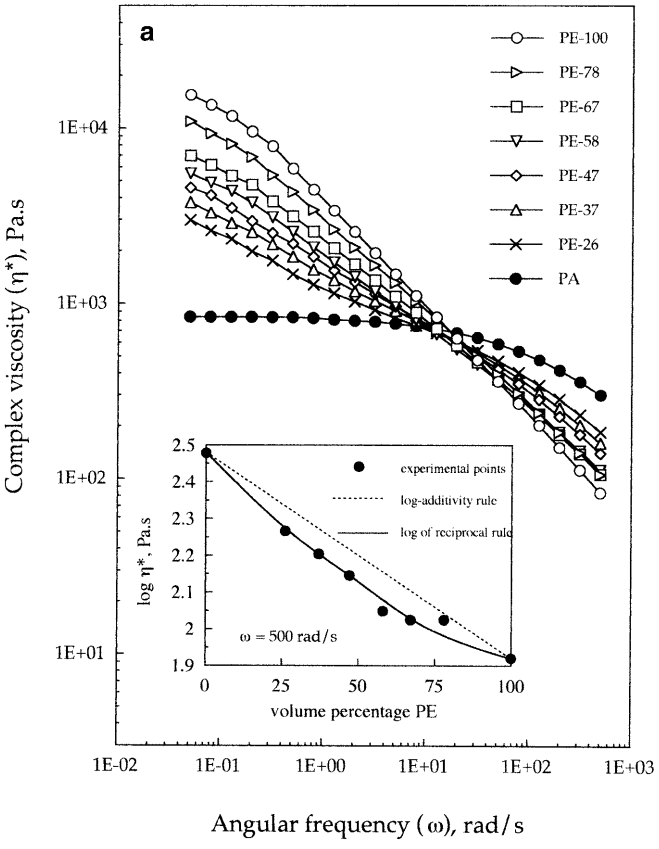
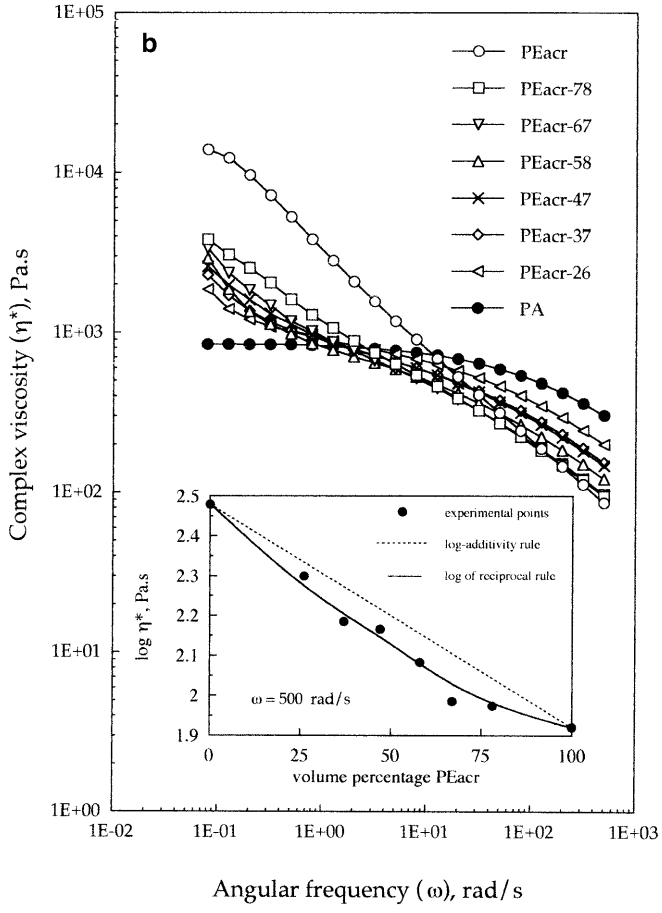


Fig. 4 a Complex viscosity versus angular frequency for PA/PE laminates with varying volume percentage of polyolefin and logarithm of viscosity measured at 500 rad/s as a function of the volume fraction of the PE phase for all the systems. **b** Complex viscosity versus angular frequency for PA/PEacr laminates with varying volume percentage of polyolefin and logarithm of viscosity measured at 500 rad/s as a function of the volume fraction of the PEacr phase for all the systems. **c** Complex viscosity versus angular frequency for PA/PEion laminates with varying volume percentage of polyolefin and logarithm of viscosity measured at 500 rad/s as a function of the volume fraction of the PEion phase for all the systems



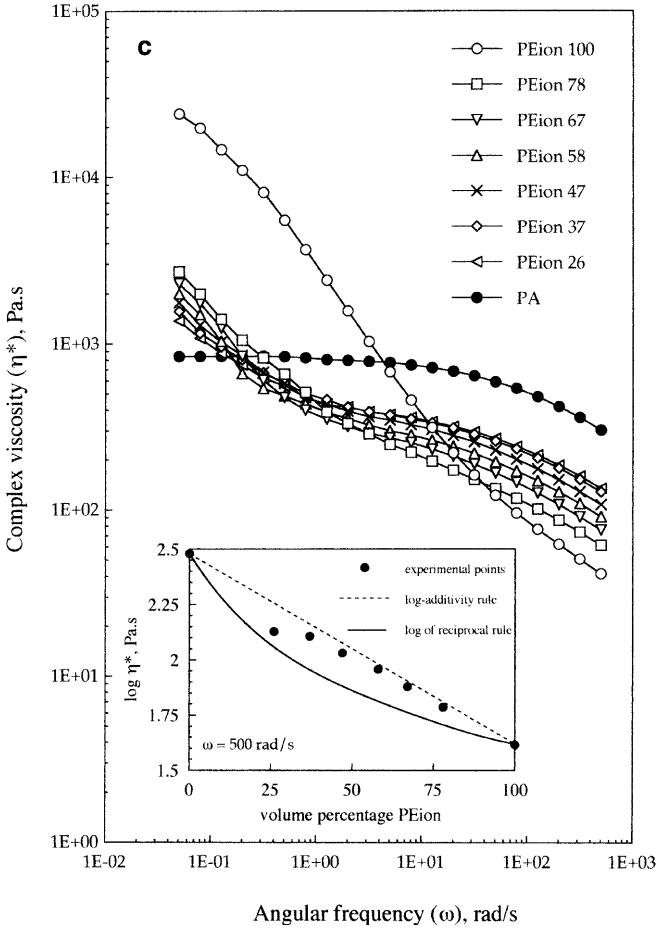


Fig. 4 (Contd.)

good agreement with the reciprocal rule, while the PA/PEion system shows good agreement with the log-additive rule at a higher volume fraction of ionomers. Once again this may be considered qualitative evidence for interfacial activity between the two different polymer phases.

Both PEacr and PEion thin films contain a considerable amount of polar or steric functionalities, some of which are oriented towards the surface of the film. This would result in an increase in the polar surface energy, thus diminishing the surface energy gap with the PA component. This would allow closer contact between the two dissimilar films, eventually improving their adhesion and subsequently their time-dependency behavior.

Due also to this interpretation, we decided to compare the behavior of such bulk modified PO systems with a system in which the PE had been significantly modified on the surface, i.e. the irradiated film quoted in the Experimental section. The corresponding results are reported in Fig. 5 in the form of complex viscosity versus angular frequency and the logarithm of η^* at $\omega = 500$ rad/s versus composition.

The melt viscosities for the different laminate systems are always higher than the corresponding values for the PEirr in the whole angular frequency range considered. With respect to pure PA an increase in melt viscosity at low ω values, followed by an inversion at higher ω values, is observed due to the significant shear-tinning behavior of the laminates systems. This is an indication of interfacial activity, due to the presence of large numbers of polar groups in irradiated and oxidized PE. These results are especially evident in terms of the logarithm of η^* versus composition, where a positive deviation, increasing with the PE volume percentage, from the additive rule, is observed.

The peeling results are reported in terms of peeling strength for all the PA/PO systems in Fig. 6. A large difference between the unmodified and all modified PE is observed, while remarkable differences due to the presence of different active groups are not to be seen.

As a conclusion we can assert that dynamic rheological measurements of stratified polymers can be used as a tool to investigate interfacial activity in multiphase systems in contrast to static measurements such as peeling.

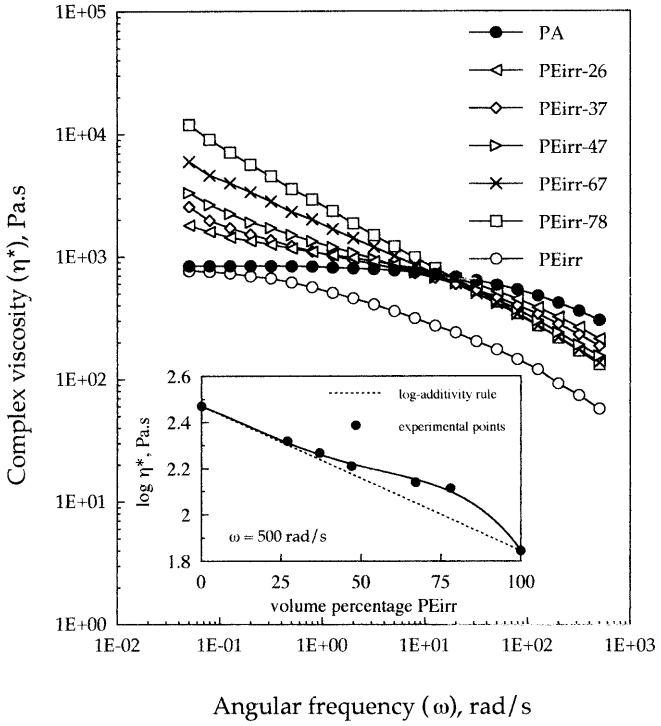


Fig. 5 Complex viscosity versus angular frequency for PA/γ-ray irradiated PE (*PEirr*) laminates with varying volume percentage of polyolefin and logarithm of viscosity measured at 500 rad/s as a function of the volume fraction of the PEirr phase for all the systems

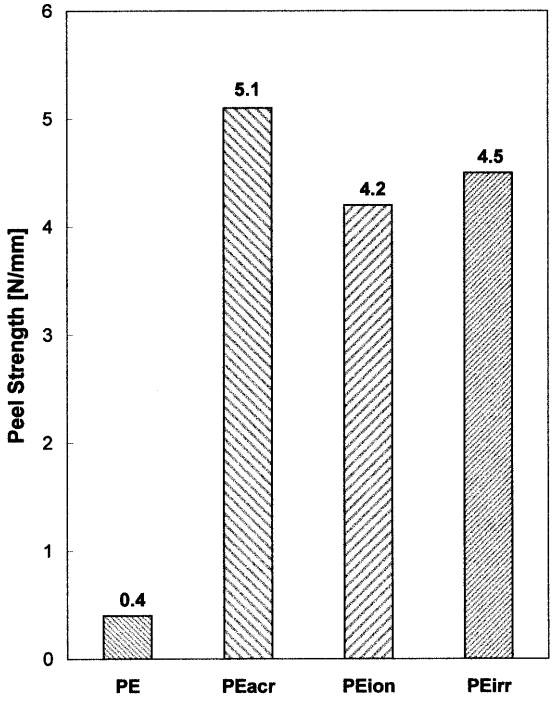


Fig. 6 Peel strength for all of the PA/polyolefin systems

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