Influence of electron beam irradiation on the microrheology of incompatible polymer blends : thread break-up and coalescence

Influence of electron beam irradiation on the microrheology of incompatible polymer blends: Thread break-up and coalescence

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Synopsis

The microrheology of polymer blends as influenced by crosslinks induced in the dispersed phase via electron beam irradiation, is systematically investigated for the model system polystyrene/low density polyethylene (PS/LDPE). Both break-up of threads and coalescence of particles are delayed to a large extent, but are not inhibited completely and occur faster than would be expected for a nonirradiated material with a comparable viscosity. Small amplitude, dynamic rheological measurements indicated that in the irradiated materials a yield stress could exist. In contrast, direct microrheological measurements showed that this yield stress, which would prevent both break-up and coalescence, could not be realized by EB irradiation. Apparently, the direct study of the microrheology of a blend system is important for the prediction of the development of its morphology and it is not possible to rely only on rheological data obtained via other methods.

INTRODUCTION

The properties of an incompatible polymer blend are determined, to a large extent, by the morphology of the blend, i.e., the particle size, shape, and the distribution of the constituents. The main problem of such a morphology is its intrinsic instability in the molten state. It is determined by material parameters such as viscoelasticity, viscosity ratio, and interfacial tension. The morphology continuously adapts to changes in shear and elongational stress, deformation rate, total strain, processing time, and temperature [see e.g., Utracki (1989), Han (1981), Paul and Newman (1978), Paul and Barlow (1980), Meijer *et*

al. (1988), and especially the references in Elmendorp (1986) and Elemans (1989)]. In order to obtain the desired properties in the final product, it is important to control the morphology during the different processing steps involved.

In the case of rubber-toughened blends the use of compatibilizers, added to the system or made *in situ* by reactive extrusion, is well known to stabilize a droplet-in-matrix structure [see, e.g., Heikens *et al.* (1978), Fayt *et al.* (1982), and Saleem and Baker (1990)]. However, in order to fix other possible morphologies, e.g., layered or thread-in-matrix structures, more rigorous methods are required. In previous papers by Elemans *et al.* (1988) and Van Gisbergen *et al.* (1989), it was shown that crosslinking via electron beam irradiation of the dispersed phase is a promising route to stabilize (or even fix) any morphology. In this method electron beam irradiation should occur between the mixing (e.g., extrusion) and processing (e.g., injection moulding) step. Provided that the constituents are selected with appropriate beam response, only the dispersed phase will crosslink and the matrix will not change or will only degrade in a controlled and desired way [Van Gisbergen *et al.* (1989)].

In this paper the influence of crosslinks, induced by electron beam (EB) irradiation, on the two major processes, which play an important role in the formation of the morphology, is discussed: i.e., break-up of the dispersed threads via Rayleigh distortions, see Elemans *et al.* (1990b), and coalescence of already dispersed particles. Both processes occur at relatively low shear rates and cause the morphology to develop into a structure of spherical particles in a matrix. Results of our investigations will be discussed related to a model system: a blend of relatively inert PS as a matrix and LDPE as the crosslinkable dispersed phase [Charlesby (1960)]. In a first attempt to analyze the experiments, model descriptions developed for pure Newtonian fluids are used.

EXPERIMENTAL

The low density polyethylene (LDPE) used was obtained from DSM (Stamylan 1808 AN, MFI = 7.5 dg/min) and the polystyrene (PS) was supplied by Dow Chemical (Styron 638, MFI = 25 dg/min).

Three series of experiments were performed.

(1) A blend of 80 wt. % PS and 20 wt. % LDPE was prepared on a Berstorff corotating twin screw extruder at an average barrel temperature of 200 °C. Strands with nonequilibrium morphologies were quenched in water and exposed to electron beam irradiation to various

doses. Both nonirradiated and irradiated strands were subsequently heated to 200 °C for various periods of time in a Fontijne press at very low pressure. Care was taken not to induce any shear deformation in the material. Afterwards the changes in morphology of these blends were visualized using scanning electron microscopy (SEM). A Cambridge Stereoscan S 200 was used. Before examination, the samples were first microtomed at -196 °C using a glass knife. Subsequently the LDPE phase was etched in an oxygen plasma and the surface was covered with a thin gold layer.

(2) Special samples were prepared for a more detailed investigation of the break-up process, because the thread-like morphology induced via extrusion is not very uniform, see Fig. 2, upper left corner. More-over, coalescence and thread break-up occur simultaneously during re-heating in experiment 1 and this should be avoided.

Therefore, threads of LDPE were spun (radius, $R \approx 100$ μm) and placed between two PS plaques (thickness, $d \approx 1000$ μm), following the procedure described in Elemans et al. (1990b). Upon heating these samples at 200 °C for 40 min, Rayleigh distortions with various amplitudes developed on the LDPE threads. (The typical time for complete break-up was approximately 80 min for this system, where the threads are extremely thick compared to blends prepared by extrusion.) Before complete break-up occurred the samples were cooled down, freezing in the distortions. Distortion amplitudes and wavelengths could be analyzed using a Zeiss optical microscope.

Subsequently the samples were irradiated to 50, 100, or 200 kGy and reheated for 2700 and 9900 s. The distortion amplitudes generated in the first heating step act as the initial distortions in the second heating step. It was determined whether distortions did grow until breakage or did not, after the periods of reheating imposed. A schematic procedure of this process is given in Fig. 1.

Effects of orientation of the LDPE threads on break-up during the second heating treatment can be ruled out since complete relaxation has already occurred during the first heating step. The long aspect ratio of the fibers, $L_0/R_0 \approx 1000$, ensures a homogeneous break-up via Rayleigh distortions without the danger of retraction of the threads followed by end pinching [Elemans et al. (1990b), Stone and Leal (1989), Carriere et al. (1989), note the comments on this article of Elemans and Janssen (1990a)].

(3) To study the coalescence process, the extrusion blend from experiment 1 (Fig. 2, 0 kGy, $t = 0$) was heated at 200 °C for 120 s. A morphology of LDPE droplets, with an average diameter of 1.5 μm, in
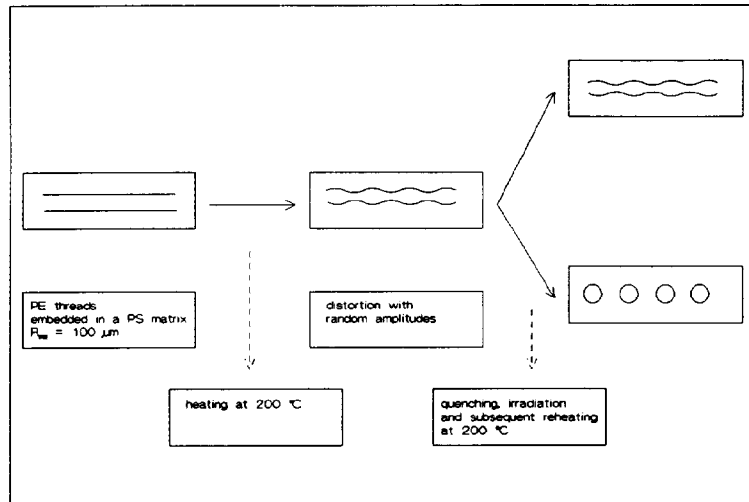
FIG. 1. Schematic representation of the experimental setup for detailed investigation of the thread break-up process.

a PS matrix resulted, see Fig. 2, 0 kGy, $t = 2$. Irradiation of these samples to 40, 100, and 180 kGy before a second reheating step, again at a temperature of 200 °C and for times up to 2×10^4 s, resulted in different coalescence rates. The average (particle) size of the droplets after heating for different periods of time was measured to determine these rates, using SEM.

Viscosity/frequency curves (0.1–100 rad/s) of nonirradiated and irradiated homopolymers were determined with a Rheometrics RDS II, at a temperature of 200 °C and a strain of 1%. A parallel plate geometry was used.

Irradiation was performed with a 3 MeV "van de Graaff" electron beam accelerator at the Interfaculty Reactor Institute (IRI, Delft, the Netherlands), under atmospheric conditions, at room temperature.

From literature, e.g., Charlesby (1960), Chapiro (1962), Makhblis (1975), and Zosel (1972), as well as from our present investigations [see Fig. 3(c)], it is known that polystyrene is rather insensitive towards irradiation: only at very high doses crosslinking will occur. On the other hand, polyethylene will rapidly crosslink and the crosslinks will be preferentially formed in the amorphous phase. Nevertheless, irradiation induced crosslinking is homogeneous on a relatively macroscopic scale,
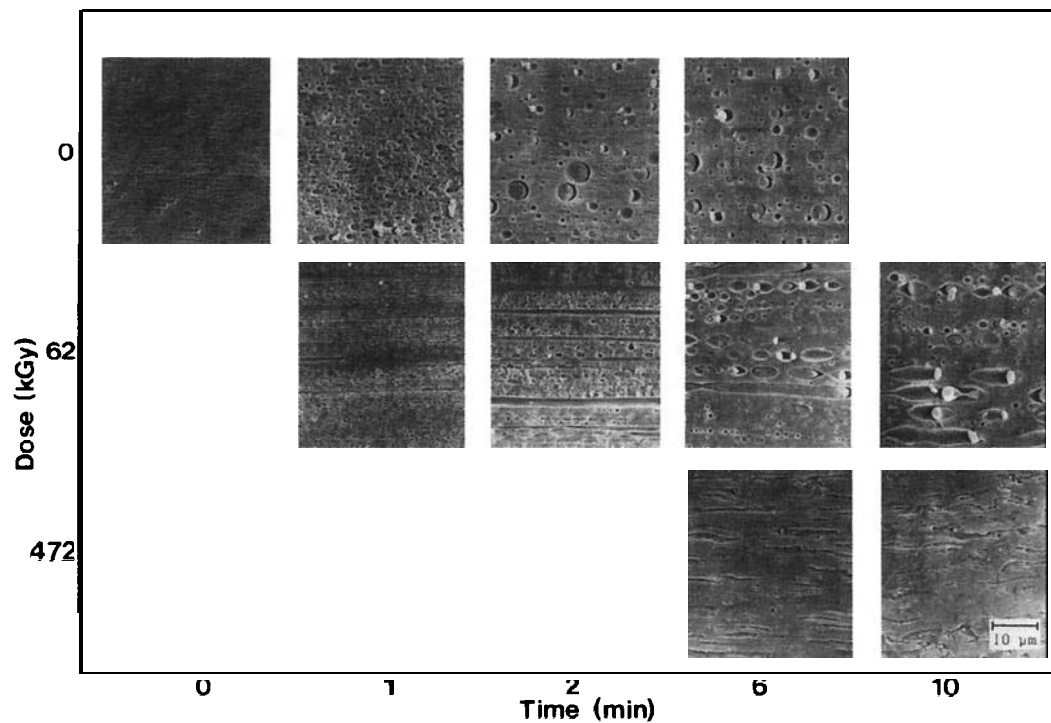
FIG. 2. Stabilizing effect of radiation induced crosslinks in the dispersed LDPE phase in a PS/LDPE 80/20 blend prepared on a corotating twin screw extruder and reheated for various periods of time at a temperature of 200 °C. Irradiation in between the extrusion and reheating step. SEM micrographs parallel to the direction of extrusion.
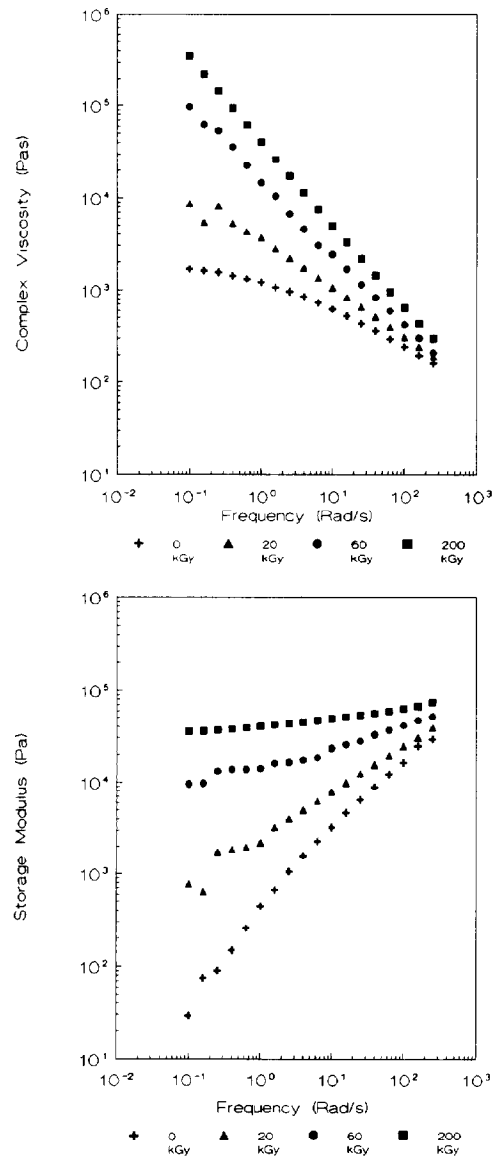
FIG. 3. (a) Complex viscosity of LDPE at 200 °C as a function of angular frequency. Parameter: irradiation dose. (b) Storage modulus of LDPE at 200 °C as a function of angular frequency. Parameter: irradiation dose. (c) Complex viscosity of PS at 200 °C as a function of angular frequency. Parameter: irradiation dose.
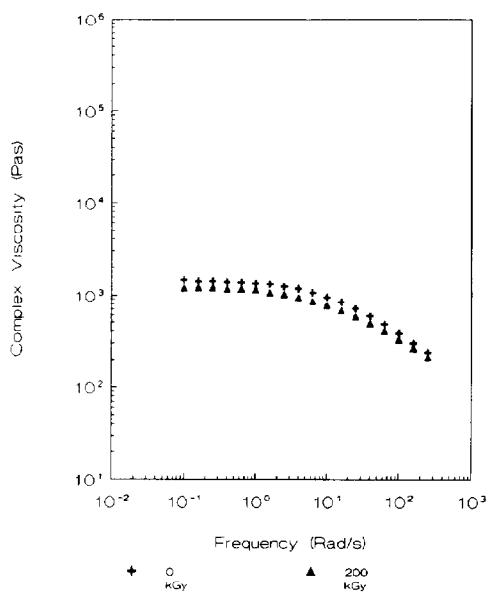
FIG. 3. (continued).

i.e., typical dimensions $\geqslant 10$ nm. At higher doses chain scission will become more important and consequently a crosslinked fraction of 100% will never be obtained.

RESULTS AND DISCUSSION

As can be inferred from the SEM micrograph in the upper left corner of Fig. 2, a morphology of small LDPE threads in a PS matrix is induced via twin screw extrusion. This intrinsically unstable morphology rapidly transforms into a droplet-in-matrix morphology when the sample is reheated at 200 °C for various periods of time, see Fig. 2 upper row. The two processes, thread break-up via Rayleigh distortions and coalescence, occur simultaneously. Irradiation of the blend before reheating, with an intermediate dose of 62 kGy, delays the droplet formation. Irradiation of the blend with a maximum dose of 472 kGy (using higher doses would also affect the PS matrix) prevents the formation of droplets in the typical time scale of the experiment (600 s).

However, complete preservation of the original thread-in-matrix morphology is not possible, even for this high dose. Deformation of threads and coalescence still continues.

In Fig. 3(a) it is shown that the viscosity of LDPE strongly increases upon irradiation, especially at low shear rates. It can also be inferred that, as a result of irradiation, a Newtonian plateau is no longer observed in the frequency range investigated and that the crosslinked material shows pronounced elasticity. This elasticity of the irradiated LDPE is reflected in the strong increase in the storage modulus G' of LPDE upon irradiation, see Fig. 3(b). On the other hand, PS is hardly affected by an irradiation dose of 200 kGy. A slight but negligible decrease in viscosity is observed compared to the nonirradiated blend, see Fig. 3(c).

It is evident that the strong increase in viscosity (or viscoelasticity) of the LDPE decreases the mobility of the dispersed LDPE phase. This decreased mobility results in the delay in thread break-up and a decrease in coalescence rate, as shown in Fig. 2. However, questions arise about the effectivity of radiation induced crosslinks with respect to the complete prevention of break-up and coalescence. In this paper a first attempt will be given to relate changes in viscosity, elasticity, and viscosity ratio to a change in break-up and coalescence rates.

THREAD BREAK-UP

Assuming that the break-up of molten polymer threads in a molten polymer matrix can be described, in a first approximation, with the development and growth of sinusoidal distortions as derived for Newtonian fluids [Lord Rayleigh (1879), Tomotika (1935 and 1936), Rumscheidt and Mason (1962), Chappelaer (1964), Elemans et al. (1990b)], the time to break can be expressed as

$$t_b = (1/q)\ln(0.816R_0/\alpha_0) \tag{1}$$

and

$$q = (\sigma/2\eta_m R_0)\Omega(\lambda, p), \tag{2}$$

where

$\quad t_b$ = time to break (s),
$\quad R_0$ = initial thread radius (m),
$\quad \alpha_0$ = initial distortion amplitude (m),
$\quad \sigma$ = interfacial tension (N/m),
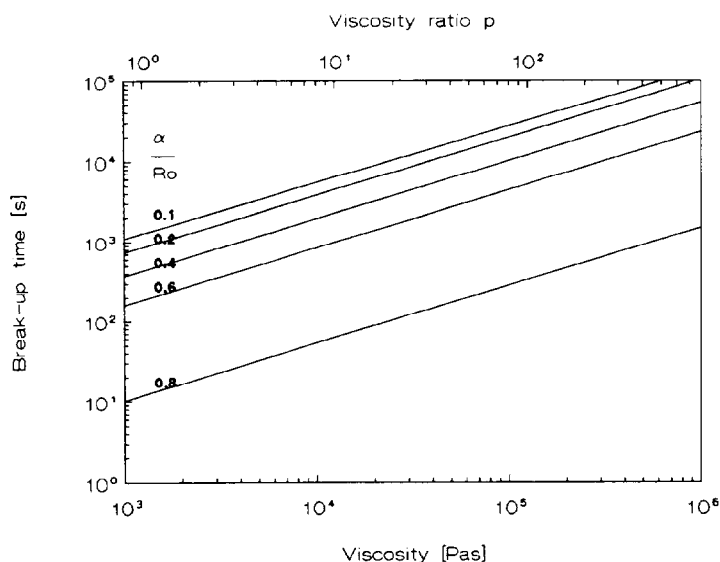$\quad \eta_m$ = viscosity of matrix (Pa s),

λ = wavelength of sinusoidal distortion (m),

p = viscosity ratio between the dispersed phase and matrix phase (η_d/η_m),

$\Omega(\lambda,p)$ = tabulated function of λ and p [Tomotika (1935 and 1936), Chappelaer (1964)].

Since break-up occurs at a very low shear rate, the zero shear viscosity can be used successfully in Eq. (2) [see Elmendorp (1986), Elemans (1989 and 1990)].

As the viscosity of PS hardly changes upon irradiation the influence of the viscosity of LDPE on the time, necessary for complete break-up of threads, can be predicted for various initial distortion amplitudes. Calculations have been performed, using for the interfacial tension a value of $\sigma = 5\times10^{-3}$ N/m [Wu (1979), Elmendorp (1986)]. This interfacial tension can be decreased via the addition of compatibilizers to the blend. Such compatibilizers can be induced *in situ* via irradiation, Van Gisbergen *et al.* (1990). However, in the blend of PS/LDPE this is rather unlikely since there is no contact in the solid state between PS and LDPE due to the crystallization shrinkage of the PE phase, see, e.g., Fig. 5 in the paper of Heikens and Barentsen (1977). For the viscosity of the PS matrix η_m, a value of 1400 Pa s was used which is the average of the zero shear viscosities of the nonirradiated and the irradiated PS as shown in Fig. 3(c). The results of the calculated time as a function of the viscosity of the dispersed LDPE phase or the viscosity ratio p are shown in Fig. 4. As a parameter the reduced amplitude $(\alpha_0' = \alpha_0/R_0)$ was used. An increase in LDPE viscosity, or in viscosity ratio p, results in a significant increase in break-up time, whereas an increase in the relative distortion amplitude has the opposite effect.

The theoretical values of the initial amplitudes, which result in breaking of the threads, after reheating during 2700 and 9900 s, respectively, can be determined as a function of the viscosity of LDPE, via interpolation in Fig. 4. Results are shown in Fig. 5 (solid lines). Threads with smaller amplitudes will, theoretically, not break up into droplets during the heating time imposed. Increasing the viscosity of LDPE increases the value of the critical amplitude.

In order to compare the theoretical value of the initial amplitudes which do not result in break up, with experimental data on crosslinked LDPE as obtained with experiment 2, the zero shear viscosity has to be known as a function of the irradiation dose. However, for the crosslinked materials no plateau value of the viscosity is found, see Fig. 3(a). Therefore, in a first approximation, the viscosity at an angular

Viscosity ratio p

FIG. 4. Theoretical break-up times of PE threads in a PS matrix as a function of the LDPE viscosity, which represents the viscosity ratio $p = \eta_{LDPE}/\eta_{PS}$ because the viscosity of the PS matrix remains constant. Parameter: the initial reduced distortion amplitude, $\alpha' = \alpha/R_0$. $\sigma = 5\times10^{-3}$ (N/m), $\eta_m = 1400$ (Pa s), $R_0 = 100$ μm, $T = 200$ °C.

frequency of 0.1 rad/s is used. According to Elmendorp (1986), break-up occurs at even lower deformation rates (order of magnitude $\approx 10^{-5}$–10^{-3} s^{-1}). Therefore the values of the viscosity used can be considered to present a kind of lower limit. In Fig. 6 the (complex) viscosity of LDPE as a function of irradiation dose is given. Using the data from experiment 2 and the viscosity data of Fig. 6, the experimental maximum amplitudes are determined. They are plotted (dashed lines) in Fig. 5. Comparing the experimental and theoretical values, it is clear that the prediction of the model is in qualitative agreement with the experiments. However, the experimental values are somewhat lower, i.e., break-up occurs faster than would be expected, particularly for the shorter reheating time.

Of course estimation of the correct viscosity of the (irradiated) LDPE is a problem in this experiment. Break-up more likely occurs at even lower shear rates than the 0.1 rad/s chosen, i.e., at an even higher viscosity of the LDPE phase. As a consequence the experimental values

Viscosity ratio p
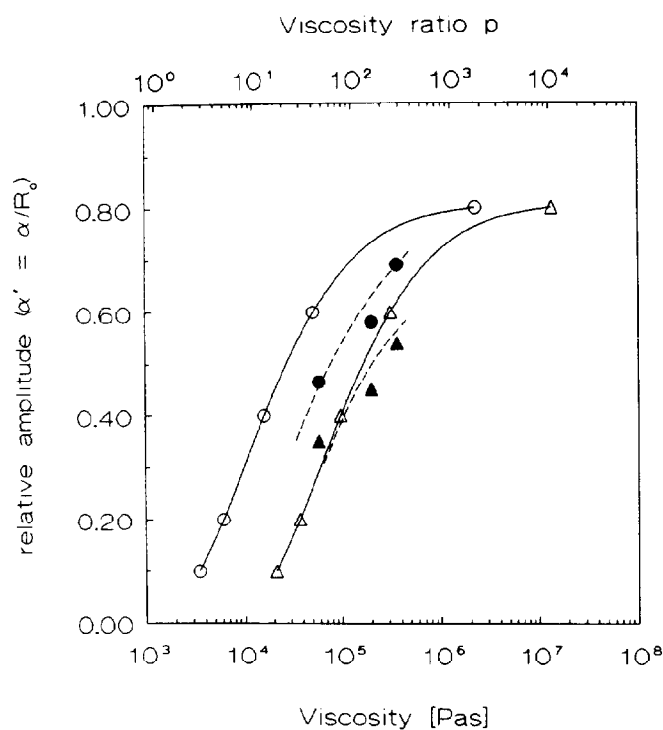
FIG. 5. Comparison between theory (open symbols, solid lines) and experiment (closed symbols, dashed lines) of maximum distortion amplitudes, which do not result in breakage of LDPE threads ($R_0 = 100 \, \mu$m) in a PS matrix, as a function of LDPE viscosity or viscosity ratio $p = \eta_{LDPE}/\eta_{PS}$. ○: heating time = 2700 s. △: heating time = 9900 s.

in Fig. 5 would shift to higher viscosities, making the discrepancy between theory and experiment worse.

Also the time determination may induce errors. However, when the heating-up time is taken into account, the difference between experiment and theory also increases. Threads with the maximum distortion amplitude are broken in an effective time which is shorter than indicated in Fig. 5.

Hence, the conclusion that break-up occurs faster than would be expected for materials, not crosslinked but with comparable viscosity, seems to be justified. This conclusion is rather surprising, since one
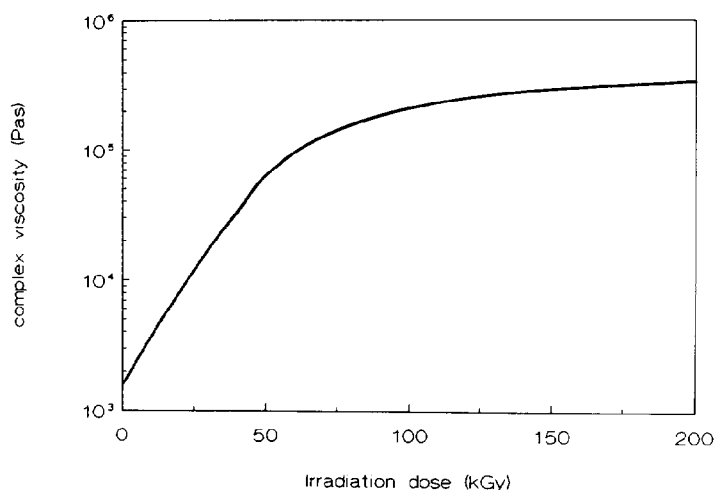
FIG. 6. LDPE viscosity as a function of irradiation dose. Complex viscosity at frequency $\omega = 0.1$ rad/s. $T = 200$ °C.

would expect that the radiation induced elasticity would slow down the process beyond the simple viscous prediction. (According to Tomotika, break-up of threads occurs at only one, dominant, wave number $\chi = 2\pi R_0/\lambda_{max}$. This wave number is a function of viscosity ratio. From the optical microscope analysis, the dominant wave number of the original LDPE threads can be determined as 0.52 ± 0.1. This is in accordance with Tomotika's theory which predicts a value of $\chi \approx 0.5$ for the viscosity ratio of our system. This check on homogeneous break up always should be performed. After irradiation the viscosity ratio is changed. As a consequence, a smaller dominant wavelength is expected, e.g., $\chi \approx 0.2$ for $p = 100$. Despite this, the threads continued to distort with the original wavelength, during the second step, maybe because the initial amplitudes, imposed during the first heating step, were already too large.)

Another possibility to study the effects of EB induced crosslinks is to investigate whether a yield stress is generated or not. Again under the assumption that break-up of threads can be described with the equations as derived for Newtonian fluids, the pressure difference between maximum and minimum of the distortion amplitude can be expressed as

$$\Delta p = -\{2\sigma\alpha/R_0^2\}\{1/[1-3/2(\alpha/R_0)^2]-(2\pi R_0/\lambda)^2\} \quad [Pa]. \tag{3}$$

The pressure difference is the driving force for the break-up process and is induced by the interfacial tension (σ/R). When the material exhibits a yield stress, higher than this pressure difference, the thread will not flow and the distortion cannot grow. In our experiments this pressure difference could be calculated using the microscopy data from experiment 2. Analysis of the threads, irradiated and subsequently reheated for 2700 or 9900 s, revealed maximum pressures: threads with amplitudes causing a smaller pressure difference than this maximum value, are not transformed into droplets in 2700 or 9900 s, respectively. In Fig. 7 the maximum pressure differences are given as a function of the irradiation dose.

As can be inferred from Fig. 7 the pressure difference at which a distortion is stable increases of course with increasing irradiation dose. However, it can also be observed that at high doses this pressure difference does not go to infinity but levels off. Heating for a longer period of time (9900 s) leads to break-up of distortions which were stable at a shorter time scale (2700 s). From these two observations it can be concluded that irradiation does delay break-up but cannot prevent it completely. Flow of the (partly) crosslinked material is still possible and a yield stress is not generated. This was confirmed by the fact that distortion amplitudes continuously increased, even if the thread did not completely break, during the heating times imposed.

A comparison with the rheological data obtained from the dynamic measurements reveals that also this conclusion is (again) rather surprising. When Fig. 3(a) is redrawn in terms of viscosity versus shear stress, it is evident that radiation induced crosslinking results in a steep increase in viscosity below a certain stress, which depends on the radiation dose used. This is indicative of the existence of a yield stress, see Fig. 8. LDPE irradiated with doses larger than 20 kGy shows a pronounced yield stress behavior. The driving force in break-up experiments, the pressure difference between the minimum and maximum of the distortion amplitude, is two orders of magnitude smaller than the yield stresses indicated by the rheological measurements. Consequently, break-up would not be expected to occur for the irradiated samples. Evidently, the crosslinked material behaves different during dynamic rheological testing than in the real, steady, situation.
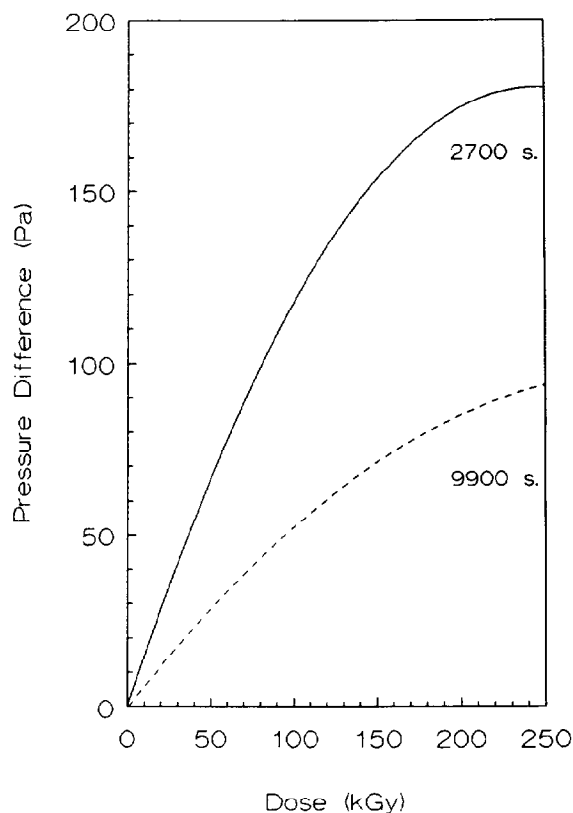
FIG. 7. Summary of experimental results concerning the stability of threads. Threads with initial distortion amplitudes, causing a pressure difference higher than indicated by the lines, break during reheating of 2700 and 9900 s, respectively at a temperature of 200 °C.

COALESCENCE

Break-up and coalescence occur simultaneously in a thread-in-matrix morphology. In order to eliminate break-up effects it is necessary to start with a droplet-in-matrix morphology. The procedure to obtain the droplet-in-matrix morphology was described in experiment 3. (From Fig. 2, upper row, it can be inferred that 120 s is enough to generate this morphology in nonirradiated blends.)

Figure 9 clearly shows that upon irradiation coalescence is delayed considerably, but not prevented. In the models describing the coalescence process, it is normally assumed that the rate of coalescence is
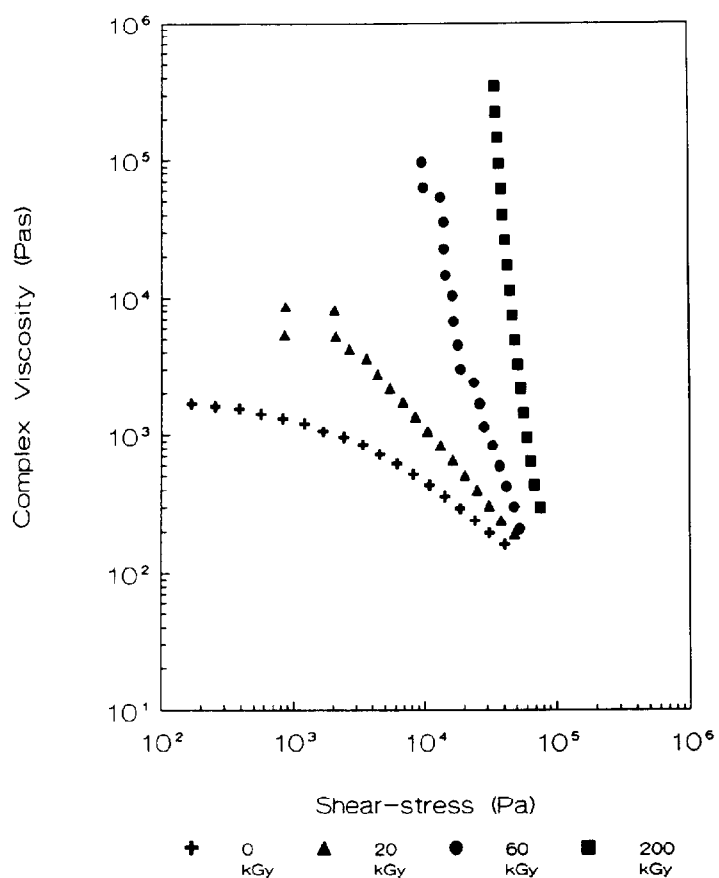
FIG. 8. Complex viscosity of LDPE at 200 °C as a function of shear stress. Parameter: irradiation dose.

determined by the film thinning rate of matrix material between the dispersed particles [Charles and Mason (1960), Elmendorp (1986), Chesters (1988)]. Based on this assumption some models were derived. For three models, the equations for the coalescence time (t_c) can be summarized as, see Charles and Mason (1960), Elmendorp (1986), and Chesters (1988):
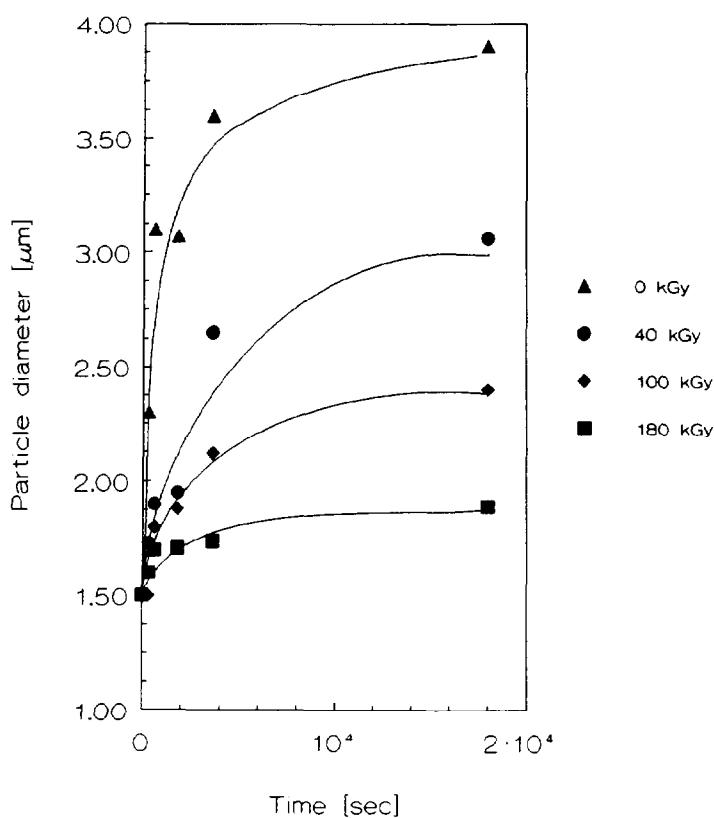
FIG. 9. Experimentally determined increase in size of dispersed LDPE particles in a PS matrix as a function of heating time at a temperature of 200 °C. Parameter: irradiation dose.

mobile interface (mi)

$$t_c = (3\eta_m R/2\sigma) \ln (R/2h_c),\tag{4}$$

immobile interface (ii)

$$t_c = (3\eta_m R^2 F/16\pi\sigma^2)[1/h_c^2 - 1/h_0^2],\tag{5}$$

partly mobile interface (pmi)

$$t_c = [\pi\eta_d F^{0.5}/2(2\pi\sigma/R)^{1.5}][1/h_c - 1/h_0],\tag{6}$$

where

t_c = time to coalescence (s),

R = particle radius (m),

h_c = critical surface-to-surface distance (m)

≈ 50 nm (Elmendorp, 1986),

h_0 = initial surface-to-surface distance (m)

$\approx 2/R$ (Mackay and Mason, 1963),

F = force (N).

The mobility of the interface is an important parameter. For fully mobile interfaces (mi) the time to coalescence (t_c) is proportional to the particle radius R times $\ln(R)$ [Eq. (4)], whereas in blends with immobile interfaces (ii) t_c is proportional to FR^2 [Eq. (5)], with $F =$ force. For gravity-induced coalescence this proportionality changes into $t_c \sim R^5$.

Immobilization of the interface can be obtained by the addition of compatibilizers to the blend. Compatibilizers are assumed to be located at the interface between the matrix and the dispersed phase. As has already been mentioned, it is unlikely that compatibilizers will be formed *in situ* via irradiation. The rate of film thinning is directly proportional to the viscosity of the matrix, both for fully mobile and immobile interfaces, whereas the viscosity of the dispersed phase is not incorporated. The viscosity of the PS matrix does not change upon irradiation (at least for the doses used) and flow, and consequently coalescence, should be as easy as in the nonirradiated material. Unless, of course, the mobility of the interface is influenced by the crosslinks in the dispersed phase. However, a fully immobilized dispersed phase and consequently immobilized interface, i.e., possessing a yield stress, is not obtained upon irradiation as could be inferred from the thread break-up experiments. A recently proposed coalescence model [Chesters (1988)] assumes a partly mobile interface (pmi) and takes into account the viscosity of the dispersed phase as well [Eq. (6)]. This model assumes plug flow between the two colliding droplets and this implies that within the validity of the model, i.e., $p \leqslant 100$, the viscosity of the matrix plays a minor role.

From the three models mentioned, mobile [Eq. (4)], immobile [Eq. (5)], and partly mobile interface [Eq. (6)], the time needed for coalescence to occur can be calculated. Subsequently the time for the next coalescence step, for bigger droplets, can be calculated. The assumption
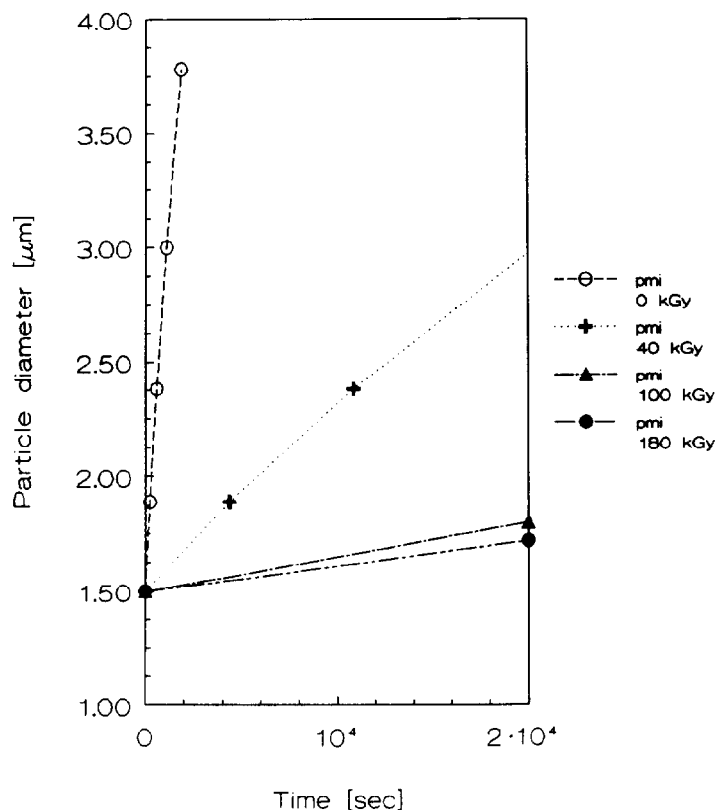
FIG. 10. Theoretically determined, stepwise, increase in size of LDPE particles in PS matrix as predicted with the pmi model as a function of heating time at a temperature of 200 °C. Parameter: irradiation dose.

has to be made that one starts with equal sized droplets which coalesce into particles with a doubled volume.

The theoretical times necessary for four coalescence processes to occur, are shown in Fig. 10, as calculated for the pmi model. For comparison with the experimental data the same time scale has been used as in Fig. 9. Calculations have been performed with LDPE viscosities at 0.1 rad/s corresponding to irradiation doses of respectively 0, 40, 100, and 180 kGy, see Fig. 6. The force F was estimated via fitting the

experimental time necessary for three coalescence steps for the nonirradiated LDPE. This force is substantially larger than would be expected for gravity-induced coalescence, where $F = \Delta \rho Vg$.

When the results are compared with the experimental data it is observed that there is a qualitative agreement, i.e., a slowdown in coalescence rate with larger particle size and higher viscosity of the LDPE. However, quantitatively the agreement is poor. Especially at high irradiation doses, the experimental coalescence times are much shorter than would be expected for nonirradiated materials with a comparable high viscosity.

It has to be remarked that the pmi model is only valid for viscosity ratios smaller than 100. For higher values the ii model should yield better predictions of the coalescence times [Chesters (1988)]. This high viscosity ratio is already achieved at the lowest irradiation dose of 40 kGy. In Fig. 11 a comparison has been made between the three models with the theoretical values for four coalescence steps to occur. In order to be able to compare, a logarithmic time scale is used, since the differences in characteristic coalescence times are very big. For the ii model the same force F has been used as in the pmi model.

As can be inferred from Fig. 11 the models of mobile and immobile interfaces give two extreme situations: very short and very long coalescence times, respectively. The pmi model leads to intermediate values and takes into account changes in viscosity of the LDPE. When a comparison is made with the experimental data (plotted on the same logarithmic scale, see Fig. 12) it can be observed that the ii model gives worse prediction than the pmi model. The qualitative agreement is the best for the partly mobile interface model.

The predictions of the coalescence rates are based on many assumptions and, consequently, it can not be expected that they are correct in a quantitative sense. Nevertheless, it can be concluded that irradiation of a blend does not delay coalescence more efficiently, although this could have been expected from the more pronounced elasticity.

EFFECTIVITY OF IRRADIATION

For the experimental verification of the calculated values in a first approximation viscosities were used, which were not correct in an absolute sense but indicated the lower limit. From the comparison between the experiments and the calculations it can be concluded that radiation induced crosslinking of the dispersed phase is less effective in delaying thread break-up and coalescence than would be expected for
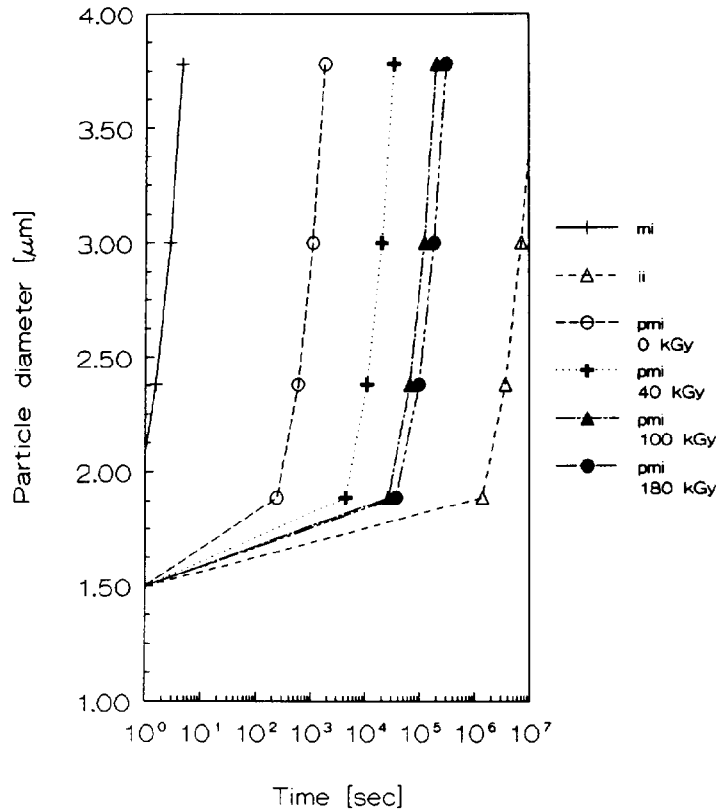
FIG. 11. Comparison of theoretical coalescence times, needed for four subsequent coalescence steps to occur, predicted according to the mi, pmi, and ii models. Due to big differences in characteristic times, the time scale is logarithmic.

pure Newtonian materials with the same high viscosity. This is rather surprising since the high elasticity of the crosslinked LDPE is believed to contribute to an enhanced stability compared to pure viscous materials, which has been shown by Van Oene (1972) and Elmendorp (1986).

A possible explanation for the observed behavior may be a nonuniform crosslinking on the molecular scale of the LDPE phase. Via irradiation it is impossible to incorporate all LDPE chains in the network, even at high doses, since also some chain scission occurs. In the PS/
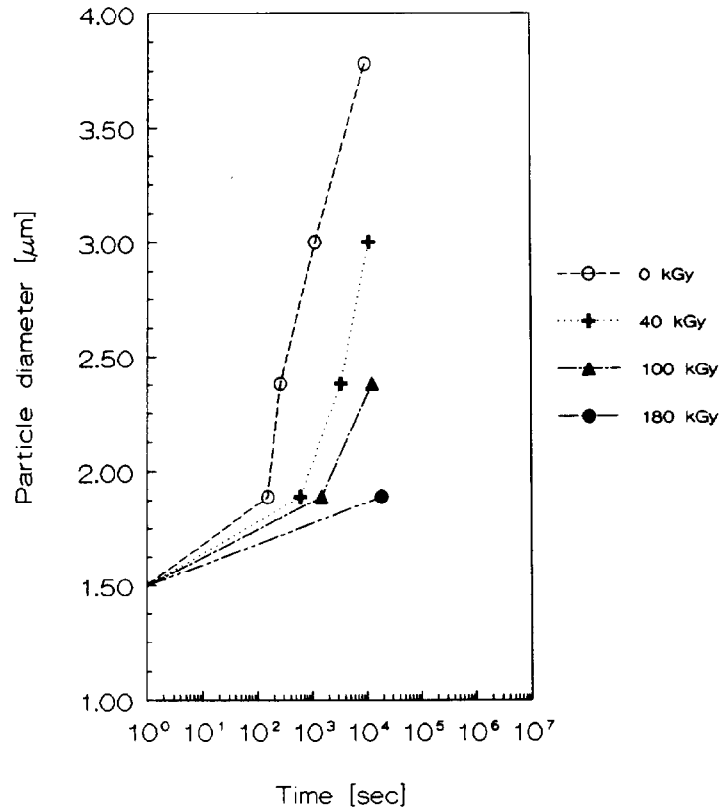
FIG. 12. Experimental coalescence times of Fig. 9 plotted on the logarithmic times scale of Fig. 11. The points indicate the experimental times, needed for subsequent (stepwise) coalescence steps to occur (similar to the calculated values in Fig. 11) and are obtained from the drawn curves in Fig. 9.

LDPE blend the maximum degree of crosslinking of the LDPE phase was approximately 70% at a dose of 200 kGy. This implies that there still is a considerable amount of noncrosslinked material (= sol) present, which has a lower viscosity than measured for the complete material (= sol + gel). This noncrosslinked material may flow during the long period of steady testing (break-up and coalescence) and very low shear rates, and hardly influences the results under dynamic testing conditions during the dynamic mechanical measurements.

Another explanation for the observed phenomenon may be that crosslinking of the LDPE phase occurs less efficient in a PS surrounding. This implies that the viscosity of LDPE in the blend may be somewhat lower than measured for the irradiated homopolymer. This shielding effect of the phenylrings has been observed by some researchers in a polymer blend with an intimate contact between the two phases [Nguyen and Kausch (1984), Schulz and Mankin (1976)]. Witt (1959) reported that in a blend of immiscible PS and polybutadiene (PB) the radiation induced crosslinking of PB occurred to the same extent as for pure PB. However, our experiments showed that there is some shielding in an extrusion prepared blend of PS and LDPE. Witt does not report about the characteristic dimensions in his experiments and, compared to our experiments, measured the degree of crosslinking with relatively low PS content (< 75%). The extent of shielding very likely depends on the amount of contact between matrix and dispersed phase, i.e., the typical particle dimensions and adhesion between matrix and dispersed phase. Consequently, the effect of shielding will be negligible in the special samples of experiment 2, where the diameter of the threads is two orders of magnitude larger than in the extrusion prepared blends and where no adhesion between threads and matrix is present. Also the absence of a yield stress cannot be accounted for by shielding effects. Using higher irradiation doses will eventually yield the same crosslinked fractions in the blends as in the homopolymer. Therefore at least at the highest dose a yield stress should be observed, but even at this dose the distortion amplitudes continuously increased in time, see experiment 2. In the samples for the coalescence experiment (with small LDPE dimensions, see experiment 3), some shielding might occur. However, again at the highest doses, the differences in crosslinked LDPE fraction between the blends and the homopolymer are small, whereas also at these doses the differences between the model prediction of the coalescence rates and experimentally determined ones are large.

The validity of the prediction of the coalescence rate is, however, somewhat doubtful, at least quantitatively. Formulas have been used which were originally derived for two equal sized colliding droplets. However, in the blends there is a distribution of particle sizes and particles influence each other.

All the results nevertheless indicate that irradiation is less effective than one should expect.

CONCLUSIONS

Both break-up and coalescence are delayed to a large extent if the dispersed phase of a blend is crosslinked with electron beam irradiation. Fixation of morphologies, during a heating experiment, is only possible when heating lasts for only a short period of time. However, when heating continues, both break-up and coalescence still occur. With the model for thread break-up of Newtonian fluids the delay of the break-up process can be explained qualitatively. However, break-up occurs faster than would be expected for nonirradiated materials with a comparable viscosity. Crosslinking via electron beam irradiation does not generate a yield stress which would prohibit the flow of the dispersed phase completely and would prevent thread break-up via Rayleigh distortions. Use of the models of fully mobile and fully immobile interfaces, led to extreme, unrealistic, predictions of the coalescence rates in our model system. In addition, the predictions of coalescence times via the model of partly mobile interfaces are only in qualitative agreement. Coalescence also occurs faster than would be expected. An explanation could be that complete crosslinking of the dispersed phase is not possible. This implies that crosslinked LDPE may act as a bimodal material, i.e., a low viscous noncrosslinked material which is hindered by an incomplete network. This hindrance causes the stabilizing effect, which is however, less effective than would be expected for (homogeneous) materials with comparable high viscosities but which are not crosslinked.

Further research concerning the yield stress will be performed using other unconventional experimental methods such as the flow between two pistons [Vos *et al.* (1990)]. Moreover, the internal flow in the dispersed phase will be studied in more detail, using an elongational flow field, similar to that of Bentley (1985), adapted for measurements in the melt.

It must be emphasized that the processing step used (heating in a press) represents an extreme case, because hardly any shear deformation was induced on the materials. Preliminary research concerning stability of morphology under high shear rate conditions, in injection moulding, indicates that under these conditions the fixing of the morphology is even less pronounced.

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