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# Melt Rheology of Electron-Beam-Irradiated Blends of Polypropylene and Ethylene-Propylene-Diene Monomer (EPDM) Rubber

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A detailed rheological analysis over large shear rate intervals has been performed for electron-beam-irradiated blends of polypropylene (PP) and ethylene-propylene-diene monomer (EPDM) rubber. At high frequencies, a lower viscosity results from irradiation compared with unirradiated blends, which implies that the irradiated blends are easily processable via injection molding. At low shear rates, however, the irradiated blends behave like a network, and the viscosity may even exceed the viscosity of the unirradiated blends. This particular behavior can result in the formation of weak weld lines. Aggregation of the dispersed, cross-linked EPDM particles into a skeletal structure is the most probable explanation. In a first attempt, it was tried to correlate the network behavior to the average (shortest) interparticle distance (ID) between two rubber particles, which takes into account both volume fractions and particle size of the dispersed phase. Provided that the EPDM rubber is sufficiently cross-linked, the network behavior becomes more pronounced; i.e., increase in viscosity with decreasing interparticle distance. Above a critical value of the ID, the viscosity does not change and is determined by the PP matrix. As a vast amount of literature indicates, the rheology of blends proves to be difficult to understand. Because of the more stable morphology, compared with usual blends, induced by irradiation, a more valuable interpretation of the rheological behavior is possible.

## INTRODUCTION

Impact toughening of polypropylene (PP) via the addition of ethylene-propylene-diene monomer (EPDM) rubber is a topic of widespread interest (1–6). Much attention has been paid to the relation between morphology, i.e., the state of dispersion of the rubber in the PP matrix, and the mechanical properties. The best impact properties are obtained when a homogenous distribution of small EPDM particles (diameter,  $d \approx 0.3 - 0.5 \mu\text{m}$ ) in the PP matrix is induced. Due to the intrinsically high viscosity of the EPDM phase, this morphology can only be obtained when a high-molar-mass, i.e., high-viscosity, PP is used, since the best dispersion is achieved when polymers of equal viscosities are blended (7). However, easy processing, e.g., injection molding, requires a low (overall) blend viscosity. In a previous paper, it was shown that this contradiction could, in

principle, be solved by applying electron beam (EB) irradiation between the mixing and processing step (8). In this procedure, an optimum morphology for impact toughening is introduced during compounding using a high-molar-mass PP. Subsequently the blend is irradiated, which results in controlled chain-scission of the PP matrix and cross-linking of the dispersed EPDM phase: controlled rheology and fixation of morphology, respectively (8).

In this paper, results are presented concerning a more detailed rheological characterization of EB-irradiated PP/EPDM blends, as measured with dynamic mechanical analysis. The influence of chain-scission of the PP matrix, the extent of cross-linking of the EPDM phase, and the (possible) grafting of PP onto EPDM on the resulting rheological properties is reported. Because, in general, the analysis of the melt rheology of polymer blends is hampered by a continuous change of the blend morphology (9–11), it is interesting to investigate whether an enhanced stability of the morphology of the blend can facilitate the interpretation of rheological measurements.

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## EXPERIMENTAL

Some characteristics of the materials used are listed in Table 1. The PP used is an extrusion-type homopolymer with a relatively high molar mass. Three different grades of EPDM containing different amounts of termonomer (diene) were used: a high (EP-H) and low diene content (EP-L) and no diene at all (EP), and an increasing ethylene/propylene ratio in this sequence. As well-documented in the literature (12-14), the rate of cross-linking increases with increasing diene content and the use of ethylene norbornene as the termonomer results in faster cross-linking compared with dicyclopentadiene. A high ethylene content and high molar mass are also favorable for cross-linking (12-14). All EPDM grades used in this study will undergo cross-linking; however, the mechanism and rate of cross-linking (beam response) differ markedly.

Blends were prepared via two-roll milling at a temperature of 200°C during 10 min. Subsequently, the blends were compression-molding at a temperature of 200°C during 8 min into square plates with dimensions of 240 by 240 by 1 mm. The pure PP and EPDM samples were compression-molded under the same conditions, but were not milled.

The plates were irradiated with a dose of 50 kGy using a 3 MeV 'Van de Graaff' electron beam accelerator at the Interfaculty Reactor Institute (IRI, Delft). Irradiation was performed at ambient temperature in air.

Rheological characterization was performed with dynamic mechanical analysis (DMA) using a Rheometrics RDS II at a temperature of 226°C. A parallel plate geometry was used. To confine measurements to the linear viscoelastic region, a strain of 5% was used for the PP homopolymers and the blends, whereas a strain of 1% was applied for the pure EPDM samples. Investigations were performed in the frequency range of  $10^{-2}$  to approximately  $10^3$  rad/s. However, a large scattering of data points was observed in the frequency range of  $10^{-2}$  to  $10^{-1}$  rad/s for irradiated PP and irradiated blends with low EPDM content because of their low viscosity. Therefore, this frequency range is not incorporated in the results for these samples.

Scanning electron microscopy (SEM) was used to characterize the morphology of the blend. Blends were first microtomed at liquid nitrogen temperature, using a glass knife. Subsequently, the samples were immersed during 15 min in xylene in an ultrasonic bath to extract the rubbery phase. Finally, the samples were covered with a thin gold layer using an argon plasma.

## RESULTS

## Rheology of Pure Polymers

In Fig. 1a the viscosity of pure PP, unirradiated and irradiated with a dose of 50 kGy, is given as a function of frequency. The viscosity decreases upon irradiation, and the irradiated PP shows a more pronounced Newtonian behavior. As well-documented (8, 12, 15), this can be explained by random scission of the PP main-chain.

The EPDM rubbers show a different behavior upon irradiation. Figure 1b clearly shows that the storage modulus  $G'$  at low frequencies increases upon irradiation. A plateau is observed (EP-H and EP-L) or will be formed (EP) because of cross-linking. This result is in accordance, at least qualitatively, with the previously mentioned dependence of the rate of cross-linking on the amount of diene, ethylene content, and molar mass. Evidently, the relatively high ethylene-propylene ratio in the EP rubber can not compensate for both the absence of double bonds and the relatively low molar mass.

## Rheology of Unirradiated Blends

In Fig. 2, some rheological data are shown for the unirradiated blends. At high frequencies, the viscosities of the unirradiated blends with various amounts of EPDM (5 and 30 wt%,) are independent of the amount and type of EPDM used, and the rheological behavior is dominated by the PP matrix (compare with Fig. 1a). However, at low frequencies some differences arise for blends with higher EPDM concentrations. For each type of EPDM rubber, the blends with 30% EPDM possess a viscosity that is much higher than the viscosity for blends containing only 5% EPDM rubber. The "5% blends" pos-

Table 1. Characteristics of the Materials used

Polypropylene				
Code	Grade	$M_n$ (kg/mole)	MFI <sup>230°C</sup> (dg/min)	
PP	13E10, DSM	62	1.1	
EPDM Rubber				
Code	Grade	Diene (mole %)	Ethylene (mole %)	Mooney Viscosity (ML(1 + 4), 125°C)
EP-H	Keltan 512, DSM	4*	55	46
EP-L	Keltan 740, DSM	1†	60	63
EP	Vistalon 808, Exxon	—	77	46

\*Ethylidene norbornene.

†Dicyclopentadiene.

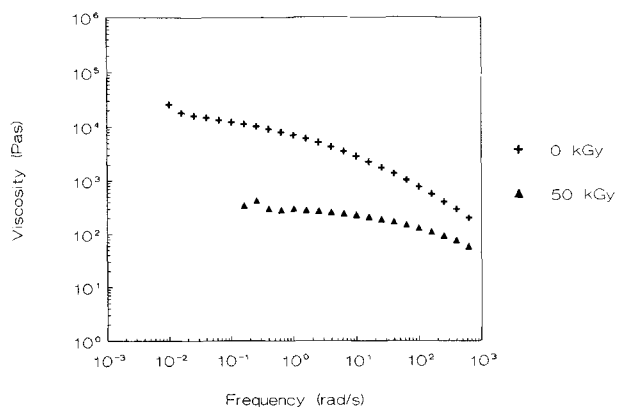


Fig. 1a. Complex viscosity as a function of the frequency of unirradiated PP and PP irradiated with a dose of 50 kGy ( $T = 226^\circ\text{C}$ ).

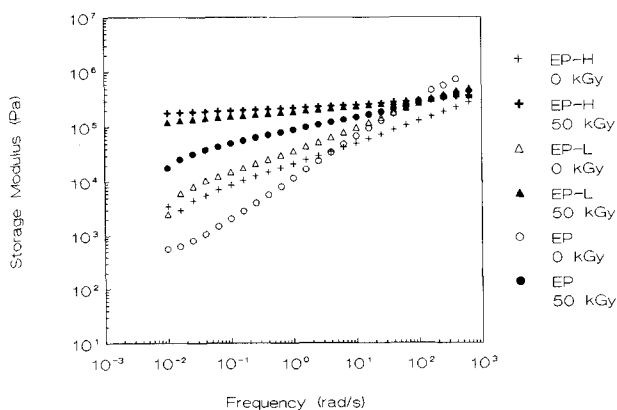


Fig. 1b. Storage modulus as a function of the frequency of unirradiated EPDM and EPDM irradiated with a dose of 50 kGy ( $T = 226^\circ\text{C}$ ).

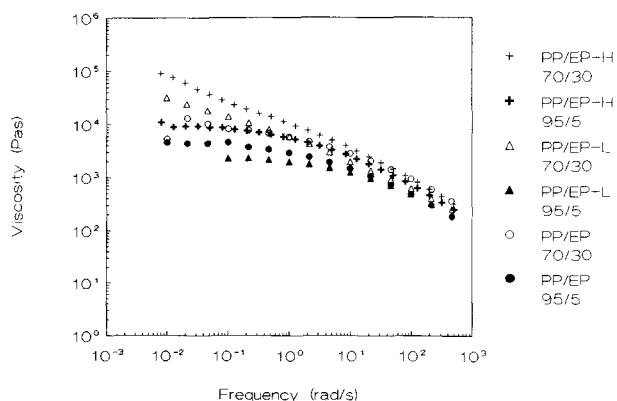


Fig. 2. Complex viscosity of unirradiated PP/EPDM blends as a function of the frequency ( $T = 226^\circ\text{C}$ ; parameter: blend composition).

sess a Newtonian plateau, whereas this plateau is not (yet) observed for blends with 30% rubber.

Differences between the blends with the same rubber concentration but with different rubber grades

exist as well. The viscosity of the blend of PP with 5% EP-H is much higher than for blends with 5% EP-L and EP and even equals the viscosity of the PP/EP 70/30 blend. The viscosity of the PP/EP-L and PP/EP blends with 5% rubber is even lower than that of pure PP.

An unambiguous interpretation of the observed rheological behavior of the unirradiated blends is difficult. It is hampered by the instability of the morphology of the blend, which changes continuously during the rheological measurement. Moreover, differences in thermal-mechanical-oxidative degradation of the PP matrix during processing may also play a role, although we have minimized this effect by keeping the processing conditions constant.

### Rheology of Irradiated Blends

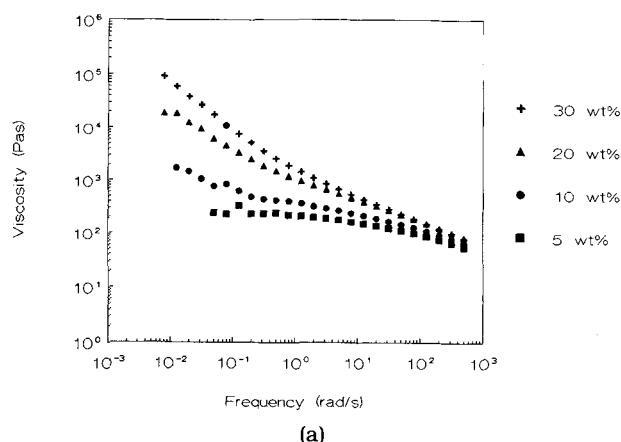
The rheological behavior of the irradiated blends of EP-H, EP-L, and EP is shown in Figs. 3a, 3b, and 3c, respectively. At high frequencies, which represent normal polymer processing conditions ( $10^2$ – $10^3$  rad/s), the viscosity of all irradiated blends is lower than the viscosity of the unirradiated blends (compare Figs. 3 and 2). Consequently, processing via injection-molding is, in principle, easier for the irradiated blends. At these frequencies, the viscosity curves of the various irradiated blends tend to overlap, similar to the unirradiated blends (Fig. 2), albeit to a lesser extent.

At low frequencies, the blends with low EPDM concentrations behave like the irradiated pure PP; i.e., low viscosity and with a Newtonian plateau. A relatively high viscosity is observed, however, at low frequencies for irradiated blends with high EPDM contents (compare Fig. 3 with Fig. 1a). The difference between blend and homopolymer is much more pronounced than for unirradiated blends. Moreover, at low frequencies, the complex viscosity of the irradiated blends may even exceed the viscosity of the unirradiated blends and of the pure PP. This high viscosity may cause serious difficulties, for example, the formation of weak weld lines in injection-molded products.

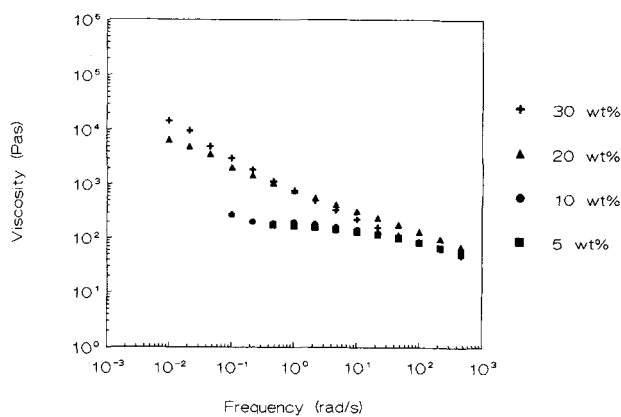
To investigate whether a Newtonian plateau would occur at still lower frequencies for the irradiated blends with higher EPDM contents, rheological experiments at various temperatures were performed. In Fig. 4 the results are shown for the storage modulus  $G'$  of the PP/EP-L 70/30 blend irradiated with a dose of 50 kGy. From Fig. 4, it can be inferred that there is hardly any influence of temperature, which implies that the irradiated blend demonstrates a typical network behavior. The high viscosity mainly results from an increase in elasticity of the blend, as can be concluded from the appearance of a second plateau modulus at low frequencies.

### DISCUSSION: NETWORK BEHAVIOR

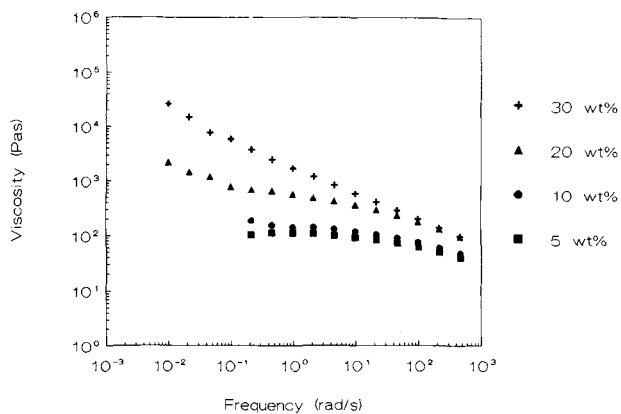
The unirradiated blends show an elastic behavior to some extent with increasing rubber content.



(a)



(b)



(c)

Fig. 3. Complex viscosity of PP/EPDM blends irradiated with a dose of 50 kGy as a function of the frequency ( $T = 226^\circ\text{C}$ ; rubber concentration as a parameter): (a) EP-H, (b) EP-L, and (c) EP.

However, this elasticity is small compared with the elastic behavior of the irradiated blends. An unambiguous explanation for the observed rheological behavior of the unirradiated blends is hindered by changing morphology during the rheological measurements (9-11). A more stable, and better characterized, morphology is expected for the irradiated blends (8). Therefore, attention is focused to the

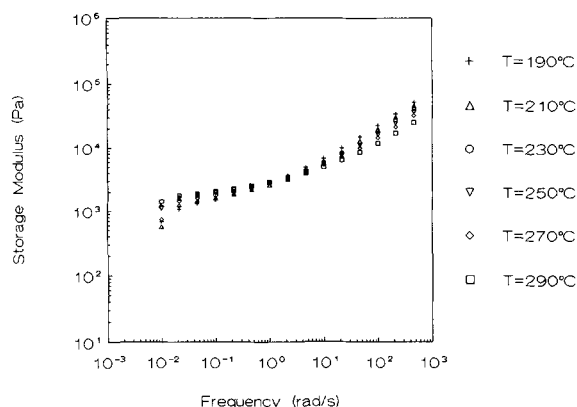


Fig. 4. Storage modulus of the PP/EP-L 70/30 blend irradiated with a dose of 50 kGy as a function of the frequency and measured at different temperatures.

origin of such a network mainly based on results obtained for the irradiated blends.

### Elasticity of Heterogeneous Mixtures

An elastic behavior of melts, as observed for the (irradiated) PP/EPDM blends, has been reported for other rubber-modified thermoplastics (11, 16-21), for polymer melts with solid particles (17, 22, 23), and even for a mixture of two Newtonian liquids (17, 24). A common feature is that the elasticity of the dispersed phase is higher than that of the matrix. (In the mixture of Newtonian liquids, the elasticity results from the interfacial tension  $\sigma/R$ ). Upon irradiation, the elasticity ratio  $G_{EPDM}/G_{PP}$  strongly increases, which causes in principle the increase in elastic behavior of the irradiated blends compared with unirradiated blends. However, the rheological behavior of the irradiated blends, presented in Fig. 3, is not uniquely proportional to this elasticity ratio, represented in Fig. 1b by  $G'$  of EPDM.

### Grafting and Aggregate Formation

A possible explanation can be found in the mechanism of network formation. In his paper on rubber-modified styrene acrylonitrile (SAN), Münstedt (18) mentioned two possible mechanisms for network formation in blends:

1. Aggregation of the dispersed rubber particles during dynamic motion, forming a skeletal structure, which prevents the matrix from flowing at low shear rates.
2. Bridging between dispersed particles via chemical grafting on the rubber particles.

For the unirradiated PP/EPDM blends, chemical grafting of PP onto EPDM can be excluded, since the blend is just a physical mixture of the two components. Consequently, aggregate formation is the most plausible mechanism for the network formation in the unirradiated blends, already suggested by Lee (16) for impact-modified PP. However, upon irradiation, some part of the PP matrix might be

grafted onto the EPDM-rubber particles. Recently, Harnischfeger, *et al.* (25) concluded that upon irradiation of similar PP/EPDM blends, some grafting occurred.

To investigate the occurrence and, if so, the extent of grafting,  $^{13}\text{C}$ -NMR (nuclear magnetic resonance) measurements were performed on the residue of irradiated and subsequently extracted blends. The measurements indicated that some grafting may occur, but is less than 1 wt% based on the total blend (26). This quantity is small compared with blends where the grafting-bridging concept was the main explanation for the network behavior and degrees of grafting were reported of more than 40% (18-20). Consequently, network formation in irradiated PP/EPDM blends does not occur via grafting-bridging.

Figure 5a shows the morphology of the PP/EP-L 70/30 blend before DMA testing, and Fig. 5b and 5c show the morphologies of the unirradiated and irradiated blends, respectively, after DMA testing. The EPDM particles in the unirradiated blend coalesce during measurement (compare Figs. 5a and 5b). This implies that the morphology of the unirradiated blends is not stable and ill-defined during the rheological measurements. However, there is no indication for aggregation and the formation of a skeletal structure. In the irradiated blend, the particles are not really coalesced but are clustered together as a result of the dynamic motion (see Fig. 5c, which could indicate a skeletal structure).

### Interparticle Distance

It has been reported in literature that the elasticity of a rubber-modified blend (18) and particulate-filled polymer melts (23) increases with increasing volume fraction of the dispersed phase as well as decreasing particle size. To take into account both volume fraction and particle size, the concept of interparticle distance (ID) in rubber-toughened polyamide blends has been introduced successfully and correlated to the toughness (27, 28). It is investigated here whether a relation also exists between the rheological properties and the interparticle distance. For this purpose, in a first approximation, the average shortest end-to-end distance between the rubber particles in the blends before the rheological measurements was measured, as obtained from the SEM micrographs. (For sake of simplicity, the particle size distribution is not taken into account). As a measure for the network behavior, the viscosity at a frequency of  $10^{-1}$  rad/s was taken. At this frequency, the differences between various blends are still large and all data points are beyond the scattering region.

In Fig. 6, these viscosity data are plotted as a function of the ID. It can be inferred from this figure that a critical value exists above which the rheological properties are independent of the ID and are mainly determined by the viscosity of the PP matrix (compare Fig. 1). Below the critical value, the vis-

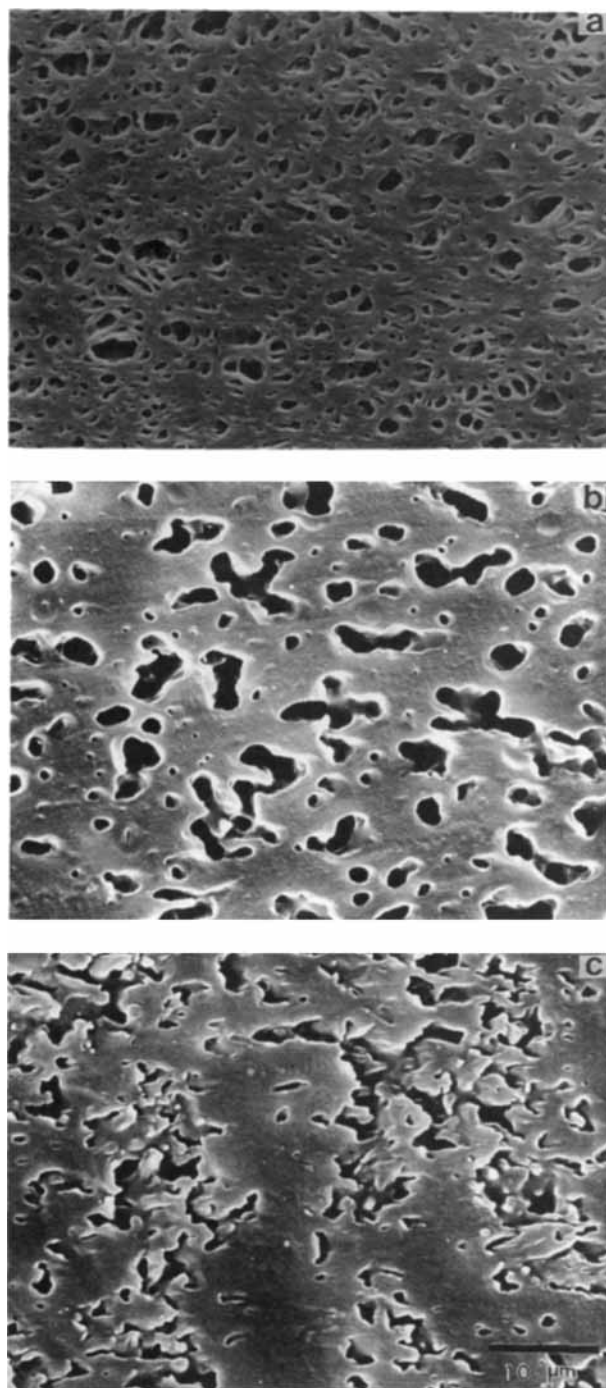


Fig. 5. Morphologies of the PP/EP-L 70/30 blend: (a) unirradiated, before dynamic mechanical analysis (DMA); (b) unirradiated, after DMA; (c) irradiated, after DMA.

cosity (or elasticity) of the blend gradually increases with decreasing ID. This critical value is similar for blends with EP-L and EP-H rubber, whereas it is slightly lower for the blend with EP rubber. Due to the small ID in this blend, a higher viscosity would be expected, but the EP rubber cross-links to a lesser extent than both others (see Fig. 1b). A comparative experiment with injection-molded blends, irradiated with a dose of 100 kGy (to cross-link EP

sufficiently), reveals that the viscosity of the PP/EP blend was higher than the viscosity of the PP/EP-L blend (26). Hence, a general trend of an increase in viscosity below a critical ID exists, as indicated with the drawn line in Fig. 6, provided that the dispersed phase is sufficiently cross-linked. The mechanism of cross-linking as well as the interaction between rubber and matrix seems less important. Above the critical value, the interaction between the rubber particles is too low to form a skeletal structure under the given test conditions.

### CONCLUSIONS

EB irradiation of PP/EPDM blends yields a low viscosity at high frequencies and, consequently, these blends can easily be processed via common injection-molding. The influence of type and amount of rubber as well as the particle size is marginal. At low shear rates, however, a pronounced network behavior is observed, which can be explained by aggregation of rubber particles into a skeletal structure. Formation of weak weld lines in injection-molded products may result from the high viscosity at low shear rates. The network behavior becomes more pronounced with increasing elasticity of the rubber and shorter interparticle distances. For interparticle distances above a critical value, the viscosity is mainly determined by the PP matrix. The existence of such a critical interparticle distance could be revealed via the enhanced stability of the morphology of the irradiated blends.

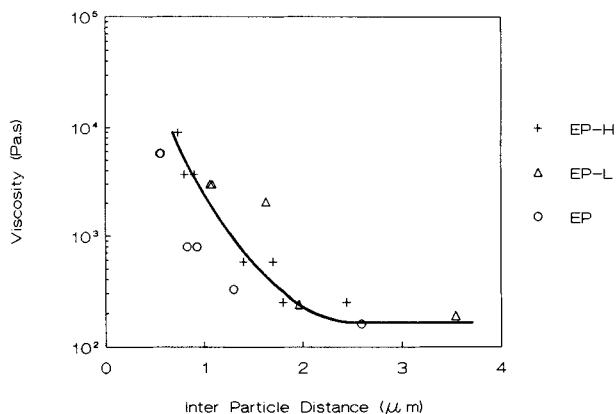


Fig. 6. Complex viscosity at  $10^{-1}$  rad/s as a function of the interparticle distance for the PP/EP-H, PP/EP-L, and PP/EP blends, unirradiated and irradiated with a dose of 50 kGy.

### ACKNOWLEDGMENT

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