Electron beam irradiation of polymer blends

Citation for published version (APA):
Gisbergen, van, J. G. M. (1991). *Electron beam irradiation of polymer blends*. [Phd Thesis 1 (Research TU/e / Graduation TU/e), Chemical Engineering and Chemistry]. Technische Universiteit Eindhoven. https://doi.org/10.6100/IR347807

DOI:
10.6100/IR347807

Document status and date:
Published: 01/01/1991

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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• The final published version features the final layout of the paper including the volume, issue and page numbers.

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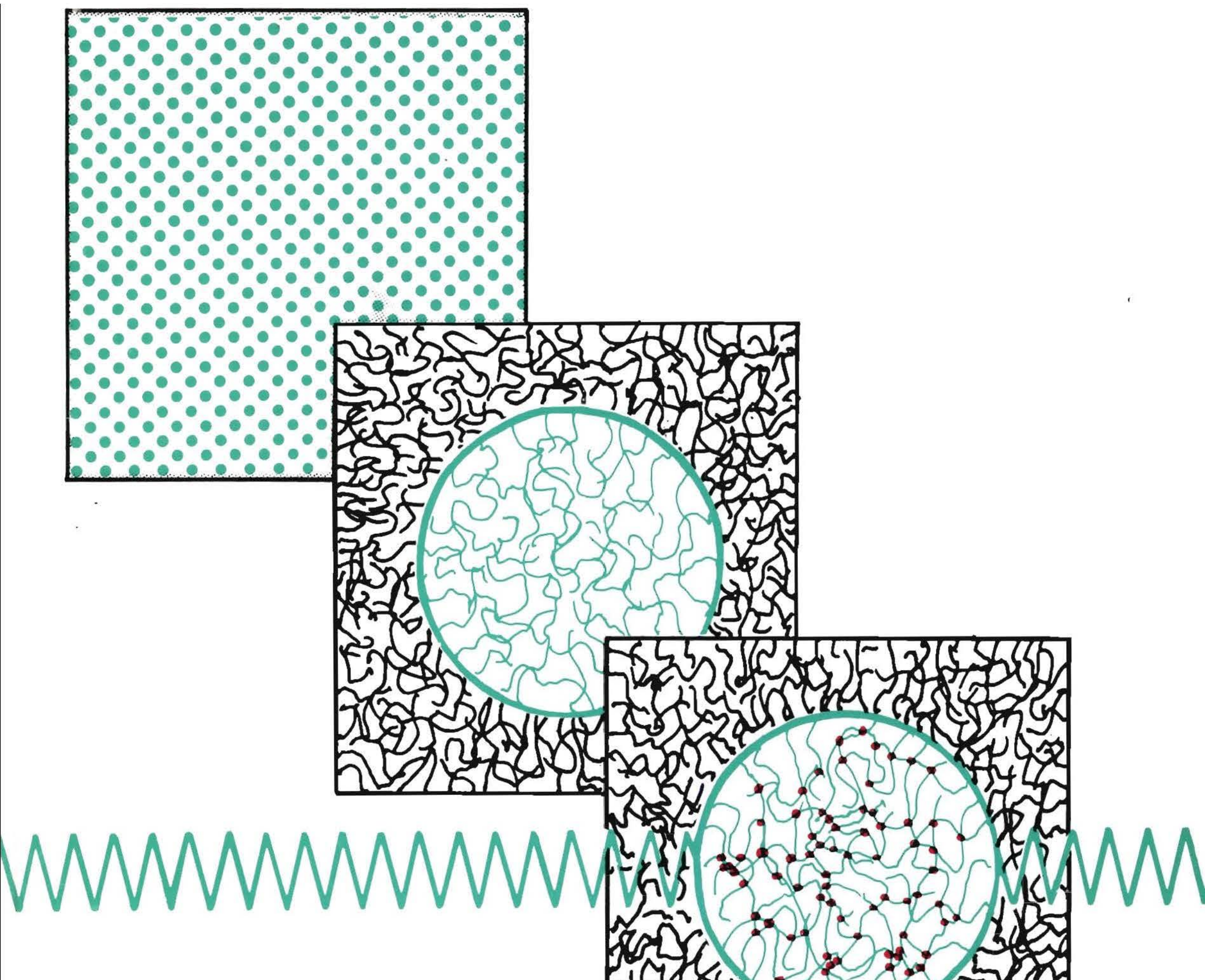
ELECTRON BEAM IRRADIATION OF POLYMER BLENDS



JOS VAN GISBERGEN

ELECTRON BEAM IRRADIATION
OF
POLYMER BLENDS

Omslag ontwerp: Sijbrand van Eck

ELECTRON BEAM IRRADIATION
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POLYMER BLENDS

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof. ir. M. Tels, voor een commissie aangewezen door het College van Dekanen in het openbaar te verdedigen op dinsdag 26 februari 1991 te 16.00 uur

door

JOSEPHUS GERARDUS MARIA VAN GISBERGEN

geboren te Hooge en Lage Mierde

Dit proefschrift is goedgekeurd door
de promotoren : prof. dr. P.J. Lemstra
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en de copromotor : dr. N. Overbergh

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Abbreviations of polymers used in this thesis

ABS	acrylonitrile butadiene styrene blend
EPDM	ethylene propylene diene monomer rubber
EPR	ethylene propylene rubber
HDPE	high-density polyethylene
HIPS	high-impact polystyrene
(L)LDPE	(linear) low-density polyethylene
PA	polyamide
PB	polybutadiene
PE	polyethylene
PIB	polyisobutylene
PP	polypropylene
PMMA	polymethylmethacrylate
PPE	polyphenylene-ether, (poly 2,6 dimethylphenyl-1,4 oxide)
PS	polystyrene
PTFE	polytetrafluoroethylene
PVC	polyvinylchloride
PVME	polyvinylmethylether
SAN	styrene acrylonitrile copolymer
SB	styrene/butadiene diblock copolymer
SEP	styrene/ethylene-propylene diblock copolymer

Symbols

A = interfacial area [m^2]
Ca = Capillary number
E = Young's modulus [N/m^2]
F = Force [N]
G_c = G-value for crosslinking [$(100\ ev)^{-1}$]
G_s = G-value for chain scission [$(100\ ev)^{-1}$]
h = thickness of layer between two colliding droplets [m]
M_n = number average molar mass [kg/mole]
M_w = weight average molar mass [kg/mole]
p = viscosity ratio
R = radius [m]
S = sol fraction
t = time [s]
V_1 = specific volume [m^3/kg]
V_2 = fraction of uncrosslinked material

α = amplitude of distortion [m]
γ = total shear
γ = shear rate [s^{-1}]
ε_b = elongation at break [%]
η = viscosity [Pas]
λ = wavelength of distortion [m]
ρ = density [kg/m^3]
σ = interfacial tension [N/m]
σ_y = yield stress [Pa]
τ = shear stress [Pa]
ϕ = volume fraction of polymer in swollen sample
χ = Flory Huggins interaction parameter or
χ = wavenumber
ω = frequency [rad/s]

CHAPTER 1

INTRODUCTION

1.1 Structured Polymer Blends

Blending of polymers is, in principle, a flexible method to generate new polymeric materials. Moreover, a large number of unique properties can only be obtained when different polymers are combined, despite the continuous development of *new* polymers via direct chemical synthesis [1-5].

One has to distinguish between *miscible* and *immiscible* polymer pairs. Due to the high molar mass, the entropy of mixing is relatively low and consequently specific interactions are needed to obtain polymer blends which are miscible on a molecular scale. For this reason, the number of miscible polymer pairs is limited to about 300 [6]. Despite the fact that processing of miscible blends is relatively straightforward and tailor-made properties can be obtained by just changing the volume fractions, only a few pairs have been commercialized. A well known example is the blend of polystyrene (PS) and polyphenylene-ether (PPE).

In the case of immiscible pairs, homogeneous mixing on a molecular level cannot be obtained and, consequently, a heterogeneous mixture results after blending. The ultimate properties are strongly influenced by the morphology, i.e. the size, shape and the distribution of the constituents in the blend.

The distinction between miscible and immiscible polymer blends is less straightforward than suggested above. The miscibility of a polymer pair A and B depends on the temperature, pressure, composition and shear (rate) and a miscibility region may be observed in relation to these parameters [1].

Another term frequently encountered in polymer blending is *compatibility*. Utracki [3] defines a compatible polymer blend as: " a commercially attractive *immiscible* polymer mixture, normally homogeneous by visual inspection". In order to achieve this goal, compatibilizers (surface active copolymers, located at the interface of the constituents) are often added to the blend or are generated in situ, in order to decrease the interfacial tension and increase the adhesion.

A classical example of an immiscible polymer blend is the dispersion of rubbery particles in a glassy polymer to improve the impact strength. The impact properties of such a blend not only depend on the total volume fraction of rubber, but also on the rubber particle size and shape and on the adhesion between matrix and rubber [7]. These immiscible, but compatible, polymer blends are usually prepared via reactor blending with optimum control of particle size, for example acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS).

An alternative method is melt-blending, which offers great flexibility in terms of mixing various polymer pairs and generating a tailor made morphology for a specific application: *a structured polymer blend.* Various morphologies can be induced during mixing of one immiscible polymer pair: fibrillar vs. co-continuous morphologies, matrix/ dispersion and layered structures, illustrated in Figure 1.1 for the model system polystyrene/high-density polyethylene (PS/HDPE). Layered structures find, for example, application as barrier blends for packaging to combine the resistance against water- and gas transport. A layered structure of the blend constituents with the layers perpendicular to the direction of transport, will result in optimum barrier properties [8,9].

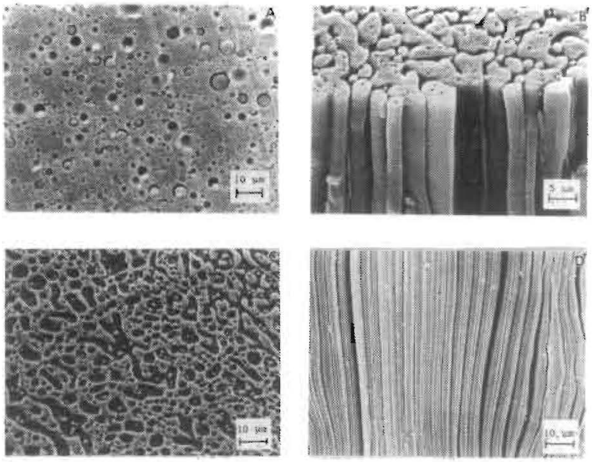

Figure 1.1 Different morphologies for a blend of PS and HDPE, obtained via melt-blending: droplets (a) or fibrils (b) in a matrix, a co-continuous (c) and a stratified structure (d). Reproduced from ref [29], with permission.

The major complicating factor in the case of melt-blending is the intrinsic instability of a morphology in the melt which depends on shear or elongational stress and rate, viscosity ratio, volume fraction and temperature, and adapts continuously to changes in processing conditions. In practice, this implies that a morphology, carefully induced by the (raw material) manufacturers, could be completely lost upon further processing by (custom) moulders. Consequently, detailed knowledge of mixing and processing equipment, as well as micro-rheological characterization of the mixing process, is necessary to understand how different morphologies can be prepared and preserved through various subsequent processing steps.

In this thesis, results will be presented concerning electron beam (EB) irradiation of *immiscible* polymer blends. EB irradiation is a type of high energy radiation involving energies in the order of 100 keV to 10 MeV [10,11]. Despite the large difference in energy levels between the EB irradiation and the bond energy in organic matter, 10-30 eV, no complete deterioration occurs (see chapter 2 for details). Depending on their chemical structure, polymers may be relatively inert towards irradiation, undergo crosslinking or show pronounced chain scission [10,11].

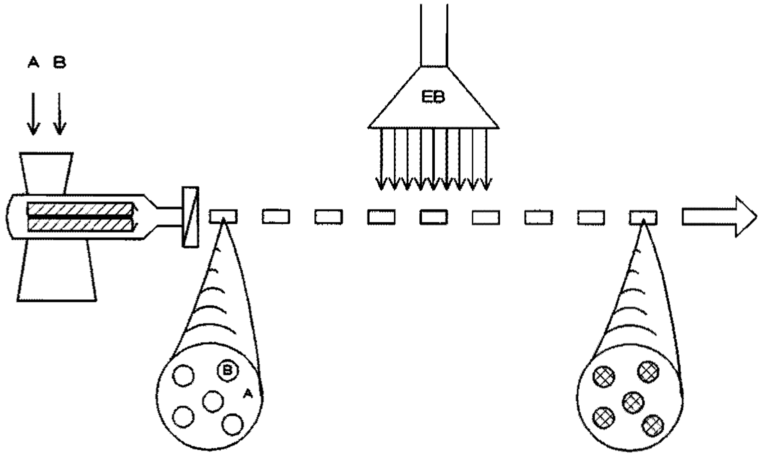

Figure 1.2 *Schematic view of crosslinking a dispersed phase B using electron beam irradiation between the blending and final processing step in order to achieve morphology fixation.*

A possibility to use EB irradiation in melt-blending, is illustrated in Figure 1.2. Two polymers are selected with appropriate beam response, for example polymer B crosslinks and polymer A is either inert or will undergo chain scission. Polymer B is dispersed in polymer A and, after quenching, the blend is pelletized. Upon subsequent EB irradiation the dispersed phase B will crosslink and the morphology is fixed for subsequent processing steps, solving the problem mentioned above.

Before presenting the aim of the thesis, in detail in paragraph 1.4, some basic aspects are discussed concerning impact modification of polymers, the paradigm of the importance of a morphology, and micro-rheology in polymer blending.

1.2 Impact Modification

Upon deformation, polymeric materials may fail differently, depending on their chemical structure and the test geometry used. Two mechanisms can be distinguished [7,12-27].

1) Crazing, followed by fatal crack formation. A craze can be considered as a microcrack, bridged by microfibrils. Upon further loading the microfibrils will break and the microcrack will grow until brittle fracture of the material occurs [12].
2) Shear yielding, with energy dissipation via shear band or diffuse shear zone formation. Although the material behaves tough, a sensitivity towards flaws and notches is still present in these materials.

Failure via crazing or yielding is to some extent determined by the internal coherence of the material as reflected in the entanglement density [17]. Crazing is favoured by a low entanglement density, whereas a higher entanglement density results in shear yielding. PS, styrene acrylonitrile (SAN) and polymethylmethacrylate (PMMA) are well known examples of polymers which craze upon loading, whereas PPE and polyamide-6 (PA-6) are examples of yielding materials. Often both mechanisms occur simultaneously, for example in polypropylene (PP) [19]. Depending on the testing conditions, deformation rate, temperature and geometry of the test samples, one of the mechanisms will dominate.

Fracture is normally initiated at flaws or notches, which act as stress concentrations in the material and further deformation occurs, uncontrolled, in a relatively small volume. In order to control the initiation and concentration of crazes or shear bands, rubbery particles may be dispersed in the polymer. Since the modulus of a rubber is generally lower than the one of the matrix material, stress concentrations near the equator of the rubber particle result. Craze or shear band formation will start at these stress concentrations. A larger deformation volume will be generated, which implies more energy dissipation. At constant rubber concentration, smaller rubber particles will result in a more homogeneous and larger deformation zone.

1.2.1 Multiple Crazing

It was reported that, for various polymers which craze upon loading, different optimum particle sizes exist for maximum impact properties at constant rubber volume fraction. For HIPS this optimum particle size is approximately 2-5 µm, for ABS 0.3 µm and for polyvinylchloride (PVC) 0.1 µm [7,20,21]. Donald and Kramer [20,21] showed experimentally, that particles with smaller sizes than the optimum one will not initiate crazes. The deformation volume induced becomes too small for generation of even the thinnest craze [22].

This optimum particle size for impact toughening of the polymers, demonstrates the importance of the morphology. Another example can be found in the blends HIPS and ABS, which are prepared directly in the

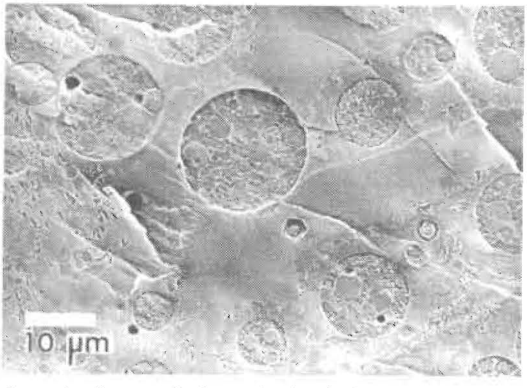

Figure 1.3 A typical morphology in high impact polystyrene (HIPS). A composite dispersed phase is present, consisting of small PS inclusions in a dispersed PB phase.

reactor. Butadiene rubber is polymerized (and crosslinked) and subsequently styrene or styrene-acrylonitrile mixtures are added. A typical morphology results, as shown for HIPS in Figure 1.3. Small inclusions of the matrix material, PS, can be found in the dispersed rubbery particles, increasing the effective volume of the dispersed phase. As a consequence, an efficient impact modification is obtained with a relatively small (overall) rubber content.

Apart from the controlled generation of crazes, rubber particles also slow-down the growth of crazes into a fatal crack. Good adhesion between the rubber and the matrix can improve the impact properties, as a result of retarding craze propagation. In HIPS and ABS, prepared via chemical synthesis, sufficient adhesion is present as a result of grafting of the PS or SAN onto butadiene. However, in most blends prepared via melt-blending, compatibilizers have to be added to the blend or have to be formed in situ to ensure sufficient adhesion. The use of a compatibilizer simultaneously results in a reduction of the particle size due to a decrease in interfacial tension.

Craze initiation and growth can be influenced by the degree of crosslinking of the dispersed rubber phase [7]. Crosslinking enhances the inherent coherence of the dispersed rubber and will delay craze propagation as such, provided that sufficient adhesion is present. If the modulus of the rubber phase increases too much, the controlled initiation of crazes is seriously affected [7].

1.2.2 Multiple Shear Yielding

Rubbery particles in a yielding matrix release, locally, the hydrostatic tension via cavitation or delamination of the rubber. Subsequently, energy dissipation may occur via excessive yielding of the matrix, which is initiated at the particle/matrix interface [16,23,24]. Experimental results have been reported by Borggreve [16,26,27] and Wu [14,25] for PA/EDPM blends. It was shown that a "Brittle-to-Tough" (BT) transition exists at a well defined temperature, which uniquely depends on the interparticle distance, taking into account both the effect of volume fraction and the average rubber particle size. The general condition for toughening is that the interparticle distance should be below a critical value. At a constant rubber volume fraction, this implies that a lower BT transition temperature can be obtained at a smaller particle size, see figure 1.4. This toughening criterion is valid for all polymer blends which are toughened by increased shear yielding of the matrix. An unambiguous explanation for this transition is still lacking.

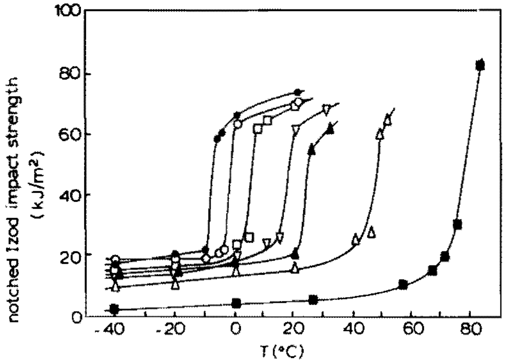

Figure 1.4 Brittle-to-Tough transitions for PA-6/EPDM blends at a constant EPDM volume fraction of 26%. Parameter: particle size (μm). Reproduced from ref [16], with permission. ■, *PA-6,* Δ, *1.59,* ▲, *1.20,* ▽, *1.14,* □, *0.94,* ○, *0.57,* ●, *0.48.*

In order to obtain a small particle size in PA-6/EPDM blends, maleic anhydride modified EPDM was used [26]. This in situ compatibilization, in principle, increases the adhesion between matrix and rubber as well. This does, however, not influence the impact properties of the blend, provided that a minimum level is present [26].

On the other hand, improved impact properties were obtained with an enhanced cavitation ability of the dispersed rubber [27].

1.3 Micro-rheology in Polymer Blending

The importance of the morphology of immiscible polymer blends has been illustrated in § 1.2. In this paragraph, some basic micro-rheological processes and parameters will be discussed which are important in the development of the morphology during processing.

A review on existing literature on micro-rheology during mixing of Newtonian fluids, extended to polymeric systems, has been given by Elmendorp [28]. Elemans [29] combined these results with a detailed analysis of continuous mixers, yielding expressions for the temperature, residence time, shear stress, shear rate and total shear, in dependence of screw geometry and operating conditions.

Traditionally, two processes are distinguished in blending of polymers: *distributive* and *dispersive* mixing. The first process describes the homogeneous distribution of the second phase over the matrix, whereas the second one causes large particles to break up into smaller ones. During actual mixing, both processes occur simultaneously.

1.3.1 Distributive Mixing

At the start of a blending process, the size of the second phase is relatively large and will deform affinely with the matrix. Two counteracting stresses are operative: the deforming shear stress (τ) and the interfacial stress (σ/R). Their ratio is usually expressed as the, so-called, capillary number (Ca), see eq. 1.1.

$$Ca = \tau R/\sigma = \eta_m \dot{\gamma} R/\sigma \qquad (1.1)$$

where: $\dot{\gamma}$ = shear rate (s^{-1})

η_m = viscosity of matrix (Pas)

σ = interfacial tension (N/m)

R = local radius of particle (m)

Typical shear stresses in polymer melts are in the order of 10^4 N/m^2. The local radius of a dispersed droplet, in the early stages of the mixing process, is approximately 10^{-3} m (size of a pellet) and σ is typically 10^{-2} N/m. It is evident that the deforming shear stresses are much larger than the counterbalancing interfacial stress and consequently affine deformation will occur.

The total shear (γ) and the number of reorientations (n) are the only factors determining the affine deformation in distributive mixing. This was clearly demonstrated by the "classical" experiments of Ng and Erwin [30]. Coloured slices of polymers were placed between two concentric cylinders. After melting the polymer, one of the cylinders was rotated, see Figure 1.5. The total interface (or number of radially formed layers) is a measure for distributive mixing and is, in the absence of reorientation, directly proportional to the total shear γ, see Figure 1.5a.

$$A = A_0\gamma \qquad (1.2)$$

where: A = interfacial area

A_0 = initial interfacial area

If the layers are reoriented with respect to the shearing direction, distributive mixing becomes much more efficient. This is illustrated in Fig. 1.5b. The rotation is stopped and the polymer melt is quenched. Subsequently the polymeric ring is cut into parts, which are turned over 90 °, an ideal reorientation, and are further sheared after reheating.

This procedure can be repeated n-1 times, and equation 1.2 transforms into:

$$A = A_0(\gamma/n)^n \qquad (1.3)$$

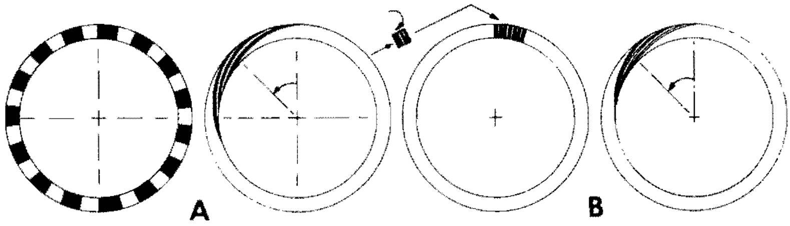

Figure 1.5 Effect of total shear (a) and reorientation (b) of black and white segments on the efficiency of distributive mixing. Reorientation is achieved by stopping the shearing motion in step (a), cutting the ring in parts, and rotation of the parts over 90°. After reference [30], and reproduced from [29].

Static mixers are the best examples of this very effective, exponential, way of distributive mixing. However, also in corotating twin screw extruders, material is continuously reoriented relative to the shearing direction, due to the take over of the melt from one screw to the other in the intermeshing region.

1.3.2 Dispersive Mixing

As discussed above, the dispersed phase deforms affinely with the fluid motion and long slender bodies will result. This process will continue until the Capillary number approaches unity. Consequently, if local radii are in the order of 10^{-6} m, resulting in $\sigma/R = 10^4$ N/m^2, this limit is reached. The long slender bodies become unstable due to interfacial tension driven Rayleigh distortions, which result in the formation of droplets as illustrated in Figure 1.6 [31-33]. The growth

shown in Figure 1.6. The rate of coalescence is mainly determined by removal of the layer of matrix material between two colliding droplets rate of the distortion is maximum at one, dominant wavelength and depends on the diameter of the thread. During shearing, a continuous thinning of the thread occurs and the dominant wavelength changes continuously. Consequently, the threads are stabilized because break-up via Rayleigh distortions is retarded [34]. In regions of relatively stagnant flow, threads break up very quickly because of the large driving force σ/R (and R is very small).

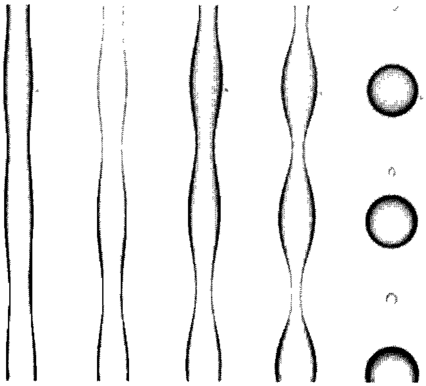

Figure 1.6 Break-up of molten PA-6 threads in a PS matrix, via interfacial driven Rayleigh distortions, after ref. [29,39], with permission.

The droplets formed are, subsequently, subjected to shear stresses. Depending on the local Capillary number, the droplets can either be deformed in new (long slender) threads in regions with relatively high stresses, they can be deformed and broken in regions of intermediate stresses or can be deformed only slightly because of the counterbalancing interfacial tension. The dependence on the Capillary number has been investigated thoroughly by Grace, who performed a large number of experiments in shear and elongational flow, using Newtonian liquids with a large range of viscosity ratios [35]. The critical value of the Capillary number leading to break-up was determined and proved to be strongly dependent on the viscosity ratio p, see Figure 1.7.

$$p = \eta_d/\eta_m \tag{1.4}$$

where: η_d = viscosity of dispersed phase

As can be inferred from Figure 1.7, dispersive mixing is most efficient when liquids are mixed with approximately the same viscosity. Figure 1.7 further shows that a large difference exists between the (efficiency of) shear and elongational flows, especially if $p \neq 1$. For high viscosity ratios ($p>4$), break-up of dispersed particles is not possible in shear, which is caused by rotation of the particles in these types of flow. Elongational flows, however, are irrotational and consequently dispersive mixing is still possible.

Addition of a compatibilizer, located at the interface between matrix and dispersed phase, will result in a decrease in the interfacial tension. This will cause a smaller particle size at the same viscosity ratio and applied shear stress.

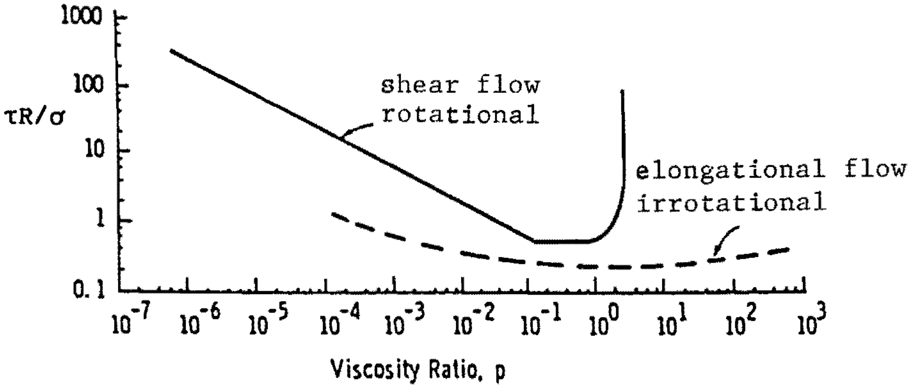

Figure 1.7 *Critical capillary number as a function of viscosity ratio in shear and elongational flow. For Ca numbers below this critical value, the droplets are stable. Data from reference [35], reprinted from [29].*

Up to now, individual droplets have been considered. In practice, droplets will interact and, already at relatively low concentrations, coalescence of particles will play an important role. Coalescence is shown in Figure 1.8. The rate of coalescence is mainly determined by removal of the layer of matrix material between two colliding droplets

[28,36]. The rate of gravity-induced coalescence can be expressed as:

$$dh/dt \sim h^{\alpha}/(\eta_m R^{\beta}) \qquad (1.5)$$

where: h = thickness of the matrix layer between two colliding particles

α and β are adjustable parameters

The parameters α and β are determined by the mobility of the interface of matrix and dispersed particle. Immobilization of an interface can, for example, be obtained via the addition of a compatibilizer. For fully mobile interfaces α and β are both 1. For immobile interfaces they are 3 and 5 respectively. This implies that coalescence is much slower for immobilized interfaces.

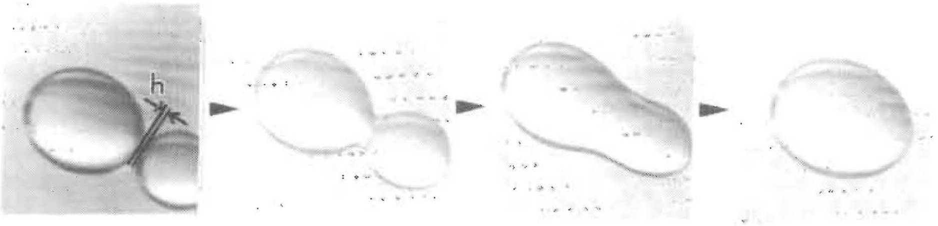

Figure 1.8 Example of coalescence of droplets

Processes and equations mentioned above were, in principle, introduced for Newtonian systems. The applicability for polymeric systems is still a matter of debate, although it has been shown that these processes also occur during polymer blending [28,29,37-39]. Moreover, Elemans et al. [29,39] showed that equations derived for thread break-up in Newtonian systems can be used quantitatively to calculate interfacial tensions in polymeric systems, provided that the zero shear viscosity of matrix and thread can be determined accurately.

which now has been cooled only after some time. As a consequence, the threads are fully desintegrated into droplets via Rayleigh distortions.

A preliminary study concerning the influence of time on the different processes occuring in micro-rheology during mixing has been performed by Janssen [42]. The translation of the typical timescale of the processes with model liquids to real polymer blends, is performed with the dimensionless time (t*):

$$t^* = t(\sigma/\eta_m R) \qquad (1.6)$$

where: t = actual time of process

Compared to real polymer blends, in systems of model liquids the typical dimensions (R) are approximately a factor 1000 larger and, consequently, easy accessible for observations. The viscosity (η_m) of model liquids is reduced by the same factor. Hence, the factor $\eta_m \cdot R$ stays approximately constant, which implies that the typical timescales for the study of model liquids compare well with those of polymer blends in practice.

Via a systematical variation of volume fractions and viscosity ratios in a blend of PB and EPDM rubber, Avgeropoulos [43] composed a phase diagram based on the overall effect of coalescence, distributive and dispersive mixing during two roll milling. A schematic representation is given in Figure 1.10. In principle three morphologies can be induced: a matrix of A and dispersion of B, a co-continuous structure and a matrix of B and dispersion of A. The component with the lowest viscosity tends to form the continuous phase, even at a volume fraction less than 50%. This principle has been verified for various blends, e.g in a blend of PS and HDPE [44].

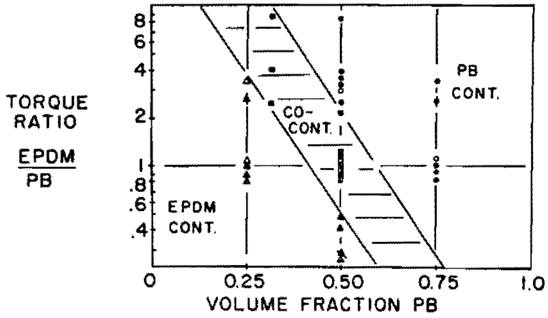

Figure 1.10 Systematic phase diagram as a function of volume fraction and viscosity (torque) ratio, based on the overall effect of coalescence, distributive and dispersive mixing, composed for a blend of PB and EPDM [43], but generally applicable to any polymer blend. Three morphologies can be distinguished: a continuous EPDM phase, a co-continuous structure and a continuous PB phase.

1.4 Scope of the Thesis

The objective of the thesis is to introduce the use of Electron Beam (EB) irradiation in the modification of immiscible polymer blends, focussing on (micro-)rheology and mechanical properties.

In Chapter 2, some aspects of the interaction of high energy irradiation with polymer systems are discussed, including a brief review of the existing literature on the modification of polymer blends, using radiation.

Chapter 3 deals with a fundamental study concerning the fixation of highly non-equilibrium morphologies via EB-induced crosslinks in the dispersed phase. Thread break-up via Rayleigh distortions and coalescence are investigated, using a model system of inert PS (matrix) and crosslinkable LDPE (dispersed phase).

A unique possibility for EB irradiation is in the toughening of PP with EPDM rubber as discussed in Chapter 4. Irradiation is used to solve the contradiction between excellent processability and optimum impact resistance via controlled scission of the PP matrix and sufficient stabilization of an optimum morphology via crosslinking of the dispersed EPDM phase.

In Chapter 5 results are presented concerning a more detailed rheological characterization of irradiated PP/EPDM blends. The influence of scission of the PP matrix, crosslinking of the EPDM phase as well as interaction between rubber and matrix on the resulting rheological properties will be discussed.

Morphological details of ternary PP/EPDM/HDPE blends will be presented in Chapter 6. The influence of radiation on the impact properties will be demonstrated.

In Chapter 7 the impact properties of PS/EPDM blends will be discussed in relation to radiation-induced grafting at the interface.

Chapter 8 summarizes some preliminary results concerning the applicability of controlled scission of a second phase. In a PA-6/PIB blends, the aim is to enhance the cavitation ability of the dispersed PIB rubber in order to improve the impact properties of the blend. Controlled porosity is the ultimate goal for similar experiments with LLDPE/PIB blends.

Finally, some remaining problems concerning the irradiation of polymer blends are discussed in Chapter 9.

This thesis is based on a collection of papers which have been published in, or submitted to, various journals [45-51]. Furthermore, the author has contributed to some papers on related subjects [44,52,53] not presented in this thesis.

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CHAPTER 2*

IRRADIATION OF POLYMERS AND POLYMER BLENDS: PRINCIPLES AND APPLICATIONS

2.1 Introduction

The simultaneous growth of both the polymer industry and nuclear technology in the first two decades after world war II, has resulted in an outburst of papers concerning the interaction of high energy radiation with polymeric materials. Several books cover most results from this period and still act as important references nowadays [1-4]. Also more up to date reviews with the latest developments on modification of homopolymers and blends, dosimetry and equipment appeared [5,6] or are in preparation [7]. In this chapter some main principles will be discussed.

In irradiation of polymeric materials, two objectives exist: the study and development of polymers with a *high resistance* to radiation (e.g. application in nuclear power reactors) vs. the search for materials with a high radiation sensitivity to *obtain better properties*. The distinct interest in irradiation of long chain polymers is related to the fact that, in contrast to low molar mass species, large changes in the physical and mechanical behaviour can be obtained at relatively low doses. For example, crosslinking can be induced via irradiation, involving only a few chemical changes per macromolecule, whereas the properties change completely. The same effect can usually be obtained by thermal energy (peroxide crosslinking/vulcanisation) but in this case the whole

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* *Reproduced in part from Van Gisbergen, J.G.M. and Overbergh, N., Progress in Polymer Processing, vol 3: Eds. L.A. Utracki, J. Silverman and A. Singh, Hanser Publ., Münich, in press.*

system has to be heated in order to induce only a few chemical changes per macromolecule. Especially for curing of coatings on substrates, radiation at ambient temperature is fast and efficient without the necessity of heating the whole system to the reaction temperature.

Nuclear vs. electronic sources

Several sources of high energy radiation are available, which can be divided in two categories:

1) α, β and γ-radiation from *naturally radioactive materials* and
2) radiation produced by *high voltage machines* like accelerated electrons and X-rays.

The effects produced from the various radiation sources in polymeric materials are not basically different, since the energy carried by each particle or photon considerably exceeds the typical binding energy in matter. Moreover, the secondary reactions induced by the primary photons or particles are rather similar (will be discussed below). Consequently, the choice of a radiation source is mainly determined by experimental considerations such as the beam penetration and intensity, cost, availability and, last but not least, safety. The two types of irradiation mostly used in polymer modification are accelerated electrons (EB) and γ-irradiation.

A main practical difference, due its corpuscular character, is the low penetration depth of electrons compared to γ-irradiation. In Figure 2.1, the halve value thickness (hvt, i.e. the thickness where the energy is only half of its initial value) as well as the penetration (range) are compared for various types of irradiaton and various irradiation sources as a function of their energy [8]. For electrons with an energy of 100 keV, the maximum penetration is approximately 50 μm in materials with unit density, which increases to approximately 1.5 cm for an acceleration voltage of 3 MV. The penetration depth for γ-rays can easily exceed 20 cm.

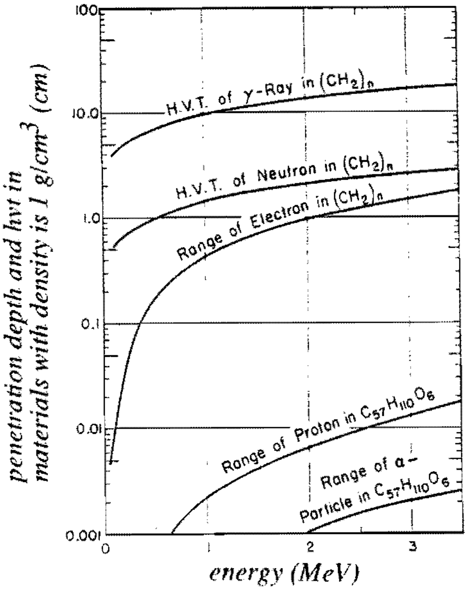

Figure 2.1 *Comparison between the penetration depth (range) or halve value thickness (hvt) of various types of irradiation in matter with a density of 1 g/cm^3 [8]*

Important disadvantages of γ-irradiation, compared to accelerated electrons are the low intensity of the source, which can differ a factor of more than 10000, and safety regulations related to nuclear energy.

Most of the processes induced by irradiation depend on the total energy absorbed and very little on the type of radiation or its intensity. Consequently, it will take much more time to induce a change in a sample using γ-irradiation compared to EB irradiation.

Both, EB and γ-radiation sources, require strict regulations for safety. In the case of EB radiation, shielding of the equipment is necessary, especially for protection related to X-rays which are generated by de-accelerated electrons (Bremstrahlung). Low energy accelerators are mainly self-shielded. In the case of γ-irradiation, shielding is even more important due to the continuous radiation and the high penetration depth.

Equipment

^{60}Co is often used as the source for γ-irradiation, which desintegrates into two discrete photons of 1.17 MeV and 1.33 MeV respectively.

Accelerated electrons can be generated in various ways and with various energies. Especially, in the low energy region, up to 500 kV, developments are still continuing. The Electrocurtain and the RPC Broadbeam are two relatively new machines worthwhile to be mentioned [9,10]. Due to the low acceleration voltage these machines are self-shielded which, however, also implies a low penetration depth. Consequently, applications are mainly found in the surface modification technique, especially in curing of coatings, and cannot be used for bulk (tubes, pellets, etc.) modification, which requires acceleration voltages above 1 MV for complete penetration of the sample. For bulk modifications, usually 'Van de Graaff' (schematically shown in Figure 2.2) and linear accelerators are used.

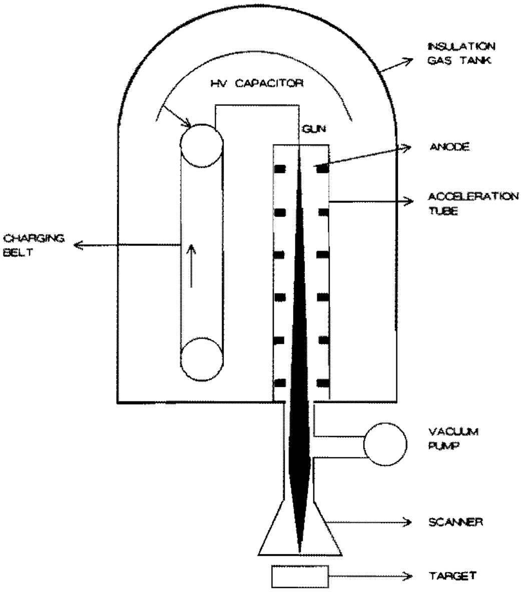

Figure 2.2 Schematic representation of a 'Van de Graaff ' electron beam accelerator.

In table 2.1 the characteristics of some radiation sources are summarized.

Table 2.1 Some characteristics of frequently used radiation sources.

source	voltage	penetration	dose rate	safety	application
Co^{60} γ-rays, photons	1.17 and 1.33 MV	high, >200 mm	low	shielding required	bulk
Van de Graaff EB HV*, corpuscular	0.5-10 MV	low, 0.3-30 mm	high	shielding required	bulk
Electrocurtain EB LV*, corpuscular	100-500 kV	very low, < 0.3 mm	high	self shielded	surface coating

**HV and LV, high and low voltage respectively*

Basic reactions

During the passage of high energy particles or photons through matter, energy is transferred via interaction with the electrons and nuclei of the medium. Charlesby [1] summarized the basic mechanisms of energy exchange as follows:

1. *Ionization* - a process in which an orbital electron is removed from its parent nucleus, giving rise to a free electron and a positively charged (ionic) atom or molecule.
2. *Excitation* in which an electron is raised to a high energy level but remains bound to its parent nucleus. In this case, the atom or molecule remains neutral.
3. *Displacement* of a nucleus with or without its attendant electrons.
4. *Capture* by an atomic nucleus and transformation of the nuclear structure.
5. *Scattering* of incident particle or photon and emission of secondary radiation.

The range of energies mostly applied in practice of polymer irradiation, give mainly rise to ionization and excitation.

Electron beams of the energies used in radiation work lose most of their energy via the interaction with orbital electrons. The bound electron may be given sufficient energy to result in (direct) ionization or excitation and the incident particle will be scattered. Compton scattering, elastic collision of a photon with orbital electrons of the medium, is the main mechanism of energy transfer for γ-irradiation. The scattered photons, but especially the ejected fast electrons, will cause further ionizations and excitations. Therefore γ-rays are often considered as internal sources of electron radiation.

These basic processes will result in a broad variety of secondary reactions. For example, electrons may be captured, either with or without dissociation of the capturing molecule, reactive radicals will be formed, which cause combination or disproportionation of molecules, charge can be neutralized and intra- or intermolecular energy, radical or ion transfer will occur. The chemical structure of the irradiated medium determines which of these reactions overrules and induces the final modifications. For polymers the most important overall reactions are *crosslinking and main chain scission.* Side chain fracture and formation of decomposition products like gases and low molar mass material, formation and consumption of double bonds, are other important side reactions.

Radiation yield

It can be concluded from the previous section that upon irradiation a multitude of reactions will occur. Although it is not possible to identify all individual reactions, the sensitivity of a system to radiation can be expressed in the number of changes, e.g. crosslinking or chain scission, produced per 100 eV energy absorbed, the so-called G value [11]. In this definition no assumptions are made concerning the mechanisms of the reaction (see below, § 2.3).

Radiation dose

Many units have been used to express the energy to which a medium has been exposed. Nowadays, the official unity for radiation dose is the Gray (Gy). One Gray corresponds to an energy absorption of 1 J/kg. Irradiation doses in polymer modification are usually in the range of 10 - 250 kGy. The classical unit, which is still encountered frequently, is the Rad. One Rad equals 10 J/g or 1 MRad = 10 kGy.

Correct measurement of the doses, dosimetry, is required for optimum understanding of radiation chemistry. A dose of 1 MRad will by definition raise the temperature of water by 2.4 °C. (Corrections have to be made concerning heat loss, energy absorbed by container walls, backscattering etc.) Using this method, more easy to handle dosimeters can be calibrated. These dosimeters can be based on known physical or chemical changes like oxidation of ferrous sulphate to ferric sulphate, colorimetric methods, photographic methods and known changes in polymers, e.g. intrinsic viscosity.

2.2 Analysis of Crosslinking and Chain Scission

Crosslinking

In order to detemine the extent of crosslinking in a polymer, several methods can be used.

Via extraction, it is possible to determine the extent of gel (= unsoluble three-dimensional network) which has been formed upon irradiation, as well as the critical dose needed for gel formation. From this gelation dose it is possible to determine the G-value for crosslinking, provided that chain scission is negligible, according to equation 2.1 [12-14]:

$$D_c = 4.81 \cdot 10^6/(G_c M_w) \qquad (2.1)$$

where: D_c = gelation dose (kGy)
G_c = G-value for crosslinking
M_w = initial weight average molar mass before crosslinking (kg/mole)

The extent of crosslinking can also be derived from swelling measurements. From these measurements the molar mass between two crosslinks (M_c) can be obtained. Based on thermodynamic equilibrium and assuming that all polymeric chains are incorporated in the network, the following equation was derived by Flory and Rehner [12,15].

$$M_c = \frac{\rho V_1(\phi^{1/3} - \phi/2)}{\ln(1-\phi) + \phi + \chi\phi^2} \qquad (2.2)$$

where: M_c = molar mass between crosslinks (kg/mole)
ρ = density of polymer (kg/m^3)
ϕ = volume fraction of polymer in swollen sample
V_1 = specific volume of solvent (m^3/kg)
χ = Flory-Huggins interaction parameter

Flory has proposed a correction factor for imperfections such as chain ends [16]:

$$M_c' = M_c M_n/(2M_c + M_n) \qquad (2.3)$$

where: M_c' = true molar mass between two crosslinks
M_c = calculated with equation (2.2)
M_n = initial average molar mass

Since crosslinking via irradiation never results in complete incorporation of all polymer chains in the network, another correction is required. A method which originally has been introduced for chemical crosslinking occuring in the presence of a non-reactive solvent [17], can also be applied to correct for the diluting effect of uncrosslinked material during radiation treatment, see equation 2.4.

$$M_c'' = M_c V_2^{2/3} \tag{2.4}$$

where: V_2 = fraction of uncrosslinked material

M_c can also be calculated from other 'equilibrium' properties such as rubber modulus or maximum drawability [18].

Chain scission

Scission of the polymer main chain results in degradation upon irradiation. Molar mass determination yields the G-value for chain scission [14], provided that this process occurs randomly in the polymer main chain:

$$1/M_n = 1/M_o + 1.04 \cdot 10^{-4} G_s D \tag{2.5}$$

where: M_o = initial number average molar mass (kg/mole)
D = Dose (kGy)

Charlesby-Pinner relation

Crosslinking and chain scission usually occur simultaneously. Charlesby and Pinner have derived a semi-empirical equation to account for both chain scission and crosslinking [19]

$$S + \sqrt{S} = G_s/(2G_c) + 1/(2G_cP_nD) \qquad (2.6)$$

where: S = Sol fraction

P_n = number average degree of polymerization

This equation however, has only limited validity. In principle, it is restricted to polymers with an initial random molar mass distribution. At high doses, however, it also holds for other distributions, provided that scission occurs randomly and is proportional to the radiation dose.

2.3 Irradiation of Homopolymers

In table 2.2, G-values for crosslinking (G_c) and chain scission (G_s) are presented for some important polymers, including the polymers used in this thesis.

From table 2.2 it can be inferred that crosslinking dominates in PE since its G-value for crosslinking is higher than for chain scission. However, it is also evident that a degree of crosslinking of 100 % will never be obtained, since a part of the PE will undergo scission. Simultaneous occurrence of crosslinking and chain scission is even more pronounced for PP. G-values for crosslinking and chain scission are of the same order. Under normal atmospheric irradiation conditions chain scission prevails in PP up to doses of approximately 200 kGy [20]. In the case of polystyrene, crosslinking predominates. However, it is a factor 100 less sensitive than PE. This insensitivity is the result of the resonant nature of the styrene: the abstraction of an electron or its excitation still leaves a relatively stable system. PIB-rubber is again much more sensitive towards irradiation and chain scission prevails.

table 2.2 G-values for crosslinking and chain scission for some polymers, inluding their average ratio, ordered in increasing rate of chain scission.

	G_C	G_S	G_S/G_C
Polybutadiene (PB)	1.55-5.8	0.16-0.5	0.09
Polystyrene (PS)	0.014-0.17	0.0012-0.055	0.1
EPDM-rubber			
56 % ethylene			
1.9 % DCPD*	0.91	0.29	0.3
2.0 % ENB**	2.18	0.57	0.3
3.75 % ENB	3.12	1.25	0.4
Polyethylene (PE)	1-3	0.5-1	0.4
EPR-rubber	0.3	0.16	0.5
Polyamide 66 (PA-66)	0.3		0.5-1.5
Polyamide 6 (PA-6)	0.35		0.5-1.5
Polypropylene (PP)	0.15-0.5	0.17-0.62	1.2
Polymethylmethacrylate (PMMA)		0.71-1.9	>2.5
Polyisobutylene (PIB)	<0.06	3.8-11.1	76

* *DCPD = dicyclopentadiene*
** *ENB = ethylidene norbornene*

In principle, polymers can be divided into a group in which crosslinking predominates and another where chain scission is more important. As a rule of thumb, it is accepted that the extent of chain scission becomes more pronounced, the more substituted groups (hydrogen excepted) the monomeric unit contains. For example, the extent of degradation strongly increases in the order: PE, PP, PIB. Unsaturated polymers, all possess a strong tendency towards crosslinking, which is demonstrated in the G-value for crosslinking of PB. Also EPDM-rubber crosslinks at lower doses when the diene-monomer content in the rubber increases.

Table 2.2 also indicates that a wide range of G-values exists for a certain polymer and not one, single, value. Differences in molar mass, branching and crystallinity play an important role in this respect. A high molar mass and a low crystallinity are normally favourable for crosslinking. In PE, crosslinks are formed preferentially in the amorphous part and especially at the crystalline/amorphous interface [5,21].

Also the irradiation conditions, e.g. temperature, atmosphere and dose rate, influence the sensitivity towards irradiation. Chain scission will be enhanced, in the presence of oxygen, especially when γ-radiation is used. Due to the relatively long exposure times for this kind of irradiation, oxygen may diffuse into the material and will enhance degradation via peroxide and hydroperoxide formation. When accelerated electrons are used as a source, the influence of oxygen is marginal [22].

Finally, not all radicals or electrons formed upon irradiaton will react immediately. These so called trapped radicals or electrons can slowly vanish without causing much damage. However, in combination with oxygen, peroxides or hydroperoxides may be formed, resulting in an enhanced degradation. Trapped radicals may also become active upon heating, causing either a further crosslinking or chain scission. The effect is, however, small compared to the effect of overall absorbed dose.

Applications

In most industrial applications benefit is taken of the crosslinking ability of polymers. Crosslinking results in improved temperature and chemical resistance and better mechanical properties, and is applied, for example, in cable insulation. Heat shrinkable materials are also often prepared via radiation crosslinking of PE, taking advantage from the fact that in PE the crosslinks are mainly formed in the amorphous phase [23]. Self regulating heaters are prepared from radiation crosslinked PE, filled with carbon [24].

Application of the scission ability of a polymer is rather limited. An example is irradiation of polytetrafluoroethylene (PTFE)scrap which is used as an additive in printing ink and lubricating oil [25].

Instead of modification of existing polymers, it is also possible to initiate polymerizations via irradiation. A rapid growing application is the curing of coatings [26]. Due to the fact that coatings are only applied in thin layers, they are extremely suitable for the low energy electron beam accelerators as discussed previously, see page 24. Surface modification via radiation induced grafting of monomers, or even polymers, onto a substrate polymer is also applied successfully, e.g. in the preparation of apolar membranes, containing polar grafts [27].

2.4 **Irradiation of Polymer Blends: Literature Review**

In contrast to irradiation of pure polymers, irradiation of polymer blends has not been studied extensively. A brief review of the existing literature on irradiation of polymer blends will be presented in this section.

Miscible blends

For most of the miscible blends, the miscibility is limited to a certain composition, temperature or pressure range [28]. Attempts have been made to extend the miscibility range, using radiation to crosslink (one of) the two polymers under conditions of complete miscibility [29]. For example Nishi and Kwei [29] studied the system polyvinylmethlyether/ polystyrene (PVME/PS) 50/50 and succeeded in raising the lower critical solution temperature (LCST) of this system with γ-irradiation via crosslinking of the PVME chains.

Immiscible blends

Irradiation of immiscible polymer blends has been studied in some more detail. Blends of two crosslinkable constituents have been irradiated in order to increase their strength and heat resistance [30,31] or to improve the morphology stability [32]. In the latter case, irradiation occurs to a point only slightly above the gelation dose (5-10% gel) in order to permit conventional processing. Irradiation of blends of PP, which normally undergoes chain scission, with crosslinkable polymers has been studied as well [33-40]. Overall crosslinking is the ultimate goal, e.g. in view of obtaining better resistance against sterilizing radiation for medical purposes, where addition of low molar mass stabilizers is often prohibited for health reasons. A good contact on a molecular scale and a co-continuous morphology are the requirements to obtain optimum properties [33,34,39,40]. In PP/EPDM blends radiation induced grafting of PP onto EPDM was observed, explaining the increase in mechanical properties, which were better than expected from additivity [36].

Protective effects in blends of styrene-polymers.

Other investigators tried to improve the radiation stability of polymers via blending with the radiation insensitive PS or styrene group containing polymers [41-44]. Although the stabilizing effect of a phenyl group is well established when incorporated in copolymers or when added to polymers as a low molar mass material, the effect of physical blending of PS with other polymers is not completely conclusive. In miscible blends the protective action of a styrene containing polymer was evident. Nguyen and Kausch [41] blended polymethylmethacrylate (PMMA) and styrene acrylonitrile (SAN) and observed a marked decrease in rate of scission of PMMA upon gamma irradiation in vacuum, which could be related to compatibility of the two constituents. This is illustrated in table 2.3 showing the decrease in G-value for chain scission of PMMA from 1.2 to 0.27 by adding 50 % of SAN [41].

Table 2.3 G-values for crosslinking and chain scission and gelation doses for gamma irradiated PMMA-SAN blends, from ref. 41.

% weight SAN	0	20	50	70	100
G_s (PMMA)	1.2	0.5	0.27	0.3	--
G_s (SAN)	--	--	0.051	0.062	0.055
G_c (SAN)	--	--	0.025	0.043	0.077
R_{gel} (kGy)			1900	870	380

Witt [42] showed that in a physical blend of PS and polybutadiene (PB), without interaction between the two phases, the rate of crosslinking of PB as a result of gamma irradiation in vacuum was constant. PS only acted as a diluent and no radiation protection was observed. Schulz and Mankin [43] also found that in an immiscible blend of coprecipitated PS and PMMA, the rate of scission was similar to that of pure PMMA. They used electron beam irradiation to show that with their freeze drying method some molecular mixing between PS and PMMA was achieved, since for these blends an appreciable amount of radiation protection was found. These results indicate that intimate contact between the two phases is required for obtaining a protective action from the styrene units. Garrett and coworkers [44], however, found a protective effect of PS in a coprecipitated immiscible blend of PS and PMMA, especially at high PS concentrations. From the results mentioned above it is evident that it is not possible to determine unambiguously whether in immiscible PS blends protection occurs or not. Contact-surface between PS and the other polymer plays a decisive role in this context, particularly in their immiscible blends.

2.5 Conclusions

Although the effects of high energy irradiation on polymers has been studied extensively, until now little fundamental work has been carried out on irradiation of polymer blends. The main aim of the studies up to now, has been the improvement of the overall properties, particulary the mechanical properties, or to diminish the negative effects of irradiation on the major component of the blend. Irradiation was mostly performed on the final article and no further melt processing took place. No studies have been presented on using gamma or electron beam irradiation to induce a controlled amount of crosslinking and/or chain scission in either of the two phases or to induce reactions at the interface, with the aim of developing specific characteristics in the blends which would be retained during subsequent processing steps. These possibilities have been investigated in the thesis and will be discussed in the next chapters.

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CHAPTER 3*

FIXATION OF NON-EQUILIBRIUM MORPHOLOGIES: A MODEL STUDY CONCERNING THREAD BREAK-UP AND COALESCENCE

3.1 Introduction

As discussed previously in chapter 1, the properties of an immiscible polymer blend are determined, to a large extent, by the morphology i.e. the particle size, shape and distribution of the constituents. The main problem of such a morphology is its intrinsic instability in the molten state. The morphology changes continuously and adapts to changes in shear - and elongational stress, deformation rate, total strain, processing time and temperature (see e.g. [1-5] and the thesisses of Elmendorp [6] and Elemans [7]).

In order to transfer the desired properties of the blend into the final product, it is important to gain control of the morphology during the various processing steps involved.

For the relatively simple morphologies like spherical particles in a matrix, as encountered for example in rubber-toughened blends, the use of compatibilizers (added to the system or made in situ by reactive extrusion) is usually an effective way to stabilize the structure [8-10]. However, in order to fix more complex morphologies, aiming at structured blends which possess, for example, layered or thread-in-matrix structures, new methods are required. In chapter 1, crosslinking via electron beam irradiation of the dispersed phase was

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* *Reproduced in part from Van Gisbergen, J.G.M. and Meijer, H.E.H. J. Rheol., 1991, 35(1), 1-25*

proposed as a route to stabilize, or even fix, any morphology, provided that the materials are selected with appropriate beam response.

In order to test this hypothesis, the fixation of a *highly non-equilibrium* morphology, threads-in-a-matrix, was selected. The influence of crosslinks on the two major processes which play an important role in the development and stabilization of the morphology, will be discussed: *break-up* of dispersed threads via Rayleigh distortions and *coalescence* of 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 will be discussed related to a model system: a blend of relatively inert PS (matrix) and LDPE as the crosslinkable dispersed phase [11-15].

In a first attempt to analyze the experiments and to obtain a reference time frame, model descriptions developed for pure Newtonian fluids will be used.

3.2 Experimental

The low density polyethylene (LDPE) sample 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.

Experiment 1. A blend of 80 % PS (w/w) and 20 % LDPE (w/w) was prepared on a Berstorff corotating twin-screw extruder at an average barrel temperature of 200 °C. Strands with non-equilibrium morphologies were quenched in water and exposed to electron beam irradiation at various doses. Both unirradiated and irradiated strands were subsequently annealed at 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. After annealing the changes in morphology of these blends were examined 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.

Experiment 2. Special samples were prepared for a more detailed investigation of the break-up process, because the thread-like morphology induced via extrusion (experiment 1) is not very uniform. Moreover, coalescence and thread break-up occur simultaneously during annealing in experiment 1 whereas seperate investigation is more interesting. Also some molecular orientation induced in the LDPE phase may hamper an unambiguous interpretation of experiment 1.

Consequently, threads of LDPE were spun (radius, R ≈ 100 μm) and positioned between two PS plates (thickness, d ≈ 1000 μm), following the procedure described by Elemans et al. [16]. Upon annealing these samples at 200 °C for 40 minutes, Rayleigh distortions with various amplitudes developed on the LDPE threads. (The typical time for complete break-up was approximately 80 minutes, whereas 1 minute was sufficient for the thin threads in the extruded blends of experiment 1.) Before complete break-up occurred, the samples were quenched to freeze-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 annealed for 2700 and 9900 seconds at 200 °C. The distortion amplitudes generated in the first annealing step act as the initial distortions in the re-annealing step. The growth of the distortions was analyzed. A schematic procedure of this process is given in Figure 3.1.

Effects of orientation of the LDPE threads on break-up during the re-annealing treatment can be ruled out since complete relaxation has already occurred during the first annealing step. The high 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 [16-19].

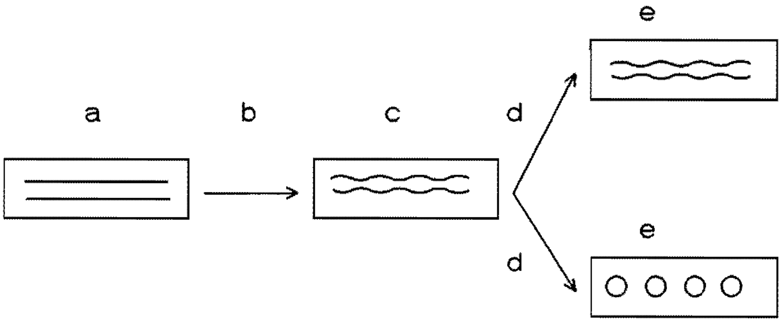

Figure 3.1 Schematic representation of the experimental set up for detailed investigation of the thread break-up process. a) PE thread, Radius = 100 μm, embedded in PS matrix, b) annealing at 200 °C resulting in c) sinusoidal distortions. d) Quenching, irradiation and subsequent re-annealing at 200 °C. e) Analysis of growth of distortions.

Experiment 3. In order to study the coalescence process, the extrusion blend from experiment 1 was heated at 200 °C for 120 seconds. A morphology of LDPE droplets, with an average diameter of 1.5 μm, in a PS matrix resulted. These samples were irradiated to 40, 100 and 180 kGy before a second annealing step, again at a temperature of 200 °C and for times up to $2 \cdot 10^4$ seconds. The average (particle) size of the droplets after annealing for different periods of time was measured to determine the rates of coalescence, using SEM.

Techniques

Viscosity/frequency curves (0.1-100 rad/s) of unirradiated 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), in air at room temperature.

3.3 Results and Discussion

3.3.1 Phenomenology

As can be inferred from the SEM micrograph in the upper left corner (0 kGy, t=0) of Figure 3.2, a morphology of thin LDPE threads in a PS matrix is induced via twin-screw extrusion. This intrinsically unstable morphology rapidly transforms into a droplet-in-matrix morphology upon annealing at 200 °C, see Figure 3.2, upper row. The two processes, thread *break-up* via Rayleigh distortions and *coalescence*, occur simultaneously. Irradiation of the blend before annealing in the press, with an intermediate dose of 62 kGy, delays the droplet formation. Irradiation of the blend up to a dose of 472 kGy (using higher doses would also affect the PS matrix) prevents the formation of droplets in the selected time scale of the experiment (600 seconds). However,

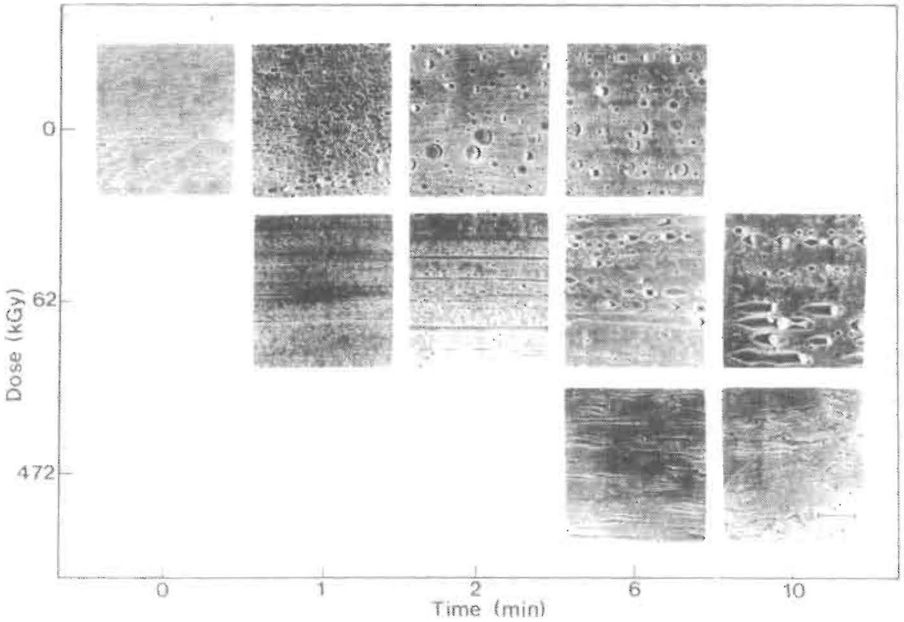

Figure 3.2 Stabilizing effect of radiation-induced crosslinks in the dispersed phase in a PS/LDPE 80/20 blend prepared on a corotating twin screw extruder and subsequently annealed for various periods of time at a temperature of 200 °C. Irradiation was performed after extrusion but before annealing. SEM micrographs parallel to the direction of extrusion.

complete preservation of the original thread-in-matrix morphology is not observed, even for this high dose. The experiments demonstrate that irradiation delays break-up and coalescence but does not prevent these processes to occur, as would be expected from a completely crosslinked dispersed phase.

Rheological experiments were performed using *pure* LDPE and PS samples as a reference to estimate the crosslinking efficiency of the constituents of the blend. In Figure 3.3a 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 Figure 3.3b). On the other

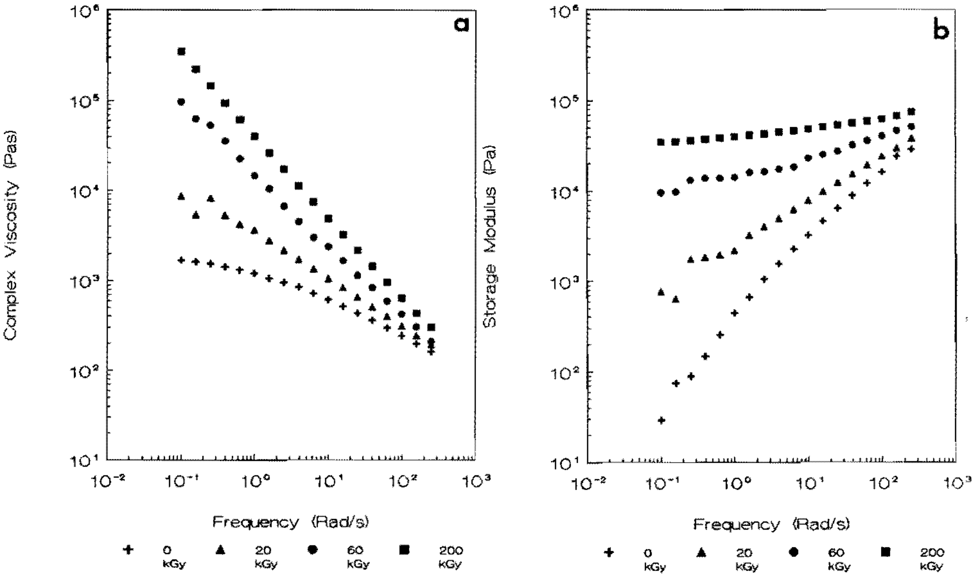

Figure 3.3 Complex viscosity (a) and storage modulus (b) of LDPE and complex viscosity of PS (c) as a function of angular frequency at 200 °C. Parameter: irradiation dose.

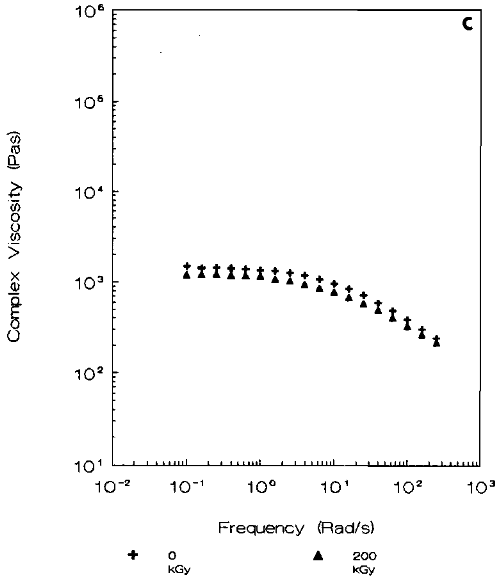

Figure 3.3 (continued)

hand, PS is hardly affected by an irradiation dose of 200 kGy. A slight but negligible decrease in viscosity is observed compared to the unirradiated blend, see Figure 3.3c.

It is clear that the strong increase in viscosity (or viscoelasticity) of the LDPE should decrease the mobility of the dispersed LDPE phase. This decreased mobility results in the delay of thread break-up and a decrease in coalescence rate, as shown in Figure 3.2, but does not prevent this process. Questions arise about the effectivity of radiation-induced crosslinks with respect to the complete prevention of break-up and coalescence. In the next sections, a first attempt will be presented to use the changes in viscosity and viscosity ratio (assuming that crosslinking in the blends and the samples of experiment 2 occurs to approximately the same extent as in the pure homopolymer, see § 3.3.4) to obtain a reference time frame for thread break-up and coalescence.

3.3.2 Analysis of Thread Break-up

In order to establish the time frame in which break-up of partly crosslinked threads should be expected it is assumed that the break-up of molten polymer threads in a polymer matrix can be described, in a first approximation, with the development and growth of sinusoidal distortions as derived for Newtonian fluids [16,20-24]. The time for break up, t_b, can be expressed as:

$$t_b = (1/q)\ln(0.816R_o/\alpha_o) \qquad (3.1)$$

In eq. 3.1, q is given by:

$$q = (\sigma/2\eta_m R_o)\Omega(\lambda,p) \qquad (3.2)$$

where:

t_b = time to break (s)
R_o = initial thread radius (m)
α_o = initial distortion amplitude (m)
σ = interfacial tension (N/m)
η_m = viscosity of matrix (Pas)
λ = wavelength of sinusoidal distortion (m)
p = viscosity ratio between the dispersed phase and the matrix phase (η_d/η_m)
$\Omega(\lambda,p)$ = tabulated function of λ and p [21,22,24]

Since break-up occurs at a very low shear rate, the zero shear viscosity can be used successfully in Eq. (3.2), [6,7,16].

Because 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 an average value of $\sigma = 5 \cdot 10^{-3}$ N/m [6,25].* For the viscosity of the PS matrix η_m, a value of 1400 Pas was used which is the average of the zero shear viscosities of the unirradiated and the irradiated PS as shown in Figure 3.3c. Finally, it is assumed that fracture occurs at the dominant wavelength, i.e. with the maximum growth rate of the distortion [21,22]. 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 Figure 3.4. 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.

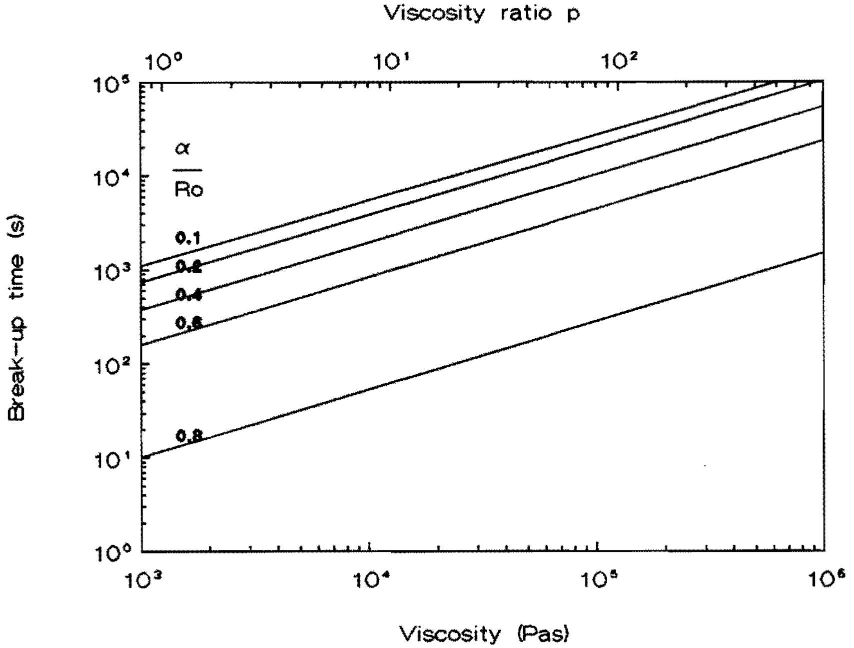

Figure 3.4 *Theoretical break-up times of PE threads in a PS matrix as a function of the LDPE viscosity, which represents the viscosity ratio $p = \eta_{ldpe}/\eta_{ps}$ because the viscosity of the PS matrix remains constant. Parameter: the initial reduced distortion amplitude, $\alpha' = \alpha/R_0$.*
$\sigma = 5 \cdot 10^{-3}$ (N/m), $\eta_m = 1400$ (Pas), $R_0 = 100$ µm, T = 200 °C

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* *As mentioned in chapter 1, the interfacial tension can be decreased via the addition of compatibilizers to the blend. Compatibilizers can be induced in situ via irradiation [26-28]. However, in the blend of PS/LDPE this is rather unlikely since there is no intimate contact in the solid state between PS and LDPE due to the crystallization shrinkage of the PE phase, see e.g. figure 5 in the paper of Heikens and Barentsen [29].*

The theoretical values of the initial amplitudes, which result in breaking of the threads, after re-annealing during 2700 and 9900 seconds respectively, can be determined as a function of the viscosity of LDPE, via interpolation in Figure 3.4. Results are shown in Figure 3.5, (open symbols, 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.

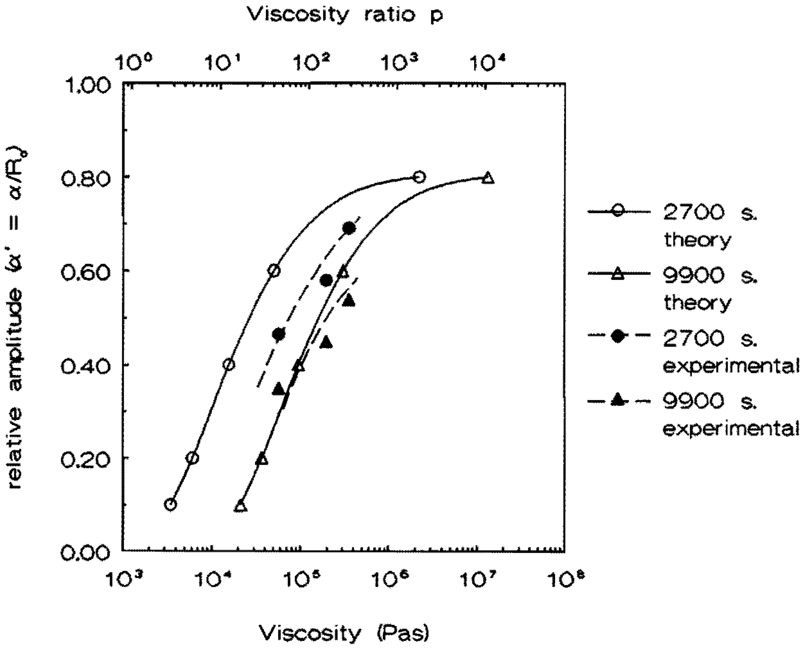


Figure 3.5 *Comparison between theory (open symbols, solid lines) and experiment (closed symbols, dotted lines) of maximum distortion amplitudes, which do not result in breakage of LDPE-threads (R_0 = 100 μm) in a PS matrix, as a function of LDPE viscosity or viscosity ratio $p = \eta_{ldpe}/\eta_{ps}$. Parameter: annealing time at 200 °C: (○,●), 2700 s. and (Δ,▲), 9900 s.*

In order to compare the theoretical value of the initial amplitudes which do not result in break up, with experimental data on irradiated 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

Figure 3.3a). Therefore, in a first approximation, the viscosity at an angular frequency of 0.1 rad/s is used. According to Elmendorp [7], break-up occurs at even lower deformation rates (order of magnitude ≈ 10^{-5} - 10^{-3} s^{-1}). Consequently, this viscosity can be considered to be a lower limit. In Figure 3.6 the (complex) viscosity of LDPE as a function of irradiation dose is given. Using the data from experiment 2 and the viscosity data of Figure 3.6, the experimental maximum amplitudes are determined. They are plotted (closed symbols, dashed lines) in Figure 3.5. 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 re-annealing time.

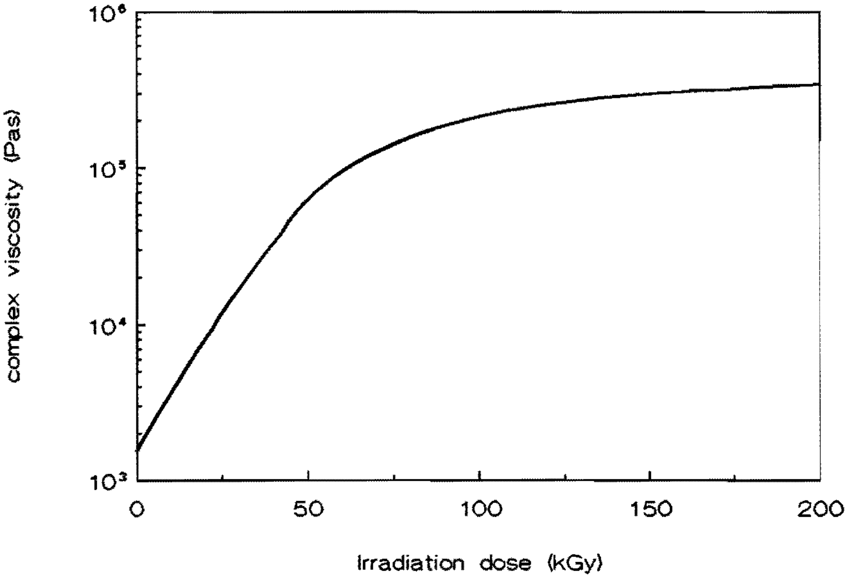


Figure 3.6 LDPE viscosity as a function of irradiation dose. Complex viscosity at frequency ω = 0.1 rad/s. T = 200 °C.

Of course estimation of the correct viscosity of the (irradiated) LDPE is a problem in this experiment. Break-up occurs more likely at even lower shear rates than the 0.1 rad/s chosen, i.e. at an even a higher viscosity of the LDPE phase. As a consequence the experimental values in Figure 3.5 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 Figure 3.5.

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 would expect that the radiation-induced elasticity would slow down the process beyond the simple viscous prediction.*

Another possibility to study the effects of EB induced crosslinks is to investigate whether a yield stress is generated. Again assuming 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:

$$\Delta p = -2\sigma\alpha/R_0^2 \cdot [1/(1-3/2(\alpha/R_0)^2)-(2\pi R_0/\lambda)^2] \quad [\mathrm{Pa}] \qquad (3.3)$$

---

* *According to Tomotika [21,22], break-up of threads occurs at only one, dominant, wavenumber* $\chi \approx 2\pi R_0/\lambda_{max}$. *This wavenumber is a function of viscosity ratio. From the optical microscope analysis, the dominant wavenumber 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 of this, the threads continued to distort with the original wavelength, during the second step, maybe because the initial amplitudes, imposed during the first annealing step, were already too large. Consequently, theoretically, a slower break-up is expected.*

The pressure difference is the driving force for the break-up process and is induced by the interfacial tension (σ/R_0). When the material exhibits a yield stress, higher than this pressure difference, the thread will not flow and the distortion is not able to grow. Analysis of the threads of experiment 2 revealed maximum values: threads with amplitudes causing a smaller pressure difference than this maximum value, are not transformed into droplets in 2700 or 9900 seconds respectively. In Figure 3.7 the pressure differences at which a distortion is stable are given. They increase with increasing irradiation dose but do not go to infinity at high doses and level off. Annealing for a longer period of time (9900 s) leads to break-up of distortions which were stable at a shorter timescale (2700 s). From these two observations it can

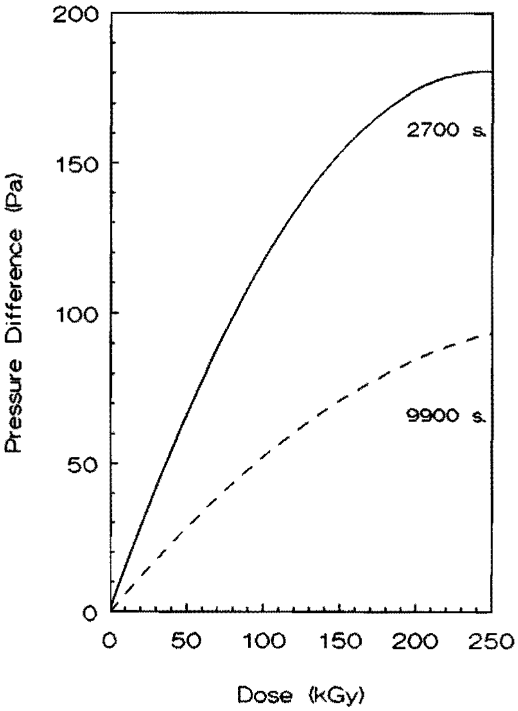


Figure 3.7 Summary of experimental results concerning the stability of threads: Threads with initial distortion amplitudes, causing a pressure difference higher than indicated by the lines, break during reheating during 2700 (solid line) and 9900 seconds (broken line) respectively at a temperature of 200 °C.

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 Figure 3.3a 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 Figure 3.8. LDPE irradiated with doses larger than 20 kGy shows a pronounced yield stress behaviour. 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 dynamic rheological

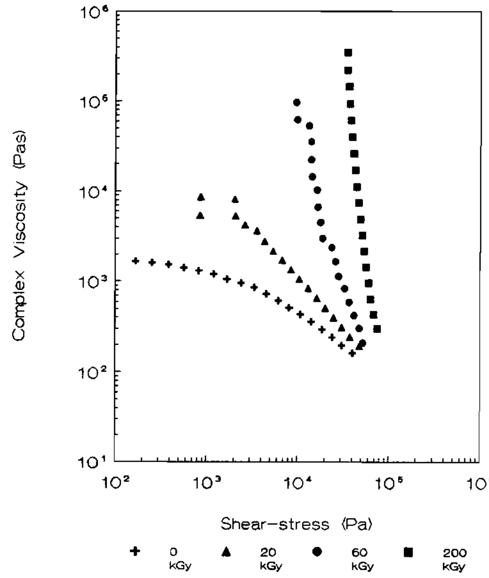


Figure 3.8 Complex viscosity of LDPE at 200 °C as a function of shear stress. Parameter: irradiation dose.

measurements. Consequently, break-up would not be expected to occur for the irradiated samples. Evidently, the crosslinked material behaves different during dynamic rheological testing compared to the flow in micro-rheology.

3.3.3 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 Figure 3.2, upper row, it can be inferred that 120 seconds is sufficient to generate this morphology in unirradiated blends.)

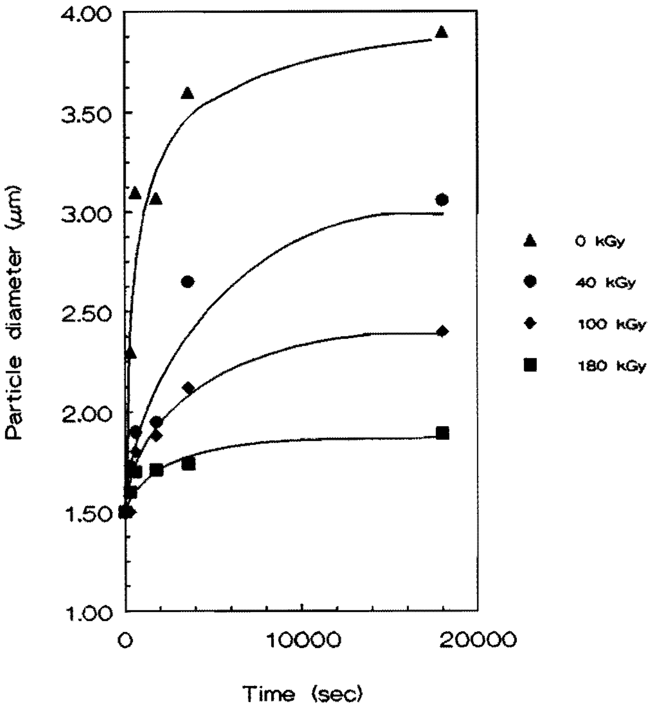


Figure 3.9 Experimentally determined increase in size of dispersed LDPE particles in a PS matrix as a function of heating time at a temperature of 200 °C. Parameter: irradiation dose.

Figure 3.9 clearly shows that upon irradiation coalescence is delayed considerably, but not prevented. In the models describing the coalescence process, it is usually assumed that the rate of coalescence is determined by the film thinning rate of matrix material between the dispersed particles [6,30,31]. For three models, the equations for the coalescence time (t_c) can be summarized as, [6,30,31]:

mobile interface (mi)

$$t_c = (3\eta_m R/2\sigma)\ln(R/2h_c) \tag{3.4}$$

immobile interface (ii)

$$t_c = (3\eta_m R^2 F/16\pi\sigma^2)[1/h_c^2 - 1/h_o^2] \tag{3.5}$$

partly mobile interface (pmi)

$$t_c = (\pi\eta_d F^{0.5}/2(2\pi\sigma/R)^{1.5})[1/h_c - 1/h_o] \tag{3.6}$$

where:

t_c = time to coalescence (s)
R = particle radius (m)
h_c = critical surface-to-surface distance (m) ≈ 50 nm [6]
h_o = initial surface-to-surface distance (m) ≈ 2/R [32]
F = Force (N)

The mobility of the interface is an important parameter. For fully mobile interfaces (mi) the time for coalescence (t_c) is proportional to the particle radius R times ln(R) (Eq. (3.4)), whereas in blends with immobile interfaces (ii) t_c is proportional to FR^2 (Eq. (3.5)), with F =

force. For gravity-induced coalescence this proportionality changes into $t_c \sim R^5$, compare with chapter 1.

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 (see footnote page 47), it is unlikely that compatibilizers will be formed in situ via irradiation in the system investigated.

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 unirradiated 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 by Chesters [31] assumes a partly mobile interface (pmi) and takes into account the viscosity of the dispersed phase as well (Eq. (3.6)). This model assumes plug flow between the two colliding droplets and this implies that within the validity of the model, i.e. $p \leq 100$, the viscosity of the matrix plays a minor role.

From the three models mentioned, mobile (Eq. (3.4)), immobile (Eq. (3.5)) and partly mobile interface (Eq. (3.6)), the time needed for coalescence to occur can be calculated. Subsequently the time for the next coalescence step, for larger droplets, can be calculated. The assumption has to be made that one starts with equal sized droplets which coalesce into particles with a doubled volume.

The theoretical times necessary for 4 coalescence steps to occur, are shown in Figure 3.10, as calculated for the pmi model. For comparison with the experimental data the same time scale has been used as in Figure 3.9. 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 Figure 3.6). The force F was estimated via fitting the experimental time necessary for 3 coalescence steps for the unirradiated LDPE. This force is substantially larger than would be expected for gravity-induced coalescence, where $F = \Delta\rho Vg$.

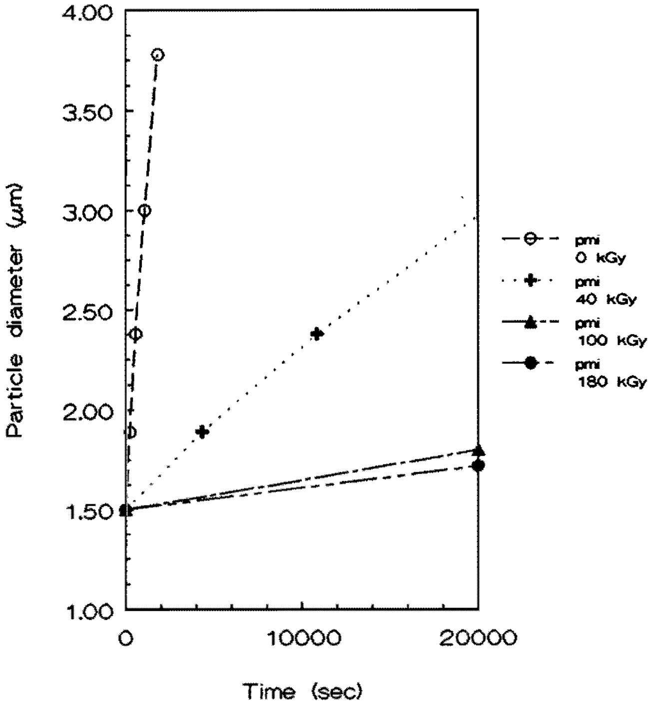


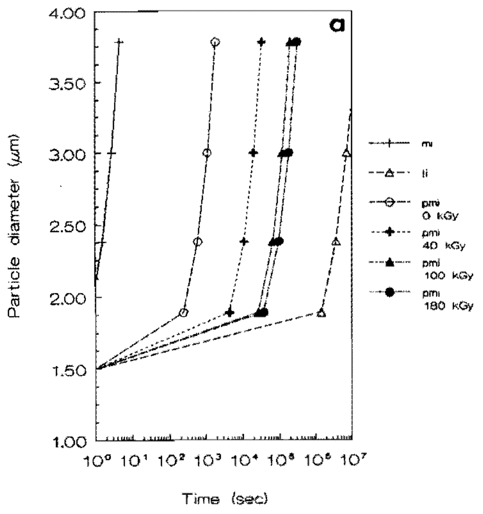
Figure 3.10 Theoretically determined, stepwise, increase in size of LDPE particles in PS matrix as predicted with the pmi model as a function of heating time at a temperature of 200 °C. Parameter: irradiation dose.

When the results are compared with the experimental data it is observed that there is a qualitative agreement, i.e. a slow-down 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 unirradiated 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 [31]. This high viscosity ratio is already achieved at the lowest irradiation dose of 40 kGy. In Figure 3.11a a comparison has been made between the three models with the theoretical values for 4 coalescence steps to occur. In order to be able to compare, a logarithmic timescale is used, since the differences in characteristic coalescence times are very large. For the ii model the same force F has been used as in the pmi model.

As can be inferred from Figure 3.11a 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 Figure 3.11b) 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 way. Nevertheless, it can be concluded that irradiation of a blend does not delay coalescence efficiently, although this could have been expected from the more pronounced elasticity.



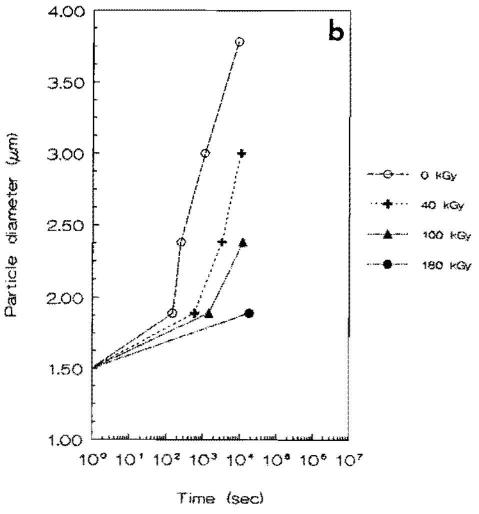


Figure 3.11a Comparison of theoretical coalescence times, needed for four subsequent coalescence steps to occur, predicted according to the mi, pmi, and ii models. Due to large differences in characteristic times, the time scale is logarithmic.

Figure 3.11b Experimental coalescence times of Figure 3.9 plotted on the logarithmic timescale of Fig. 3.11a The points indicate the experimental times, needed for subsequent (stepwise) coalescence steps to occur (similar to the calculated values in Figure 3.11a) and are obtained from the drawn curves in Fig. 3.9.

3.3.4 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 pure Newtonian materials with comparable 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, a.o., by Van Oene [33] and Elmendorp [6].

Inhomogeneity

Upon irradiation of the polyethylene, crosslinks will be formed preferentially in the amorphous phase [11-14]. Nevertheless, irradiation-induced crosslinking is homogeneous on a relatively macroscopic scale, i.e. typical dimensions $\geq$ 10 nm. On a molecular scale, however, crosslinking of LDPE is not completely uniform, which is a possible explanation for the observed rheological behaviour. 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/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 non-crosslinked material (= sol) present, with a lower viscosity than that of the complete material (= sol + gel). This non-crosslinked material may flow during the slow steady tests (break-up and coalescence) at very low shear rates, and hardly influence the results under dynamic testing conditions during the viscosity measurements.

Shielding

Furthermore, crosslinking of the LDPE phase may occur less efficient in a PS surrounding. This implies that the viscosity of LDPE in the blend will be somewhat lower than measured for the irradiated *pure* homopolymer. This shielding effect of the phenylrings has been observed in blends with an intimate contact between the two phases [34,35], whereas it does not occur in an immiscible blend [36]. Our experiments showed that there is some shielding in the extrusion prepared blend of PS and LDPE [37]. Since the extent of shielding depends on the amount of contact between matrix and dispersed phase (i.e. the typical particle dimensions and adhesion between matrix and dispersed phase, see chapter 2) it will be negligible in the samples of experiment 2: the diameter of the threads is two orders larger than in the extrusion prepared blends and no adhesion between threads and matrix is present.

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 predictions 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. Equations have been used which were originally derived for two equal sized colliding droplets. In the blends there is a distribution of particle sizes and particles influence each other.

Still, the conclusion remains that the results indicate that irradiation is less effective than expected.

3.4 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. However, complete fixation of highly non-equilibrium morphologies is not possible for the system investigated.

Adopting the model for thread break-up of Newtonian fluids, the reference time frame of the break-up process can be predicted. Break-up occurs faster than would be expected for highly viscous fluid with a viscosity, comparable to irradiated LDPE. From dynamic rheological measurements it could be concluded that upon irradiation even a yield stress is generated which would prohibit flow completely. Direct micro-rheological experiments showed, however, that break-up via Rayleigh distortions still continued.

Models of fully mobile and fully immobile interfaces, both result in unrealistic predictions of the coalescence rates. The model of partly mobile interfaces gives results which are only in qualitative agreement. Coalescence occurs faster than would be expected. However, the author hastens to add that the predictions of the coalescence rates are a little bit questionable due to the absence of a well defined driving force.

Complete crosslinking of the dispersed phase is not possible in our model system. This implies that crosslinked LDPE can be considered as a bimodal material, i.e. a low viscous uncrosslinked material which is hindered by an uncomplete network. This hindrance causes the stabilizing effect which is, however, less effective than would be expected for fluids with comparable high viscosity.

It must be emphasized that fixation of non-equilibrium morphologies was not obtained, even in the absence of shear flow. In actual processes like injection moulding, fixation was even less pronounced, as indicated by preliminary experiments in our group [37].

In the next chapters, the possibilities of using EB irradiation to stabilize less extreme non-equilibrium, droplet-in-matrix, morphologies are discussed. In chapter 4, attention is focussed on PP/EPDM blends (with some more details in chapters 5 and 6). A good interfacial contact will be assured, due to partial miscibility of these constituents and pronounced crystallization shrinkage of the PP matrix. Moreover, some radiation-induced grafting might occur, see chapter 5, resulting in an enhanced stability of the morphology. In chapter 7 results will be presented concerning a compatibilized PS/EPDM blend. (Compare to the PS/LDPE system without compatibilizer and with pronounced crystallization shrinkage of the dispersed LDPE phase and, consequently, with very poor interfacial properties.)

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CHAPTER 4*

POLYPROPYLENE/EPDM BLENDS: CONTROLLED MORPHOLOGY AND RHEOLOGY

4.1 Introduction

In rubber toughening of Polypropylene (PP) with Ethylene-Propylene-Diene Monomer (EPDM), a homogeneous dispersion of EPDM particles with a diameter of about 0.3-0.5 μm is desired [1-4]. Such a fine dispersion is rather easily obtained when the viscosities of matrix and dispersed phase are closely matched, see references [5,6]. For PP/EPDM blends this implies that, in order to achieve this desired morphology, a high-molar-mass PP is required since the melt-viscosity of EPDM is usually very high. However, for the subsequent processing step, injection moulding of the pelletized PP/EPDM blend, a lower viscosity of the PP matrix is required. This contradiction can, in principle, be solved by irradiating the blend before the subsequent processing step, see chapter 1. It is well known that the main reaction in PP, as a result of electron beam irradiation, is chain scission, whereas EPDM will crosslink preferentially [7-9]. Consequently, irradiation of a blend of highly viscous PP with EPDM will result in a low blend-viscosity and the induced (optimum) morphology may be preserved to some extent, as a result of radiation-induced crosslinks in the dispersed phase [10-13].

The influence of the irradiation dose on the chain scission reaction of the main chain of PP in both the pure homopolymer and the blend has

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* *Reproduced in part from Van Gisbergen, J.G.M., Meijer, H.E.H. and Lemstra, P.J., Polymer, 1989, 30, 2153-2157.*

been studied. Experiments concerning fixation of an optimum morphology, obtained by blending highly viscous PP with EPDM, via irradiation will be presented. A comparison will be made between rheology, morphology and mechanical properties of injection moulded blends, with and without irradiation, between the extrusion and processing step.

4.2 Experimental

The materials used, Polypropylene (Stamylan P) and EPDM rubber (Keltan), were obtained from DSM and their characteristic properties are listed in table 4.1. The third monomer in the EPDM rubber is ethylidene norbornene (ENB). The polypropylene grades are isotactic homopolymers.

Table 4.1 Specifications of the materials.

Material	MFI *230 °C* dg/min	Mooney viscosity *ML(1+4) 125°C*	ethylene content mole %	ENB content mole %	code
PP 13E10,	1.1	--	--	--	PP-H
PP 112Mn10,	45	--	--	--	PP-L
K 514, EPDM rubber	--	46	52	8	EPDM

Blends were either prepared on a two roll mill (Schwabenthan, T = 185 °C) and subsequently compression moulded into 1 mm thick sheets or prepared on a corotating twin screw extruder (Berstorff ZE 25, T = 220 °C) and pelletized. Both, sheets and pellets (also for PP), have been exposed to a 3 MeV electron beam 'Van de Graaff' accelerator at the IRI (Delft). Irradiation was performed at room temperature in air. Irradiated and unirradiated pellets were injection moulded into testpieces for Izod impact testing and stress-strain experiments on an

Arburg Allrounder (221-55-250) at a temperature of 240 °C and a mould temperature of 50 °C.

From the compression moulded sheets, samples were cut to perform rheological measurements using a Rheometrics RDS-II. A cone and plate geometry was used. The test temperature was 190 °C, rather low for PP and PP/EPDM samples. Measurements at higher temperatures, however, resulted in pronounced scattering of the data points in the low frequency region due to the low viscosity of the irradiated PP-H.

Morphologies of the blends were characterized using a Cambridge 200 stereoscan Scanning Electron Microscope. Samples were cut at low temperature and afterwards the rubber particles were extracted. A method described by F. Stehling [14] was used and somewhat modified. After microtoming, the rubber particles were extracted during 2 minutes in n-hexane in an ultrasonic bath. In order to extract even partly crosslinked particles in some cases, a method described by Rose et al. [15] was used: the smooth surfaces were held in boiling xylene vapour for 5 seconds. After extraction the surface was covered with a thin gold layer.

Izod Impact testing was performed according to ASTM (D 256) at room temperature. Tensile testing was performed on dumbbell shaped specimens at a rate of 100 mm min (ISO-R-37, type 2). Yield stress (σ_y), modulus (E) and elongation at break (ε_b) were measured.

Molar masses were determined via GPC (Waters Model 200) using TCB as a solvent at 135 °C and four columns packed with styragel (10^3-10^4-10^5-10^6 Å). The GPC facilities at DSM research were used.

4.3 Results and Discussion

Irradiation of polypropylene homopolymer

Table 4.2 shows the results of irradiating high-molar-mass PP homopolymer (PP-H) as revealed by GPC measurements. A strong decrease in the absolute values for M_w and M_n is observed as well as a narrowing of the molar mass distribution.

Table 4.2 Molar masses of polypropylene (PP-H) as a function of radiation dose, determined by high temperature GPC.

Dose (kGy)	M_w (kg/mole)	M_n (kg/mole)	M_w/M_n
0	570	82	6.9
26	250	65	3.8
44	220	68	3.2
88	180	48	3.7

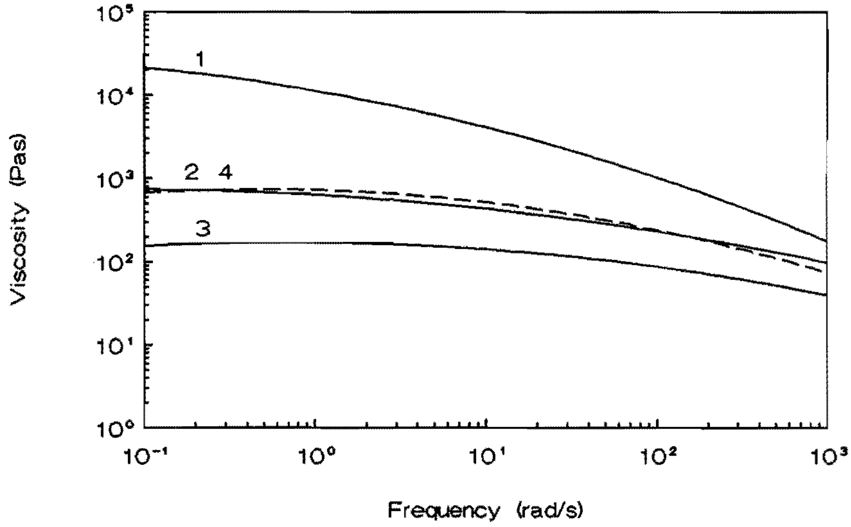

Figure 4.1 Complex viscosity of irradiated PP-H: 1) 0 kGy; 2) 44 kGy; 3) 88 kGy. As a reference, curve 4 (dashed line) is presented for the low molar mass PP-L. Measurements were performed at T = 190 °C.

The decrease in molar mass is reflected in the melt-viscosity as shown in Figure 4.1. The irradiated samples also show more pronounced Newtonian behaviour indicative of a narrowing of the molar mass distribution [16,17]. In accordance with literature data [7-9,12], it can be concluded that the molar mass of PP can easily be controlled by irradiation, at least up to doses of 100 kGy. The viscosity of the low-molar-mass PP-L is also shown in Figure 4.1 (curve 4). This reactor-modified, high flow type PP, possesses the same viscosity as the PP-H irradiated with a dose of 44 kGy and is used as a reference.

Blending and fixation of morphology

Morphologies of extruded strands of blends with 70% (wt%) PP and 30% (wt%) EPDM, obtained via mixing in a corotating twin screw extruder, are shown in Figure 4.2. The dispersed EPDM particles in the PP-H matrix are small and uniformly distributed whereas the EPDM particles in the PP-L matrix are irregular and rather large.

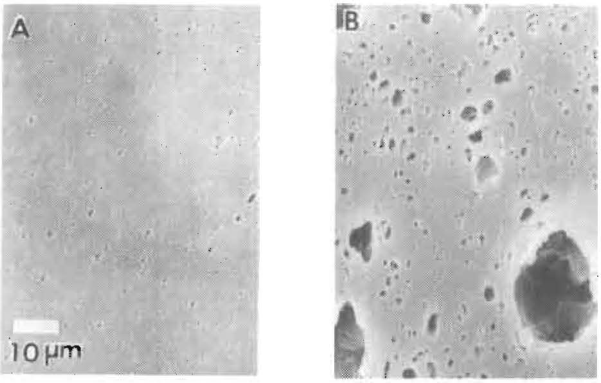

Figure 4.2 SEM micrographs of PP/EPDM 70/30 blends, extrudate, parallel to the direction of extrusion. Etched in n-hexane during 2 minutes. a) PP-H/EPDM b) PP-L/EPDM

The importance of using high viscous PP, in order to obtain small particles, is evident from these micrographs. Figure 4.3a shows that this optimum morphology may rapidly deteriorate as a consequence of subsequent processing. After injection moulding of the unirradiated, pelletized, blend the EPDM particles are still small but an orientation of the particles in the direction of injection is observed (compare Figure 4.2a). Irradiation of the extruded, pelletized, blend with a dose of 44 kGy decreased the degree of orientation as a result of injection moulding (figure 4.3b). The particles in the injection moulded blend of low viscous PP-L and EPDM are more regular and somewhat smaller than in the reference blend (compare Figure 4.3c with 4.2b) but the average particle size is still too large for acceptable impact properties (see below).

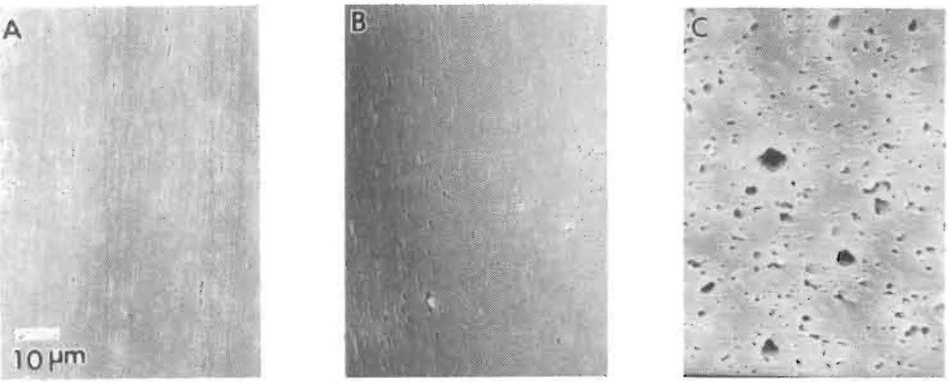

Figure 4.3 SEM micrographs of PP/EPDM 70/30 blends, etched with n-hexane during 2 minutes. a) PP-H/EPDM, extruded, pelletized and injection moulded; b) as a, but in pelletized form irradiated with a dose of 44 kGy before injection moulding; c) PP-L/EPDM, extruded, pelletized and injection moulded.

A more extreme example of morphology change during processing of these polymer blends is shown in Figures 4.4a and 4.4b for a PP-H/EPDM 80/20 blend. A droplet in matrix structure, obtained in the extrusion step, develops into a co-continuous one as a result of injection moulding. Irradiation of the blend after extrusion but before injection moulding preserves the original morphology to a large extent, as shown in figure 4.4c. The SEM micrographs 4.4b and 4.4c were taken from

The decrease in molar mass is reflected in the melt-viscosity as shown in Figure 4.1. The irradiated samples also show more pronounced Newtonian behaviour indicative of a narrowing of the molar mass distribution [16,17]. In accordance with literature data [7-9,12], it can be concluded that the molar mass of PP can easily be controlled by irradiation, at least up to doses of 100 kGy. The viscosity of the low-molar-mass PP-L is also shown in Figure 4.1 (curve 4). This reactor-modified, high flow type PP, possesses the same viscosity as the PP-H irradiated with a dose of 44 kGy and is used as a reference.

Blending and fixation of morphology

Morphologies of extruded strands of blends with 70% (wt%) PP and 30% (wt%) EPDM, obtained via mixing in a corotating twin screw extruder, are shown in Figure 4.2. The dispersed EPDM particles in the PP-H matrix are small and uniformly distributed whereas the EPDM particles in the PP-L matrix are irregular and rather large.

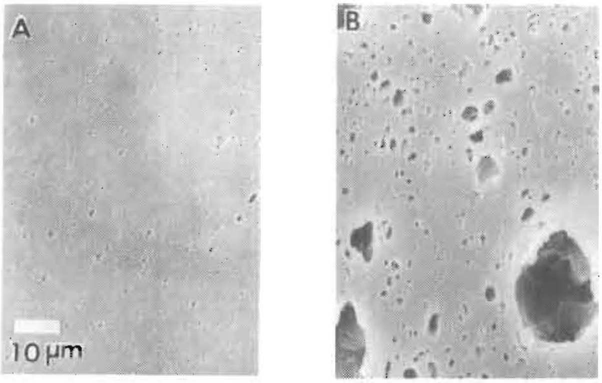

Figure 4.2 SEM micrographs of PP/EPDM 70/30 blends, extrudate, parallel to the direction of extrusion. Etched in n-hexane during 2 minutes. a) PP-H/EPDM b) PP-L/EPDM

The importance of using high viscous PP, in order to obtain small particles, is evident from these micrographs. Figure 4.3a shows that this optimum morphology may rapidly deteriorate as a consequence of

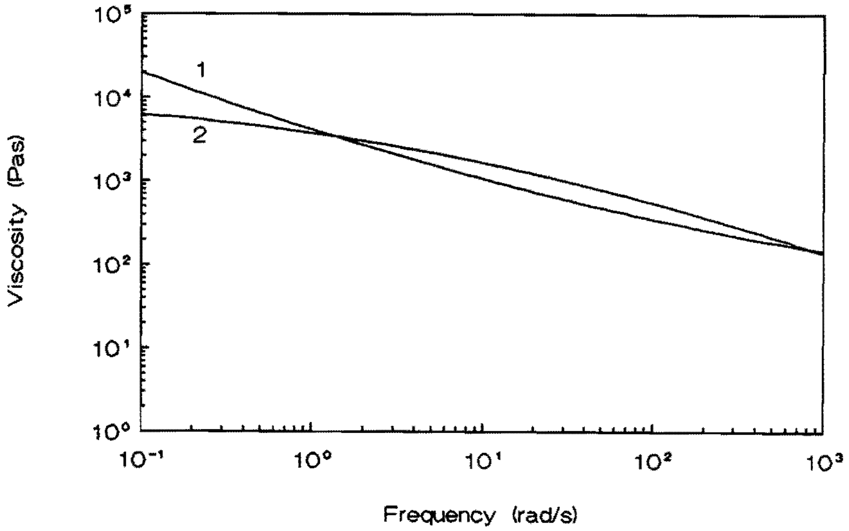

Figure 4.5 *Complex viscosity of PP/EPDM 70/30 blends; 1) PP-H/EPDM, 44 kGy; 2) PP-L/EPDM, 0 kGy. Measurement at T = 190 °C.*

In table 4.3 some results of the mechanical tests are listed. As a reference, also data are presented for an unirradiated blend and a blend irradiated with a dose of 88 kGy, possessing a higher and lower viscosity respectively, compared to the two blends shown in Figure 4.5.

Table 4.3 *Mechanical Properties for PP/EPDM 70/30 blends.*

Material		Izod kJ/m^2	σ_y N/mm^2	E N/mm^2	ε_b %	η at 100 s^{-1} Pas
PP-H/EPDM,	0 kGy	66.6	24.5	826	472	780
PP-H/EPDM,	44 kGy	57.3	17.2	804	597	400
PP-H/EPDM,	88 kGy	51.6	17.7	722	345	250
PP-L/EPDM,	0 kGy	8.1	16.4	828	460	450

σ_y = *yield stress*
E = *Young's modulus*
ε_b = *elongation at break*

The mechanical properties of the PP-H/EPDM blend irradiated with a dose of 44 kGy are superior to the PP-L/EPDM blend, especially the impact value. The properties of the PP-H/EPDM blend irradiated with a dose of 88 kGy are superior as well, which is of interest considering the low melt-viscosity, hence ease of processability. Compared with the unirradiated PP-H blend, irradiation causes a small decrease in impact, modulus and yield strength. Crosslinking of the EPDM phase could explain the decrease in impact strength, scission of the PP matrix the decrease in modulus and yield strength [18].

4.4 Conclusions

An optimum morphology for toughening can be obtained by mixing high-molar-mass PP (PP-H) with EPDM. Radiation-induced crosslinks stabilize this optimum morphology during subsequent injection moulding, resulting in good mechanical properties. Via controlled chain scission of the PP matrix, the flow properties can be adapted to the flow requirement necessary for injection moulding.

A brief optimization of the rheological and mechanical properties with respect to composition and irradiation dose is presented in the appendix. The results indicate that, in principle, easy processable blends with good impact properties can be achieved. The rheological behaviour, however, is rather complex and will be discussed in more detail in chapter 5.

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CHAPTER 5*

POLYPROPYLENE/EPDM BLENDS: MELT RHEOLOGY

5.1 Introduction

In chapter 4, it was shown that a good processability of PP/EPDM blends could be combined with good impact properties, applying electron beam (EB) irradiation *in between* the mixing and final processing step.

In this chapter, results will be presented concerning a more detailed rheological characterization of EB irradiated PP/EPDM blends. The influence of chain scission of the PP matrix, the extent of crosslinking of the EPDM phase and (possible) grafting of PP onto EPDM, in relation to the rheological properties will be discussed.

5.2 Experimental

Some characteristics of the materials used are listed in Table 5.1. The PP used is an extrusion type homopolymer with a relatively high molar mass, see also chapter 4. Three different grades of EPDM were used, containing different amounts of termonomer (diene); a high (EP-H) and low diene content (EP-L) and no diene at all (EP) respectively, and an increasing ethylene/propylene ratio in this sequence. As well documented in literature [1-3], the rate of crosslinking increases with increasing diene content and the use of ethylene norbornene as the termonomer results in faster crosslinking compared to dicyclopentadiene. A high ethylene content and high molar mass

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are also favourable for crosslinking [1-3]. All EPDM grades used in this study will undergo crosslinking. However, the mechanism and rate of crosslinking (beam response) differ markedly.

Table 5.1 Characteristics of the materials used.

Polypropylene Code	 grade	M_n kg/mole	MFI, *230°C* dg/min
PP	13E10, DSM	62	1.1

EPDM Rubber Code	 grade	diene mole %	ethylene mole %	Mooney visc. *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*

Blends were prepared via two-roll-milling at a temperature of 200 °C during 10 minutes. Subsequently, the blends were compression moulded at a temperature of 200 °C during 8 minutes into square plates with dimensions of 240x240x1 mm^3. The pure PP and EPDM samples were compression moulded under the same conditions but not milled before.

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

Rheological characterization was performed with dynamic mechancial analysis (DMA) using a Rheometrics RDS II at a temperature of 226°C. A parallel plate geometry was used. In order to confine measurement 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 datapoints was observed in the frequency range of 10^{-2}-10^{-1} rad/s for irradiated PP and irradiated blends with low EPDM content, due to 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 minutes in xylene in an ultrasonic bath, in order to extract the rubbery phase. Finally the samples were covered with a thin gold layer using an argon plasma.

5.3 Results

5.3.1 Rheology of Pure Polymers

In Figure 5.1a the viscosity of pure PP, unirradiated and irradiated with a dose of 50 kGy, is given as a function of the frequency. The viscosity decreases upon irradiation and the irradiated PP shows a more pronounced Newtonian behaviour. As well documented in literature [1,4] and discussed in the previous chapter, this can be explained by random scission of the PP main-chain.

The EPDM rubbers show a different behaviour upon irradiation. Figure 5.1b 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) due to crosslinking. This result is in accordance, at least qualitatively, with the previously mentioned dependence of the rate of crosslinking 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.

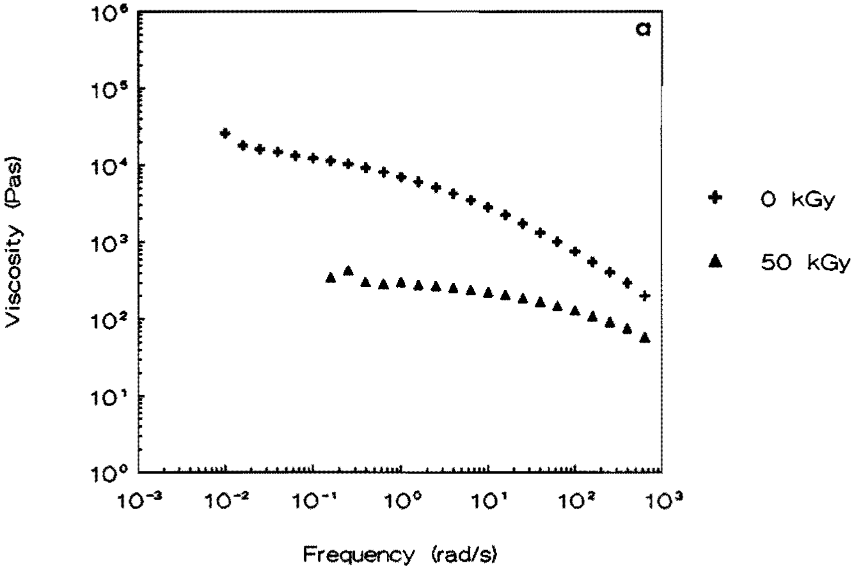

Figure 5.1a Complex viscosity as a function of the frequency of unirradiated PP and PP irradiated with a dose of 50 kGy. T=226 °C.

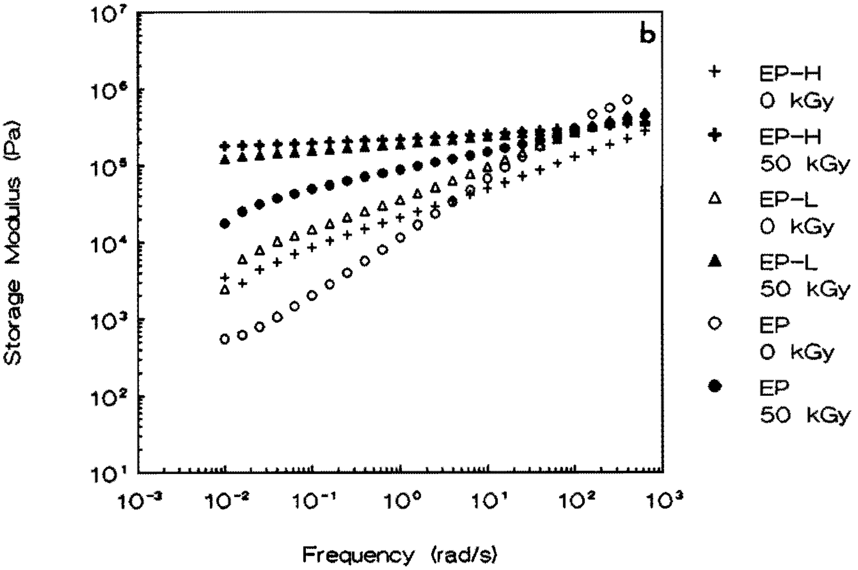

Figure 5.1b Storage modulus as a function of the frequency of unirradiated EPDM and EPDM irradiated with a dose of 50 kGy. T=226 °C.

5.3.2 Rheology of Unirradiated Blends

In Figure 5.2 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 w%,) are independent of the amount and type of EPDM used and the rheological behaviour is dominated by the PP matrix, compare with Figure 5.1a.

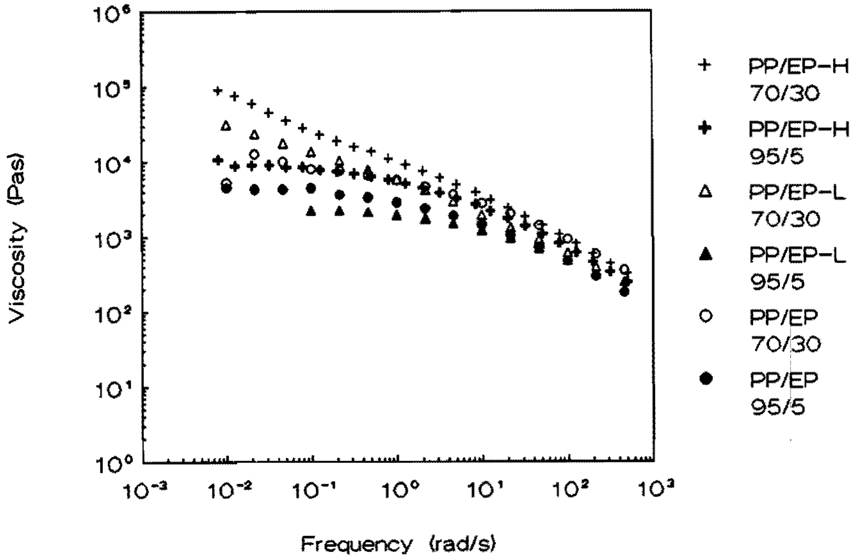

Figure 5.2 Complex viscosity of unirradiated PP/EPDM blends as a function of the frequency. T=226 °C. parameter: blend composition.

However, at low frequencies some differences arise for blends with higher EPDM concentrations. For each type of EPDM-rubber, the blends with 30% of EPDM possess a viscosity which is much higher than the viscosity for blends containing only 5% EPDM-rubber. The "5% blends" possess a Newtonian plateau, whereas this plateau is not (yet) observed for blends with 30% of 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 behaviour of the unirradiated blends is difficult. It will be 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 it has been tried to minimize this effect, keeping the processing conditions constant.

5.3.3 Rheology of Irradiated Blends

The rheological behaviour of the irradiated blends of EP-H, EP-L and EP is shown in Figures 5.3a, 5.3b and 5.3c 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 Figures 5.3 and 5.2. Consequently, processing via injection moulding 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 (Figure 5.2), albeit to a lesser extent.

At low frequencies, the blends with *low* EPDM concentrations behave similar as the irradiated pure PP, i.e. low viscous and with a Newtonian plateau. A relatively high viscosity is observed, however, at low frequencies for irradiated blends with *high* EPDM contents, compare Figure 5.3 with Figure 5.1a. 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, formation of weak weld lines in injection moulded products.

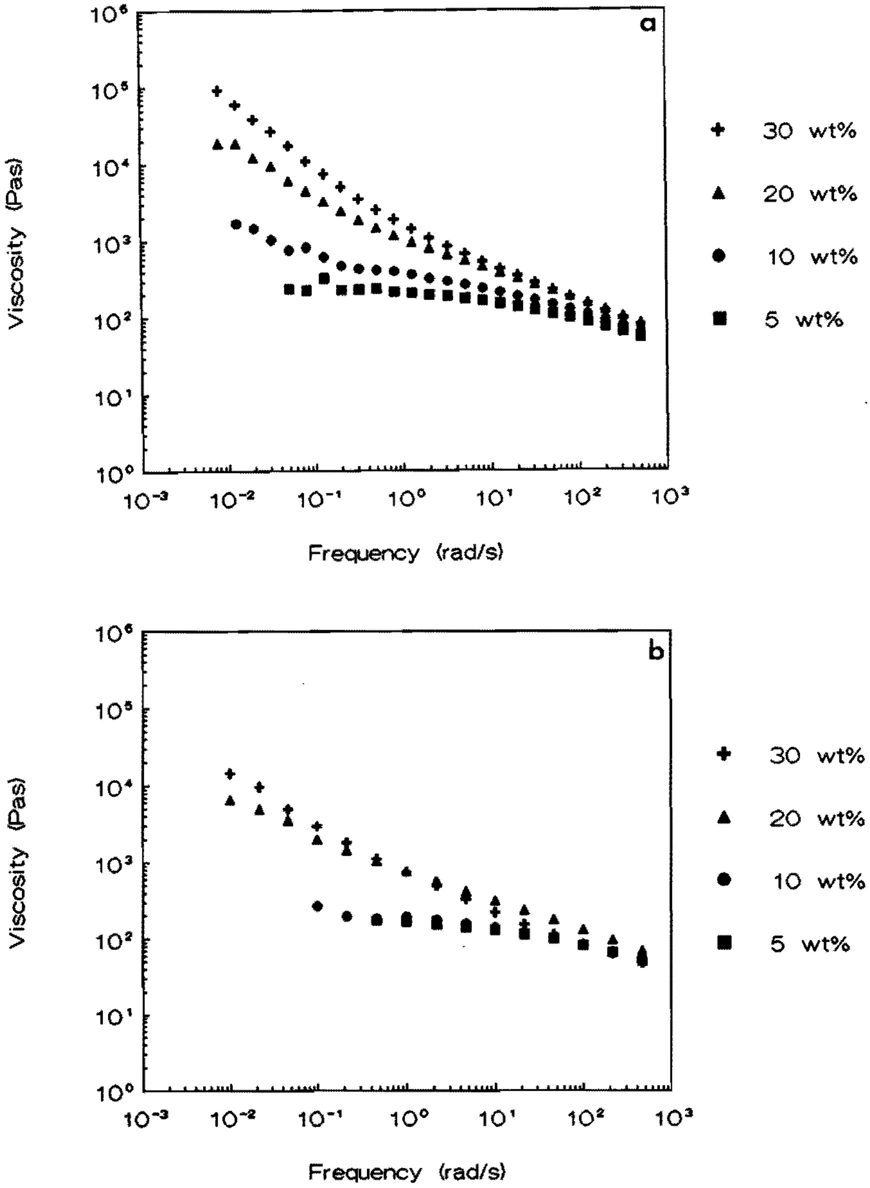

Figure 5.3 *Complex viscosity of PP/EPDM blends irradiated with a dose of 50 kGy, as a function of the frequency. T=226 °C, rubber concentration as a parameter. a) EP-H, b) EP-L and c) EP.*

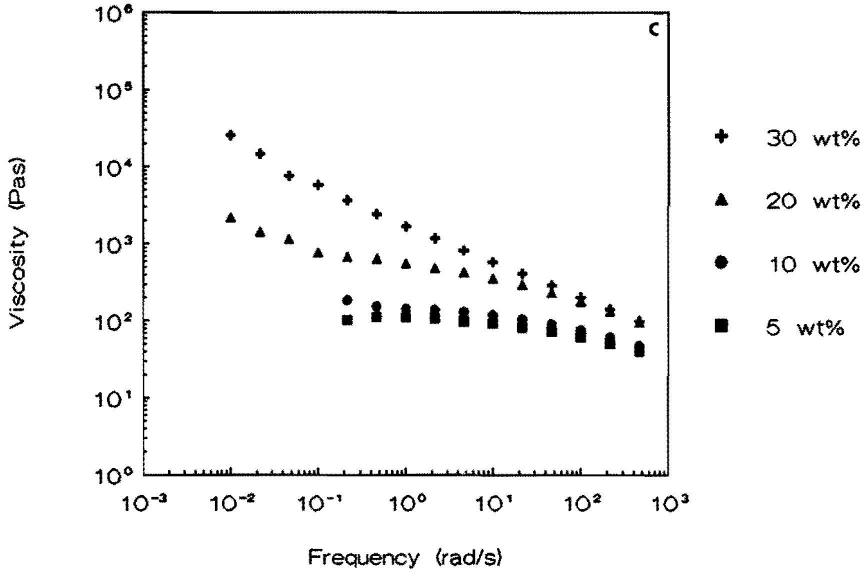

Figure 5.3 (continued)

In order 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 Figure 5.4 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 this figure it can be inferred that there is hardly any influence of temperature, which implies that the irradiated blend demonstrates a typical network behaviour. 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.

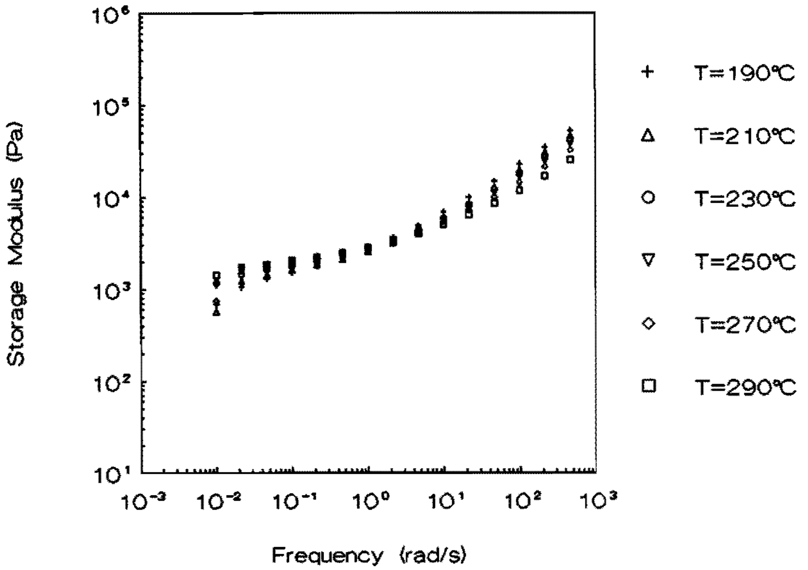

Figure 5.4 *Storage modulus of the PP/EP-L 70/30 blend, irradiated with a dose of 50 kGy as a function of the frequency and measured at different temperatures.*

5.4 Discussion: Network Behaviour

The unirradiated blends, show an elastic behaviour to some extent with increasing rubber content. However, this elasticity is small compared to the elastic behaviour of the irradiated blends. An unambiguous explanation for the observed rheological behaviour of the unirradiated blends is hindered by the changing morphology during the rheological measurements. A more stable, and better characterized, morphology is expected for the irradiated blends, as discussed in chapter 1. Therefore, attention is focussed to the origin of such a network mainly based upon results obtained for the irradiated blends.

Elasticity of heterogeneous mixtures

An elastic behaviour of melts, as observed for the (irradiated) PP/EPDM blends, has been reported for other rubber modified thermoplastics [5-10], for polymer melts with solid particles [6,11,12] and even for a mixture of two Newtonian liquids [6,13]. 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 σ/R). Upon irradiation, the elasticity ratio G_{EPDM}/G_{PP} strongly increases, which causes, in principle, the increase in elastic behaviour of the irradiated blends compared to unirradiated blends. However, the rheological behaviour of the irradiated blends, presented in Figure 5.3, is not uniquely proportional to this elasticity ratio, represented in Figure 5.1b by the G modulus 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 [7] 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 [5] for impact modified PP.

However, upon irradiation, some part of the PP matrix might be grafted onto the EPDM-rubber particles. Recently, Harnischfeger [14] concluded that upon irradiation of similar PP/EPDM blends some grafting occurred.

In order to investigate the occurrence and, if so, the extent of grafting, ^{13}C-NMR 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 [15,16]. This quantity is small compared to blends, where the grafting-bridging concept was the main explanation for the network behaviour and degrees of grafting were reported of more than 40 % [7-9]. Consequently, network formation in irradiated PP/EPDM blends does not occur via grafting-bridging.

Figure 5.5a shows the morphology of the PP/EP-L 70/30 blend before DMA testing and Figures 5.5b and 5.5c show the morphologies of the unirradiated and irradiated blends respectively, after DMA testing. The EPDM particles in the unirradiated blend coalesce during measurement, compare Figures 5.5a and 5.5b. 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 Figure 5.5c, which could indicate a skeletal structure.

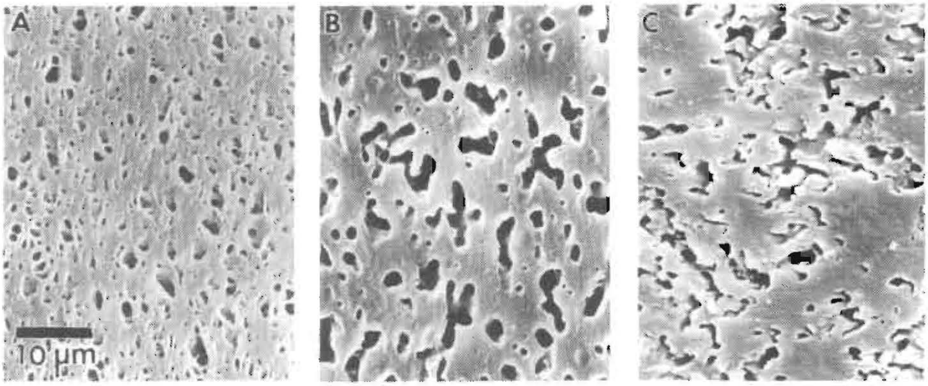

Figure 5.5 Morphologies of the PP/EP-L 70/30 blend. a) unirradiated, before dynamic mechanical analysis (DMA), b) unirradiated, after DMA c) irradiated, after DMA.

Inter particle distance

It has been reported in literature that the elasticity of a rubber modified blend [7] and particulate filled polymer melts [12], increases with increasing volume fraction of the dispersed phase and decreasing particle size. To take into account both volume fraction and particle size, the interparticle distance has been successfully introduced in rubber-toughened PA-6 blends and has been correlated to the toughness [17,18]. It is investigated, whether also a relation 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 behaviour, 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.

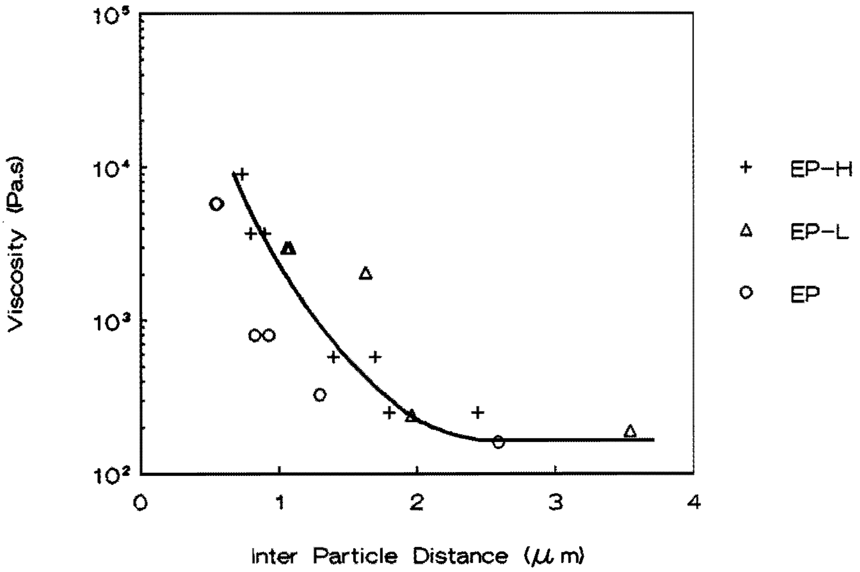

Figure 5.6 *Complex viscosity at 10 $^{-1}$ rad/s as a function of the interparticle distance for the PP/EP-H, PP/EP-L and PP/EP blends, unirradiated and irradiated with a dose of 50 kGy.*

In Figure 5.6 these viscosity data are plotted as a function of the interparticle distance. 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 figure 5.1). Below the critical value, the viscosity (or elasticity) of the blend gradually increases with decreasing inter particle distance. 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 interparticle distance in this blend a higher viscosity would be expected, but the EP rubber crosslinks to a lesser extent than than both others, see Figure 5.1b. A comparative experiment with an injection moulded blends, irradiated with a dose of 100 kGy (to crosslink EP sufficiently), reveals that the viscosity of the PP/EP blend was higher than the viscosity of the PP/EP-L blend [15]. Hence, a general trend of an increase in viscosity below a critical ID exists as indicated with the drawn line in Figure 5.6, provided that the dispersed phase is sufficiently crosslinked. The mechanism of crosslinking 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.

5.5 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 moulding. The influence of type and amount of rubber as well as the particle size is marginal.

At low shear rates, however, a pronounced network behaviour is observed, which can be explained by aggregation of rubber particles into a skeletal structure. Formation of weak weld lines in injection moulded products may result from the high viscosity at low shear rates. The network behaviour 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 inter particle distance could be revealed via the enhanced stability of the morphology of the irradiated blends.

5.6 References

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CHAPTER 6

TERNARY POLYPROPYLENE/EPDM/POLYETHYLENE BLENDS

6.1 Introduction

Toughening of PP can not only be obtained by the addition of EPDM rubber but also via the combined addition of PE and EPDM [1-7]. In these blends, EPDM merely acts as a compatibilizer and will usually be located at the PP/PE interface. Moreover, PE can act as a viscosity modifier for the EPDM and will increase the dispersability [7]. As a consequence, a synergystic effect of PE and EPDM addition on the impact strength of the ternary blend can occur [7]. Depending on the morphology of the composite dispersed phase, i.e. a core shell or interpenetrating structure, the overall modulus of the blend may increase as well [1].

In chapters 4 and 5, the effects of EB irradiation on the morphology, rheology and mechanical properties of PP/EPDM blends have been discussed. It was shown that, in principle, a good processability of the blend could be combined with optimum impact properties. In this chapter the influence of EB irradiation on PP/EPDM/HDPE blends will be presented. The principle as described in chapter 4 will be followed. Moreover, a relatively simple staining method, using RuO_4, will be introduced to characterize the morphologies with transmission electron microscopy (TEM). Details of this method are presented elsewhere [8].

6.2 Experimental

The characteristics of the materials used are listed in table 6.1.

Table 6.1 Characteristics of the materials.

	M_n kg/mole	M_w kg/mole	MFI dg/min	ethylene mole %	diene mole %
PP, 13E10, DSM	62	330	1.1 *	--	--
HDPE, 7058, DSM			4.5 **	100	--
EPDM, K740, DSM	70	200		60	1 ***

* *at T = 230 °C*
** *at T = 190 °C*
*** *dicyclopentadiene*

Blends were prepared on a Berstorff corotating twin screw extruder (ZE 25) at an average barrel temperature of 200 °C. The PP content was kept constant at 70 wt % and the HDPE/EPDM ratio was varied. Subsequently the blends were quenched and the strands were pelletized.

Part of the pellets was exposed to electron beam irradiation at ambient temperature, in air, using a 3 MeV 'van de Graaff' accelerator at the IRI (Delft). Both irradiated and unirradiated blends were subsequently injection moulded on an Arburg Allrounder (T = 230 °C) into square plates. These plates were prepared for Izod impact testing (ASTM D 256). Before mechanical testing, the samples were annealed at a temperature of 80 °C for 24 hours.

Samples for TEM were stained with RuO_4 and thin slices were cut at room temperature [8].

6.3 Results and discussion

Morphologies

The morphologies of two extruded blends are shown in Figure 6.1a and 6.1b, containing 4.5 and 25 wt% of HDPE respectively. The micrographs are perpendicular to the direction of extrusion. A clear distinction between the three constituents can be made. Relatively large HDPE lamellae can be observed in the dispersed phase whereas the continuous dark regions of the dispersed phase consist of EPDM. Evidently, the dispersed phase is a composite structure of EPDM and HDPE. The lamellae of the PP matrix can also be observed, but are smaller and less clear. A more elaborous route described by von Bassewitz and zur Nedden [9], using chlorosulfonic acid, revealed similar results for ternary PP/EPDM/PE blends.

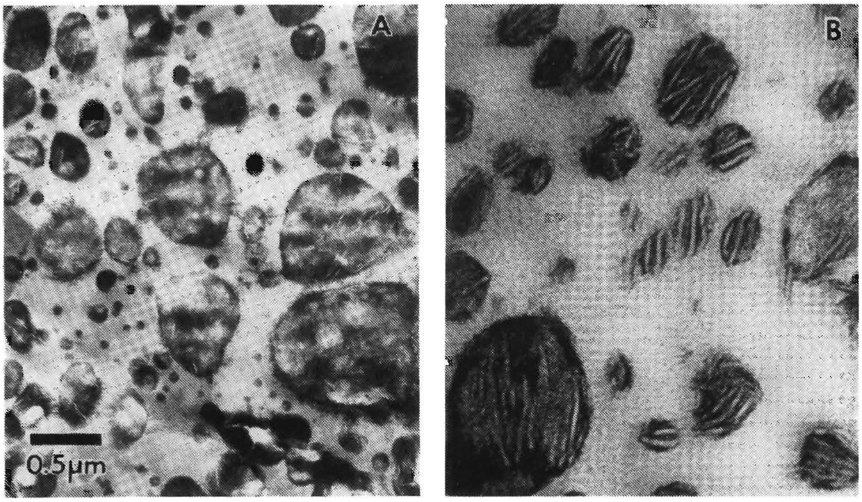

Figure 6.1 TEM micrographs of extruded PP/EPDM/HDPE blends: a) 70/25.5/4.5 (wt%) and b) 70/5/25. Photographs taken perpendicular to the direction of extrusion. In the dispersed phase, the dark continuous regions represent EPDM, the light regions the HDPE lamellae.

The EPDM-rubber shows a strong tendency to be located at the PP interface. PE lamellae, however, which penetrate the PP matrix, can also be observed. The absence of a perfect EPDM shell is a matter of time. Provided that the blends are molten (in the absence of strong deformation stresses) for a sufficiently long time, the EPDM diffuses to the interface to form a perfect shell [3,8], even up to a HDPE/EPDM ratio of 2/1.

From Figure 6.1 the orientation of the dispersed phase parallel to the direction of extrusion cannot be inferred. It is known, however, that the elongational flow in the extruder die causes this kind of orientation [10].

Morphologies of injection moulded blends are given in Figure 6.2.

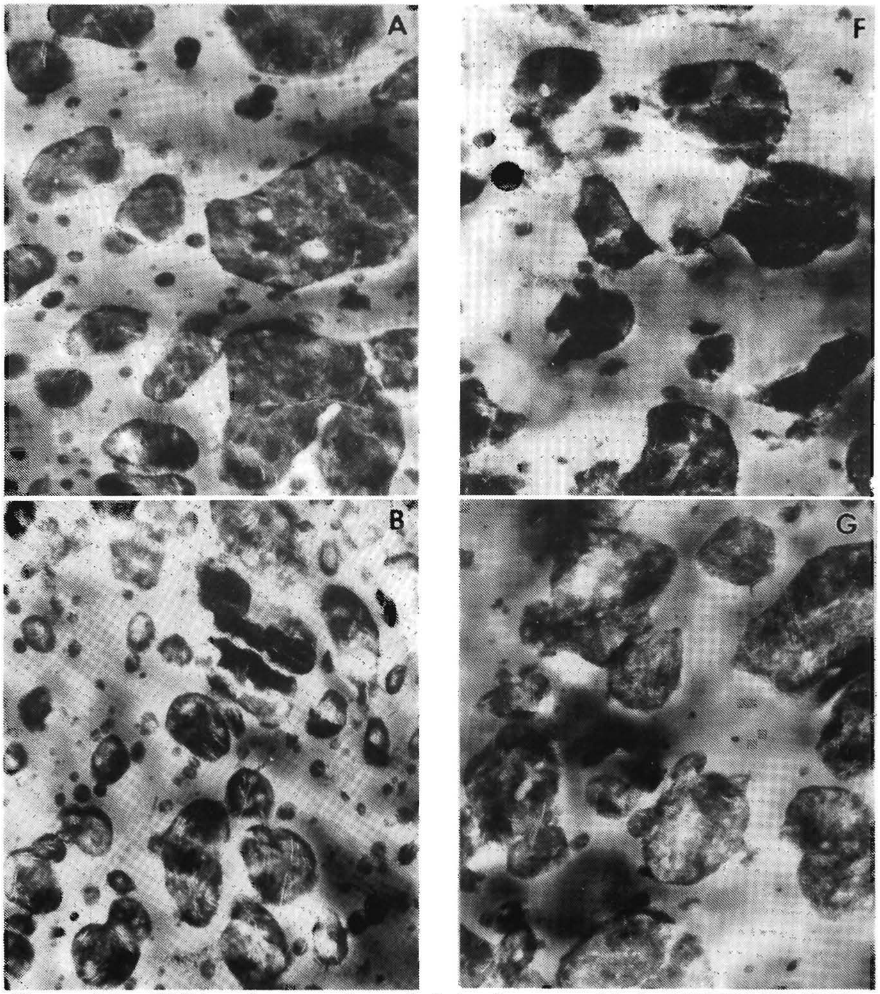

Figure 6.2 TEM micrographs of injection moulded PP/EPDM/HDPE blends. Unirradiated: a) 70/28.5/1.5, b) 70/25.5/4.5, c) 70/22.5/7.5, d) 70/15/15, e) 70/5/25. Irradiated with a dose of 50 kGy before injection moulding: f) 70/28.5/1.5, g) 70/25.5/4.5, h) 70/22.5/7.5, i) 70/15/15, j) 70/5/25.

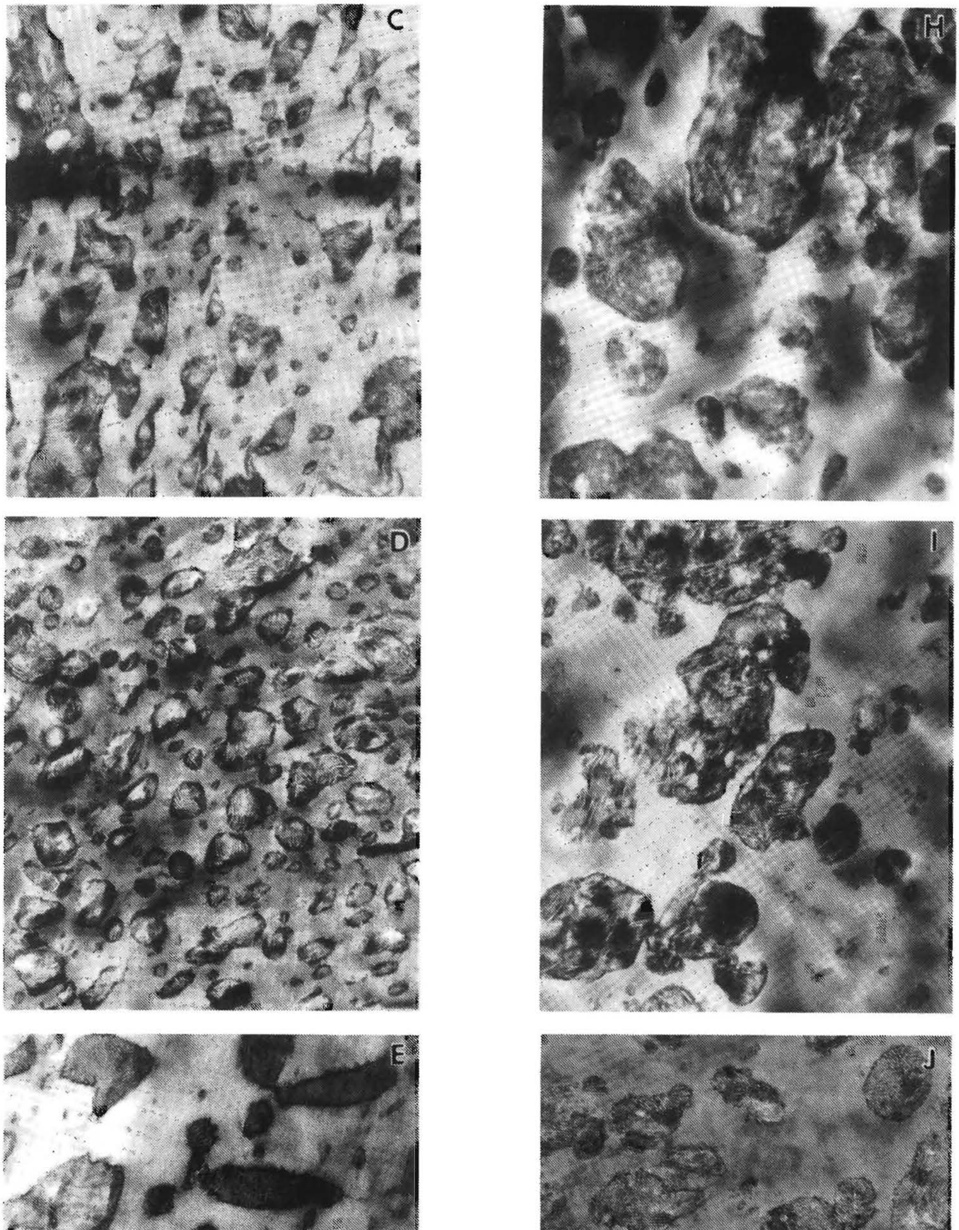

Figure 6.2 *(continued)*

For the *unirradiated* blends, the dispersed particle size gradually decreases upon addition of HDPE, passes a minimum and increases again, see Fig. 6.2a-e. This result can be related to an increased compatibility at higher EPDM contents vs. a more favourable viscosity ratio (η_d/η_m) at higher HDPE contents. The intrinsic high viscosity of EPDM hinders the dispersion process and, in principle, HDPE acts as a viscosity modifier for the dispersed phase [7].

Furthermore, it can be observed that the EPDM shell is frequently pierced with HDPE lamellae, similar to the extruded blends.

Taking into account that the extrusion prepared blends consist of threads with the perpendicular sections shown in Fig. 6.1, the average particle size in the unirradiated injection moulded blends is somewhat decreased. Evidently, the mixing (extrusion) step is not optimized and the dispersion process still continues during injection moulding.

The size of the dispersed particles in the *irradiated* blends, which implies a degraded PP matrix and a crosslinked dispersed phase, is somewhat larger and comparable to the particle size in the extruded blend, see Fig. 6.2f-j and compare with Figure 6.1. The morphology as obtained via the non-optimized extrusion step, see Fig. 6.1, is partly fixed. The size is, however, still small ($d \approx 0.5$ µm) compared to particles obtained via direct blending with a low viscous PP matrix ($d \approx$ 1.5-2 µm), see chapter 4. Differences in particle size for the irradiated blends with varying HDPE content are relatively small.

Impact toughness

At room temperature, all blends, irradiated and unirradiated, exhibit a tough behaviour, independent of the HDPE content. At -20 °C, however, a strong influence of the HDPE concentration on the fracture behaviour of the blends is observed, see Fig. 6.3. The unirradiated blend behaves tough up to a HDPE content of 7.5% and beyond this HDPE content, the impact strength gradually decreases. The irradiated blends, however, possess a much lower impact value at low HDPE content (1.5 and 4.5 wt%), show a maximum at 7.5 % HDPE and behave very brittle at higher HDPE contents. In general, irradiation results in a decrease in impact properties due to fixation of relatively large dispersed particles, which were induced via extrusion.

The large scatter in impact values of the irradiated blend at low HDPE content is caused by the fact that half of the test samples fail in a brittle way and the other half behave tough, which implies that the average particle size of the dispersed phase is at a critical value. A small reduction in particle size, difficult to observe directly from the TEM micrographs, might cause an increase in impact value, as observed for the blend with 7.5% HDPE.

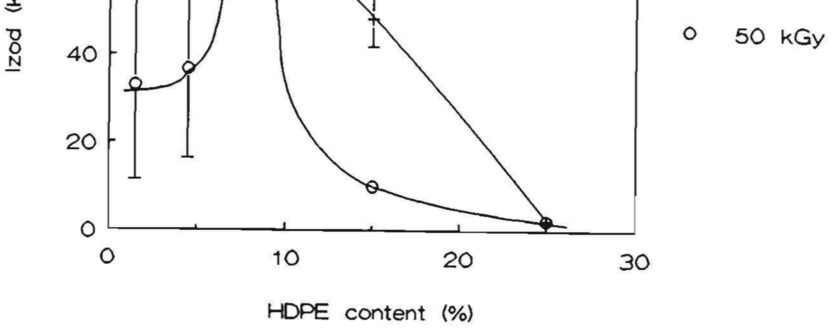

Figure 6.3 Izod values of PP/EPDM/HDPE blends, unirradiated and irradiated with a dose of 50 kGy before injection moulding, as a function of HDPE content at a temperature of - 20 °C.

The reduction in impact properties at higher HDPE concentrations for both the irradiated and unirradiated blends, can be explained by the morphology of the dispersed phase. According to Matonis [11], the behaviour of ternary blends with a perfectly surrounding soft interlayer between two stiff components, is similar to that of a binary blend with the soft material as dispersed phase, provided that the thickness of the interlayer contributes more than 4% to the total radius of the dispersed particle, for example HIPS and ABS. Evidently, the dispersed phase behaves like a pure rubber up to a HDPE content of 7.5 %, although the HDPE lamellae frequently perforate the EPDM shell. At higher PE concentrations, the effective rubber shell is too weak and the dispersed phase is more or less behaving like pure PE. The size of the EPDM shell at this HDPE concentration is far below the critical value of a perfectly surrounding EPDM layer, as would be expected from the calculations of Matonis [11].

Rheology

Compared to binary PP/EPDM blends, in ternary blends a small reduction in viscosity can be achieved, especially for irradiated blends at low shear rates [12]. The general trend is, however, very similar [12] to binary blends.

6.4 Conclusions

In ternary PP/EPDM/HDPE blends, the dispersed phase is a composite structure of HDPE and EPDM, where EPDM is preferably located at the interface between HDPE and PP. However, the EPDM shell is frequently perforated by HDPE lamellae which penetrate the PP matrix. As a consequene, the ternary blend behaves like a binary PP/EPDM blend only up to relatively low HDPE content and a decline in impact properties of the ternary system is observed for HDPE concentrations above this critical value.

For the unirradiated, injection moulded blends, a minimum in dispersed particle size exists as a function of the HDPE concentration. At low content, HDPE acts as a viscosity modifier for the dispersed phase. With increasing HDPE content, the negative effect of an increasing interfacial tension becomes more pronounced.

Irradiation in between the extrusion and injection moulding step partly fixes the morphology as obtained via a non-optimized extrusion step. As a consequence, the particle sizes in the irradiated blends are relatively large and almost independent of the HDPE content. A general reduction in impact properties compared to unirradiated blends is the result.

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CHAPTER 7*

POLYSTYRENE/EPDM BLENDS: IMPACT BEHAVIOUR

7.1 Introduction

Toughening of brittle polymers via the addition of a rubbery, low T_g, phase is a topic of widespread interest in polymer blend research [1-4], as discussed in chapter 1. The importance of the morphology has been analyzed for various systems. The adhesion between the rubbery phase and the matrix is an important parameter for matrices which craze upon loading, for example polystyrene (PS) [1,2].

In the previous chapters, it was demonstrated that electron beam (EB) irradiation can be a useful tool to control the morphology in immiscible polymer blends, via crosslinking of the dispersed phase [5,6]. In blends with a PS matrix, however, complete fixation of a morphology is very difficult to achieve [6]. Nevertheless, EB irradiation of PS/EPDM blends, with a radiation- sensitive block copolymer added as a compatibilizer, may be of interest, if a controlled change at the interface can be induced.

In this chapter, results will be presented concerning the impact behaviour of irradiated PS/EPDM blends, with polystyrene/ polybutadiene (SB) and polystyrene/ethylene-propylene (SEP) diblock copolymers used as compatibilizers. The SB copolymer crosslinks very

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* *Reproduced in part from Van Gisbergen, J.G.M., Borgmans, C.P.J.H., Van der Sanden, M.C.M. and Lemstra, P.J., Polymer Communications, 1990, 31(5), 162-164 and Van Gisbergen, J.G.M, Van der Sanden, M.C.M., De Haan, J.W., Van de Ven, L.J.W. and Lemstra, P.J., Lecture presented at IUPAC microsymposium 'Mechanisms of Polymer Strength and Toughness', Prague, 16-19 july, 1990, to be published in Makromol. Chem., Macromol. Symp.*

fast upon irradiation, due to the presence of double bonds (high beam response), whereas the SEP copolymer only crosslinks at higher doses and simultaneously undergoes pronounced chain scission [7,8]. Results of characterization by Fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR), will be presented.

7.2 Experimental

The materials used are listed in Table 7.1. Three types of commercially available compatibilizers were used: a polystyrene/ ethylene-propylene diblock copolymer (SEP) and two polystyrene/ polybutadiene diblock copolymers (SB), with a high and low PS content (h-PS and l-PS) respectively. The SEP copolymer was prepared via hydrogenation of a polystyrene/polyisoprene diblock copolymer.

Table 7.1 Specifications of the materials used.

Material	M_n kg/mole	M_w kg/mole	PS content %	Code
PS, Styron 638 (DOW)	70	200	100	PS
SB, Finaprene-410 (Fina)	70	78	48	SB/h-PS
SB, Kraton D-1118X (Shell)	53	63	30	SB/l-PS
SEP, Kraton G-1701X (Shell)	82	88	37	SEP
EPDM, Keltan 514 (DSM)	45	180	---	EPDM

All blends were prepared on a corotating twin screw extruder (Berstorff ZE 25) with a standard screw geometry (two kneading sections) at an average barrel temperature of 200 °C. Strands were quenched and subsequently pelletized. One part of the pellets was injection moulded at a temperature of 200 °C into square plates with a length of 80 mm and a thickness of 4 mm. The plates were subsequently irradiated with a dose of 50 kGy at ambient temperature, in air, using a 3 MeV 'Van de Graaff' electron beam accelerator at the IRI (Delft). The other part of the pelletized blend was first irradiated with the same dose and subsequently injection moulded. The injection moulded plates were prepared for notched Izod impact testing (ASTM D256) and were annealed during 24 hours at a temperature of 80 °C, according to the method described by Vollenberg [9]. As a reference, samples were left during three weeks at room temperature. Comparing the results of both methods it could be concluded that differences were within the experimental error.

Morphologies of the blends were characterized using Scanning Electron Microscopy (Cambridge Stereoscan 200). Samples were cut at liquid nitrogen temperature with a glass knife, subsequently etched in an oxygen plasma and finally covered with a gold layer.

The degree of crosslinking was measured via soxhlet extraction in (boiling) xylene during 24 hours. The samples were dried under vacuum at a temperature of 60 °C during 24 hours and subsequently weighed. The fraction of crosslinked material was based on the amount of rubber present in the blend.

Several methods were used to investigate possible changes upon irradiation in interfacial adhesion between rubber and matrix.

Fourier Transform Infrared (FT-IR)

A thin film of EPDM was prepared via solution-casting from cyclohexane. The SB block copolymer was dissolved in THF (ca. 10 wt%). A few droplets of the SB solution were put on the surface of the EPDM film. EPDM (slightly) swells in THF, giving the block copolymer the opportunity to diffuse into the EPDM surface layer. In order to ensure that the SB copolymer was mainly present at the EPDM surface, the THF was quickly evaporated. One part of the samples was irradiated with a dose of 100 kGy. Subsequently, the irradiated and unirradiated samples were immersed in ethyl acetate, a good solvent for the SB copolymer, but a non-solvent for EPDM rubber. Both non-crosslinked and crosslinked block copolymer which is not firmly attached to the EPDM surface will be removed [10].

It has to be mentioned that compared to the real situation, i.e. an injection moulded PS/EPDM/copolymer blend, both the concentration of copolymer and irradiation doses are relatively high. However, this treatment was necessary in order to increase the amount of block copolymer above the detection limit and for ease of handling.

Solid State Nuclear Magnetic Resonance (NMR)

Irradiated samples of PS/EPDM/SB and PS/EPDM/SEP blends were thoroughly extracted in boiling xylene during 24 hours via the Soxhlet method in order to remove polystyrene, the non-crosslinked EPDM and the non-crosslinked block copolymer. Subsequently, the samples were dried at 50 °C under vacuum during 24 hours. These dried samples were immersed in THF in order to remove residual xylene. During 24 hours THF was renewed twice and after this period the samples were dried again during 24 hours at 50 °C under vacuum. Subsequently, the residue was analyzed with cross polarization, magic angle spinning NMR, (CP-MAS NMR), using a Bruker CXP 300 spectrometer with a standard Bruker double bearing MAS probe at a frequency of 75.476 MHz for ^{13}C. Samples were spun with a frequency of approximately 3.5 kHz in standard aluminium oxide rotors. In order to ascertain that the response factors towards cross polarization were not too different for the samples studied, the signal intensities versus cross polarization times (CP-curves) were determined for the materials. These experiments proved that the rather small differences could be neglected.

7.3 Results and Discussion

Morphology

Figure 7.1 shows the morphologies of various injection moulded blends. As can be inferred from Figure 7.1, and as expected, the addition of SB block copolymer reduces the average EPDM particle size, compare Figures 7.1e with 7.1 a-d. Both SB compatibilizers used seem equally effective in reducing the average EPDM particle size. Irradiation before injection moulding (irradiation of the pelletized strands, see experimental section) only slightly effects the EPDM particle shape and size, compare Figure 7.1a with 7.1b and 7.1c with 7.1d. Based on the micrographs in Figure 7.1 one may conclude qualitatively that the

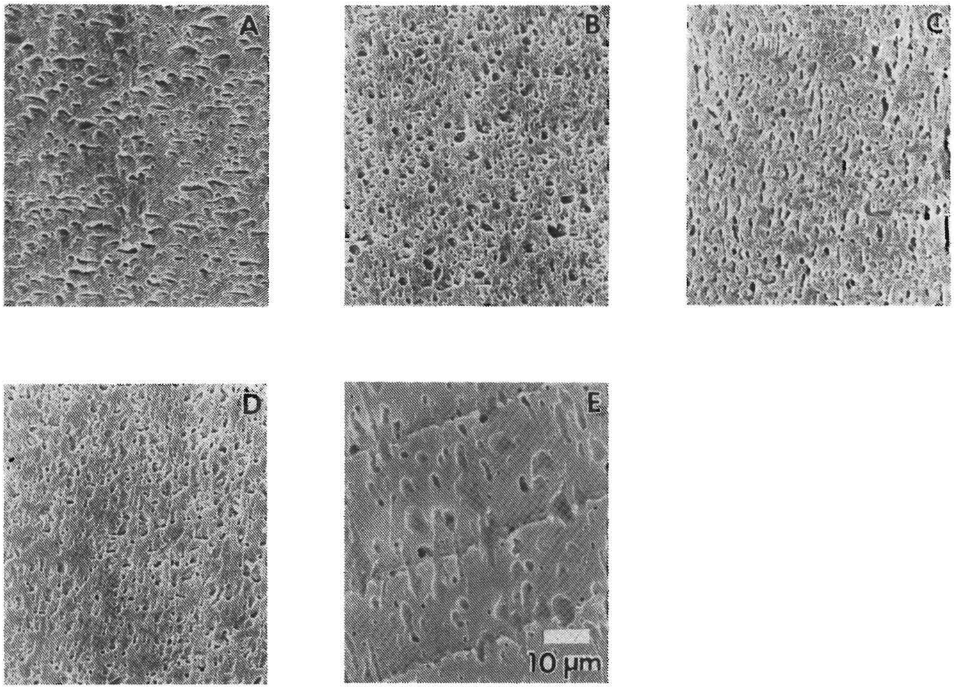

Figure 7.1 SEM micrographs of injection moulded blends (all magnifications are the same): a) PS/EPDM/l-PS 78/19/3, b) PS/EPDM/l-PS 78/19/3, irradiated with a dose of 100 kGy before injection moulding, c) PS/EPDM/h-PS 78/19/3, d) PS/EPDM/h-PS 78/19/3, irradiated with a dose of 100 kGy before injection moulding, e) PS/EPDM 80/20.

morphology of the processed blends is determined primarily by the addition of blockcopolymers, at least for the processing conditions employed for these experiments.

unirradiated blends

The impact strength data are presented in Figure 7.2. Figure 7.2a shows that an increase in impact is obtained from approximately 1 to 2.8 kJ/m^2 by the addition of 20 wt% EPDM and a further increase from 2.8 to 5 kJ/m^2 is achieved with the addition of the SB compatibilizers. This effect is related, as well documented in literature, to the combined effect of reduced particle size and an increased adhesion [1,2].

Irradiated blends

Although EB irradiation of the pelletized blend before injection moulding has no profound effect on morphology, in terms of fixation of

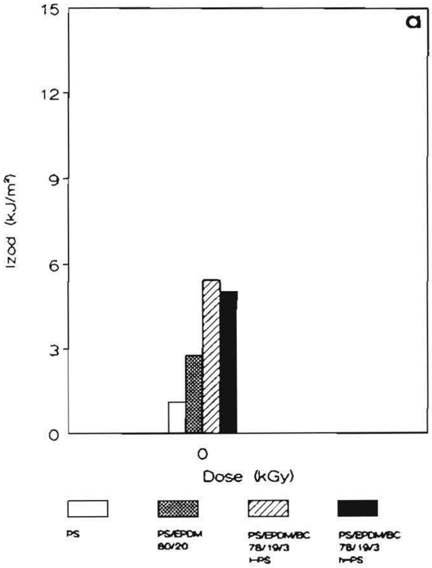

Figure 7.2 (explanation page 104)

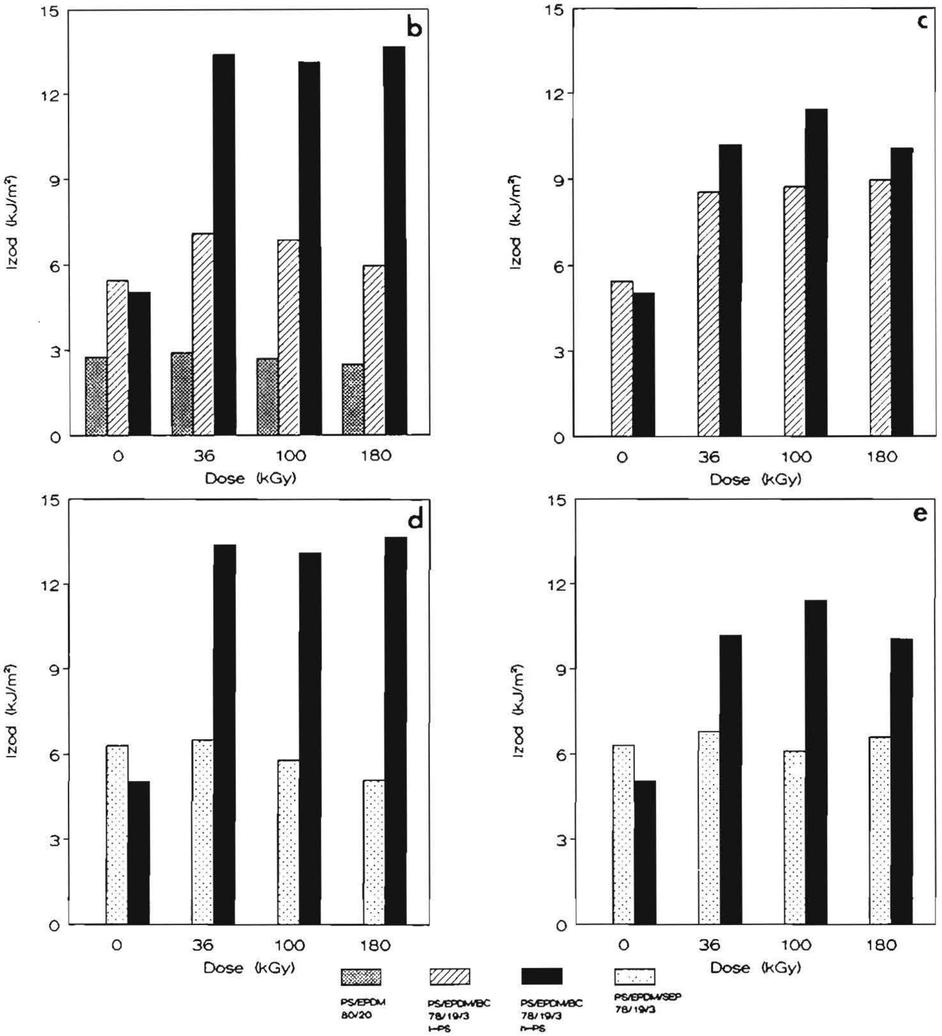

Figure 7.2 *Izod values of injection moulded blends as a function of irradiation dose: a) comparison between SB/h-PS and SB/l-PS, unirradiated blends, b) comparison between SB/h-PS and SB/l-PS, irradiated before injection moulding, c) comparison between SB/h-PS and SB/l-PS, injection moulded before irradiation. d) comparison between SB/h-PS and SEP copolymer, irradiated before injection moulding. e) comparison between SB/h-PS and SEP copolymer, irradiated after injection moulding.*

specific structures, a major increase in impact strength is observed if PS/EPDM/SB blends are subjected to irradiation either before (7.2b) or after injection moulding (7.2c). Via the latter route all influences of processing on impact strength are ruled out, i.e. there is no difference in morphology between the irradiated and unirradiated samples. At already a relatively low radiation dose, a strong increase in impact strength is observed, notably for the PS/EPDM blend with the high PS content (h-PS) block copolymer where an Izod value of approximately 14 kJ/m^2 is obtained. The differences in absolute Izod values between the two processing routes might be related to finer details in morphology or to a reorganization of the block copolymer at the interface, which cannot be explained yet. In Figure 7.2d a comparison is made between the Izod values of PS/EPDM/SB * and PS/EPDM/SEP blends, irradiated before injection moulding. For the unirradiated blends, the use of the SEP copolymer instead of the SB copolymer results in a higher Izod value. Irradiation results in a major increase in impact strength for the blend with SB diblock copolymer, whereas the Izod value for the blend with SEP copolymer remains constant or even slightly decreases. The change in processing sequence, i.e. irradiation after injection moulding does not significantly change the impact properties of the blends with SEP copolymer, see Figure 7.2e.

In addition to differences in morphology also crosslinking as such of the dispersed EPDM phase *cannot* explain the observed changes in impact properties. For example the increase in impact strength in PS/EPDM/SB blends is already achieved at a dose of 36 kGy, whereas the degree of crosslinking of the dispersed EPDM phase increases continuously, see Figure 7.3. Moreover, PS/EPDM blends, without compatibilizer and with the SEP compatibilizer, do not change in impact strength upon irradiation (see figure 7.2b), whereas the degree of crosslinking is higher or similar to that of the blends with SB copolymer [11].

Consequently, the main reason for the change in impact properties should be related to a radiation induced change in interfacial adhesion.

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* *SB/h-PS was used.*

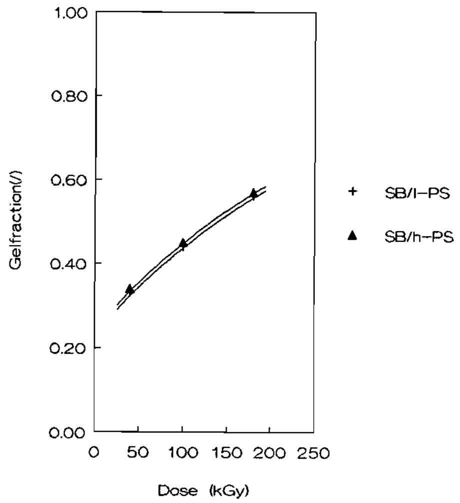

Figure 7.3 *Crosslinked fractions for PS/EPDM/SB 78/19/3 blends as a function of irradiation dose.*

Model

The block copolymer is expected to be located at the interface between the PS matrix and the dispersed EPDM particles. It can be expected that the PS part of the block copolymer (PS^b) is embedded in the PS matrix (see Figure 7.4a). If it is assumed that crack propagation of the blend during impact testing occurs via the interface, the ultimate impact value will be determined by the weakest part of the PS/EPDM interface. Cleavage may occur at two possible positions: (i) the EPDM/butadiene phase or (ii) at the PS/PS^b phase. For the unirradiated blend it is assumed that fracture will occur via the weak EPDM/butadiene phase (see Figure 7.4b). Upon irradiation of blends with the SB copolymer the EPDM phase and the butadiene part of the block copolymer will crosslink. This implies that upon irradiation the interaction between EPDM and PB may strongly increase via co-crosslinking of the two phases or possibly even grafting of PB onto EPDM. The interaction between PS and PS^b will remain constant since

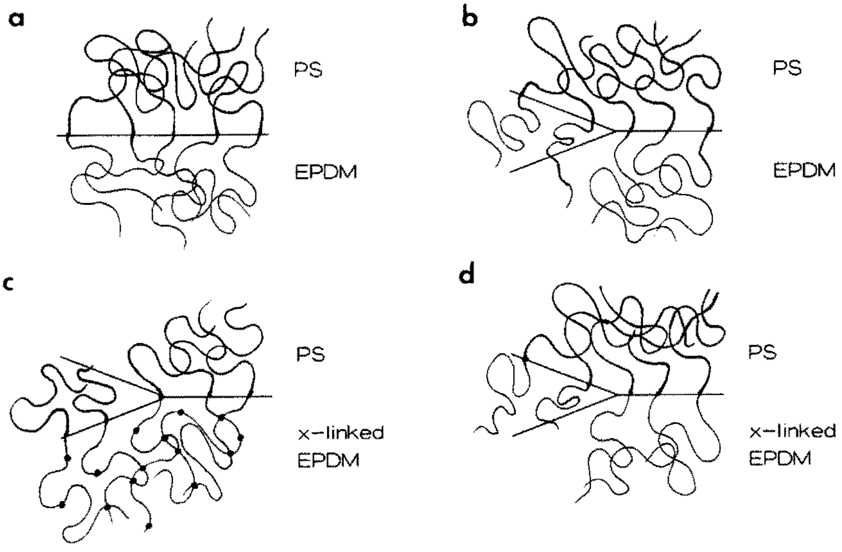

Figure7.4 *Schematic representation of the PS/EPDM interface before and during impact loading. a) Location of the block copolymer at the interface. b) Cleavage for the unirradiated blend occurs via the EPDM/SB or EPDM/SEP interface. c) Cleavage for the irradiated blend of PS/EPDM/SB occurs via the PS/SB interface, due to an increased interaction between EPDM and SB. d) Cleavage for the irradiated blend of PS/EPDM/SEP occurs via the EPDM/SEP interface. The interaction between EPDM and SEP is hardly changed upon irradiation.*

PS is very insensitive towards EB irradiation [7]. With increasing radiation dose the interaction level at the EPDM/butadiene side will exceed the interaction between PS and PS^b. Consequently, at higher doses fracture will occur via the PS/PS^b interface (see Figure 7.4c). A further increase in irradiation dose will not change the adhesion (at the PS/PS^b interface) and consequently a higher dose will not improve the impact properties. The higher effectivity of the block copolymer with the longer styrene chain can be explained as the result of a stronger interaction at the PS/PS^b interface. On the other hand, in the blend with the SEP copolymer the interaction between EP and EPDM will hardly change, since crosslinking or grafting of EP will occur at a very slow rate and will partly be overruled by chain scission [8]. Fracture will occur via the EPDM/EP interface for all irradiation doses (see Figure 7.4d). The observed decrease in impact properties for the SEP blend as a result of irradiation, might be explained by partial chain scission of the block copolymer.

Some evidence for this increased adhesion, obtained by physical analytical methods will now be presented.

FT-IR

In Figure 7.5 IR spectra are presented of unirradiated and irradiated EPDM/SB samples, extracted in ethyl acetate, which are prepared as described in the experimental section. In the spectrum of the irradiated sample, peaks at 700 and 758 cm^{-1} are clearly visible. These peaks are, among others, characteristic for the styrene part of the SB compatibilizer. The spectrum of the unirradiated EPDM/SB sample, also extracted in ethyl acetate, does not show these characteristic peaks and resembles the original EPDM sample very well. Obviously, via extraction in ethyl acetate the SB copolymer can be removed completely. Evidently, removal of the block copolymer from the EPDM film is no longer possible after irradiation, i.e. the interaction has strongly increased.

A comparative experiment was performed for both the SEP and SB copolymer using a LDPE instead of an EPDM film, with THF as a solvent [12]. Spectra of irradiated samples with the SEP copolymer hardly showed any characteristic peaks for the block copolymer, whereas these could clearly be revealed for the SB copolymer [12].

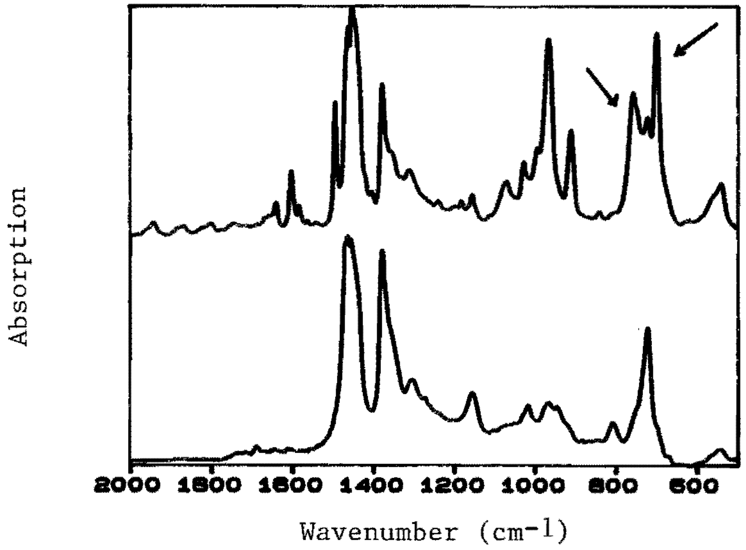

Figure 7.5 *IR Spectra of EPDM/SB samples extracted in ethyl acetate a) unirradiated, spectrum resembles original EPDM spectrum: all SB is removed. b) Irradiated with a dose of 100 kGy, characteristic peaks for SB are clearly visible at 700 and 758* cm^{-1}. *SB cannot be removed completely.*

NMR

In Figure 7.6 ^{13}C CP MAS NMR spectra of the residues of the irradiated, extracted blends are shown. For these measurements, another type of PS (higher molar mass), and larger amounts of SB/h-PS copolymer were used. The principle remains, however, intact.

The typical aromatic peaks at 127 and 144 ppm as well as spinning side-bands (at 81 and 173 ppm) are most clearly visible for the blend originally containing 5% of SB copolymer. Moreover, the backbone ^{13}C signal is visible as a shoulder near 44 ppm. For the blend with the SEP copolymer almost no aromatic groups are detected. This implies that in case of the SB copolymer there is a substantial amount of crosslinked SB copolymer present in the residue, whereas this is not the case for the SEP copolymer. Again this is an indication that the SB is much more reactive than the SEP copolymer. Assuming that the block copolymer is, as expected, located at the interface, irradiation will induce the largest changes at the interface in the blends with 5% SB block copolymer.*

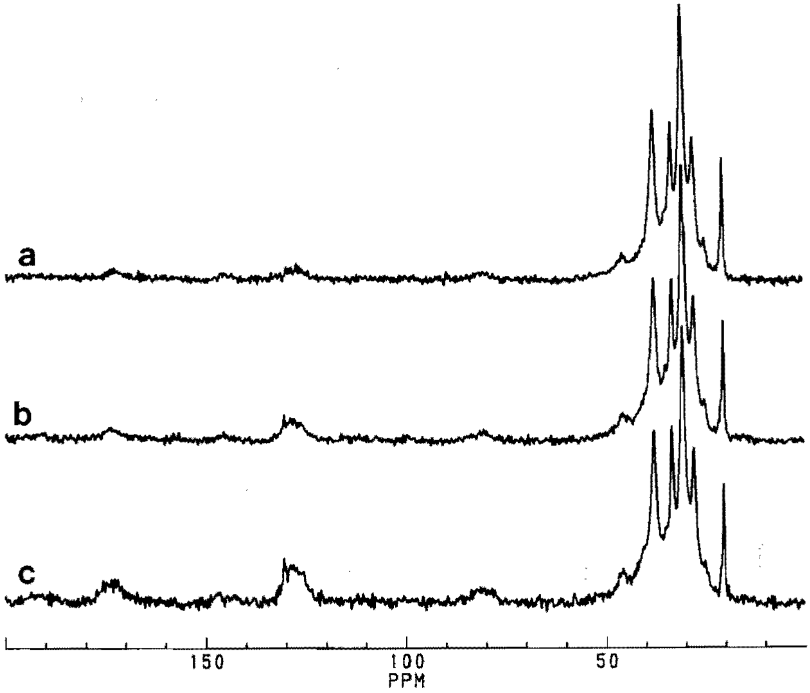

Figure 7.7 ^{13}C *CP-MAS NMR spectra of the residue of extracted samples irradiated with a dose of 100 kGy: a) PS/EPDM/SEP, 78/19/3, b) PS/EPDM/SB, 78/19/3, c) PS/EPDM/SB, 78/17/5*

A shift in the glass transition temperature of the rubber phase also provides evidence of an increased adhesion [12,13].

Although there is evidence for an increased adhesion upon irradiation, it must be mentioned that it is not completely clear whether this results from co-crosslinking of the butadiene and the EPDM, from grafting

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* *For a blend with 5% SB/h-PS as a compatibilizer an Izod value of 21 kJ/m^2 could be obtained [12].*

of the butadiene onto the EPDM phase or merely from an increase of the molar mass of the butadiene part of the block copolymer. Also the question whether breakage at the interface occurs via cleavage of the block copolymer or via pull out from the dispersed phase or matrix, respectively, is still unanswered. However, there is an indication that pull out is the main mechanism. If chain scission had prevailed, no such dependence on PS block length would have been found. In recent papers [14,15], Brown describes that chain cleavage occurs for high molar mass block copolymers. In a system of PS and polymethylmethacrylate (PMMA) pull out prevails for block copolymers with molar mass below 51 kg/mole. The block copolymers used in this study possess a comparable low molar mass.

7.4 Conclusions

It has been shown that impact properties of PS/EPDM blends can be improved significantly with EB irradiation when a suitable reactive compatibilizer is used, in our experiments a SB diblock copolymer. Differences in morphology and crosslinking of the dispersed phase could be eliminated as explanations for the observed phenomenon. It was shown that a change in interfacial adhesion is the most probable explanation. A simple model could be derived based on the assumption that via irradiation the interaction between the butadiene part of the copolymer and the EPDM increases to such an extent that the ultimate impact properties are determined by the interaction between the PS of the block copolymer (PS^b) and the PS matrix. This model basically explains (i) the necessity of a block copolymer with a high beam response (= crosslinkability) towards EB, (ii) the higher effectivity of a block copolymer with a higher PS block length (stronger interaction with matrix) and (iii) the strong increase in impact at low doses which remains constant at higher doses (the interaction between PS and PS^b

does not change upon irradiation). Via physical analytical methods, FT-IR, and NMR evidence has been found for this increased adhesion.

Some additional mechanical properties (yield stress, elongation at break and modulus) are presented in the appendix.

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    Hoeben, W.L.F.M., Masters thesis, Eindhoven University of Technology, 1990

11 In our laboratory the amount of crosslinking was determined for the blend with the SEP copolymer in the same way as done for the SB blend. The following comparison could be made.

Material	Crosslinking (%) at a dose (kGy)		
	40	100	180
PS/EPDM/SEP 78/19/3	40	55	59
PS/EPDM/SB 78/19/3	34	45	57
PS/EPDM 80/20	52	74	78

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CHAPTER 8

CONTROLLED SCISSION: NEW DEVELOPMENTS

The previous chapters were mainly focussed on selective *crosslinking of the dispersed phase* or on modifying the interface. Only in PP/EPDM blends, simultaneous scission of the PP matrix occurred. In this chapter some preliminary results will be presented concerning *controlled scission* of a polymer which either forms the *dispersed phase* or forms a co-continuous structure with the other component of the blend.

8.1 Impact Improvement of Polyamide-6/Polyisobutylene Blends*

8.1.1 Introduction

The improvement of the impact properties of polyamides (PA), via the incorporation of small, homogeneously dispersed rubbery particles has been studied extensively [1-12]. As discussed in chapter 1, for these blends a sharp Brittle-to-Tough transition exists at a critical inter particle distance.

It has been suggested that enhanced cavitation of the rubber phase, causing a local change in the stress-state, is favourable for good impact properties [4,11]. A major problem with these experiments is that variations in cavitation behaviour of the dispersed phase (using different grades of rubber) are accompanied by variations in morphology and interfacial adhesion [4,11].

**Reproduced in part from Van der Sanden, M.C.M., Van Gisbergen, J.G.M., Tauber, I.D., Meijer, H.E.H. and Lemstra, P.J., in 'Integration of Fundamental Polymer Science and Technology', vol. 5: Eds. P.J. Lemstra and L.A. Kleintjens, Elsevier Appl. Sci. Publ., London, in press.*

Gent has shown that the cavitation stress of rubbers is proportional to the modulus of the rubber [13]. Consequently, the best impact properties are expected with a low modulus, low molar mass dispersed phase, provided that a homogeneous distribution of small particles can be induced. This latter condition, however, is hard to fulfil, since such a fine dispersion can only be achieved when polymers are blended which possess approximately similar viscosities, see chapter 1 and ref. [14].

Both problems might, in principle, be solved via Electron Beam (EB) irradiation. An optimum morphology for impact toughening can be induced using well-tuned mixing and processing equipment and choosing constituents with comparable viscosity, see chapter 4. Subsequent irradiation should result in controlled scission of the dispersed phase, which implies a lower modulus and a lower cavitation stress. Moreover, matrix and interfacial adhesion should remain unaffected and, consequently, via this method the relation between impact strength and modulus of the dispersed phase can be revealed directly as well. Some preliminary results concerning EB irradiation of relatively inert polyamide-6 (PA-6) and polyisobutylene (PIB) -rubber, which is susceptible to scission, [15-17] will be presented.

8.1.2 Experimental

The matrix used is PA-6 (Akulon F135C, AKZO). The PIB rubber (Oppanol B100, BASF) was modified with maleic anhydride (MA), similar to the previously described method for EPDM-rubber [18], using Nourymix 914 (a 50/50 wt% masterbatch of MA on polypropylene, AKZO) and Trigonox 101-50PP (a 50/50 wt% masterbatch of 2,5 dimethyl-2,5-bis (t,butylperoxy)hexane on polypropylene, AKZO) as initiator.

Functionalization of PIB with MA is carried out in a Berstorff 25 mm corotating twin screw extruder at a temperature of 200 °C, using 4 wt% Nourymix and 0.8 wt% Trigonox. Free MA was removed by extracting the modified rubber with water (24 hours) at room temperature. Subsequently the PA-6/PIB blends were prepared in a 80 to 20 weight ratio in the same corotating twin screw extruder at an average barrel temperature of 240 °C. The blends were pelletized and subsequently injection moulded on an Arburg Allrounder into square plates with a length of 64 mm and a thickness of 3.2 mm. These plates were irradiated, at room temperature and in air, with various doses using a 3 MeV 'Van de Graaff' Electron Beam accelerator at the IRI (Delft).

Test samples for notched Izod impact testing were prepared from the irradiated and unirradiated plates, according to ASTM D256. Before testing at various temperatures, the samples were annealed at 80 °C during 24 hours.

Samples for scanning electron microscopy (SEM) were first microtomed at liquid nitrogen temperature using a glass knife. Subsequently, the samples were etched with an oxygen plasma and finally they were covered with an argon plasma induced gold layer.

Molar masses were determined using size exclusion chromatography. For these measurements, PA-6 was dissolved in hexafluorisopropanol and diol modified silica columns were used. The PIB samples were dissolved in THF and were measured on styragel columns.

8.1.3 Results and Discussion

Figure 8.1a shows a SEM micrograph of an injection moulded PA-6/PIB 80/20 blend, prepared as described in the experimental section. For comparison, in Figure 8.1b the morphology of an injection moulded blend is shown using an unmodified PIB rubber. It is clear that modification of the PIB rubber results in a much smaller average particle size compared to the blend with pure PIB. However, compared to EPDM particle sizes reported by Borggreve [3,4] and Wu [1], the weight average particle size in the PA-6/PIB (modified with MA) blend is still large, approximately 2 to 2.5 µm. Obviously MA modification is less effective for PIB rubber compared to EPDM rubber, due to the absence of double bonds in the PIB rubber.

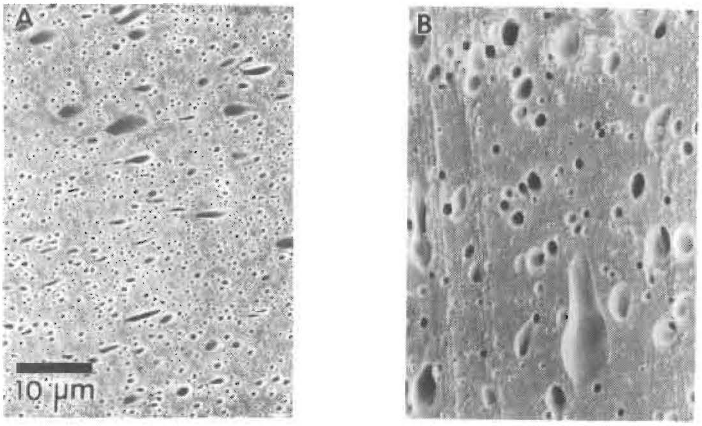

Figure 8.1 *SEM micrographs of injection moulded PA-6/PIB blends. a) PIB modified with MA, b) PIB unmodified*

The molar masses of the PA-6 and PIB homopolymers are given as a function of the irradiation dose in table 8.1. It can be inferred that PA-6 is relatively inert towards EB irradiation and does not noticeably change up to doses of 80 kGy. For PIB on the other hand a rapid decrease in

Table 8.1 *Molar masses (M_n, kg/mole) of PA-6 and PIB homopolymers as a function of the irradiation dose.*

dose (kGy)	PA-6	PIB
0	34	88
20	32	70
50	33.5	56
80	39	32

molar mass is observed upon irradiation. (The molecular weigths for PIB were measured for the unmodified PIB. The rate of chain scission of the modified PIB, determined via viscosity measurements, is similar [19].)

Figure 8.2 reflects the Izod values of the PA-6/PIB blends as a function of temperature. A small reduction in BT temperature at low doses (20 and 50 kGy) but a pronounced increase for irradiation with a dose of 100 kGy is observed. Properties of the PA-6 matrix are hardly affected at such a low dose [16].

The absolute values of the impact strength in the brittle region are not influenced by irradiation.

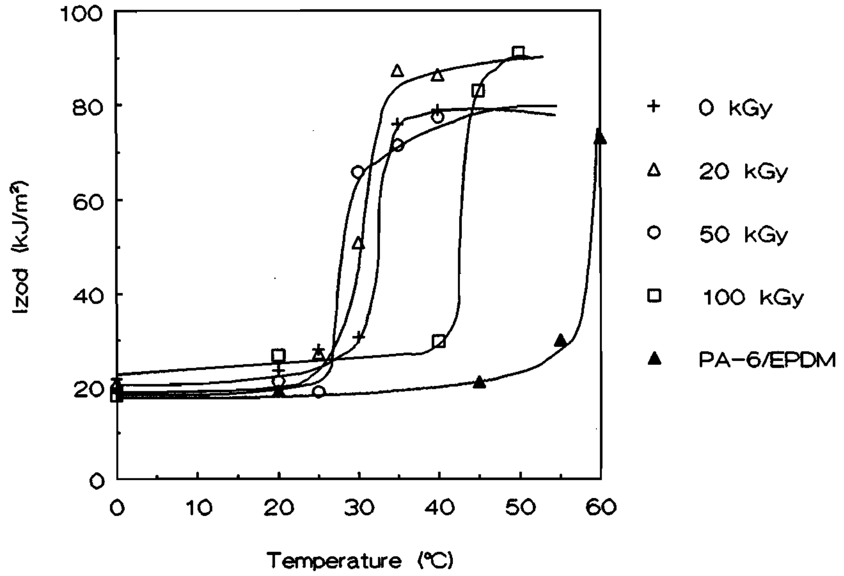

Figure 8.2 Izod values of irradiated PA-6/PIB blends, PIB modified with MA, as a function of temperature. For comparison also a curve of PA-6/EPDM is shown as obtained from Borggreve, figure 6 from ref [3].

For comparison, also a curve for PA-6/EPDM is shown in Figure 8.2, reproduced from Borggreve (figure 6 in ref [3]). This blend contains 20 wt% EPDM, with a weight average particle size of 1.94 μm and is the only blend reported by Borggreve which has a particle size and weight fraction comparable to the PA-6/PIB blend. It can be inferred that the BT transition for PA-6/PIB blends is approximately 25 °C lower than for the PA-6/EPDM blend. Probably the modulus, and consequently the cavitation stress, of the unirradiated PIB rubber is already small compared to that of EPDM and a further reduction of the modulus is not as effective as expected.

Due to the relatively large particle size, however, the absolute value of the BT temperature is high compared to results reported by Borggreve [3,4] and Wu [1,2] for blends with much smaller rubber particles.

Summarizing, the particle size of the dispersed PIB phase in PA-6 is not optimized yet. Consequently, the absolute value for the BT transition is relatively high compared to results obtained for blends with much smaller rubbery particles. Nevertheless, the method of inducing a specific morphology and subsequent controlled scission of the dispersed phase via EB irradiation is promising. The lower molar mass of the dispersed phase initially results in a decrease in the BT transition temperature but subsequently in an increase. Further research is focussed on getting a better understanding of this relation between modulus/cavitation of the dispersed phase and impact properties of the blend, as well as on inducing an optimum morphology in the PA-6/PIB blends to investigate the effectivity of the method in the low temperature region.

8.2 Porous materials

8.2.1 Introduction

The use of polymers in synthetic membranes has rapidly increased. Membranes can be applied for filtration purposes, with typical micropores between 0.1 and 10 μm radius, as well as for separation of gas mixtures, where homogeneous polymer films can be used [20,21]. In the microporous membranes, separation is based on differences in particle size, whereas for homogeneous polymer films the separation mechanism is based on solubility and diffusion. The latter mechanism is slow and, consequently, homogeneous membranes should be as thin as possible. In order to ensure sufficient strength of such a thin film, the actual membrane is supported by a porous layer. Some characteristics of such a support layer are:

a) Possibility to *support* the membrane at a given pressure, without sudden or gradual collapse.
b) Possessing such a structure that the *thin film cannot enter the pores.*
c) *Homogeneous* distribution of the pores.
d) Possessing a *pore volume as large as possible* to minimize the contribution of the support layer to the resistance against flow.

These conditions make the preparation of such a support layer complex. A typical example is biaxially drawn PP, known by the name Celgard [22].

In this study some preliminary experiments have been performed concerning the contribution of polymer blending and irradiation to the preparation of porous materials, which could either be employed as a basic membrane or as a support layer. The main idea is based on using two immiscible polymers and to generate an appropriate structure with controlled pore size. Subsequently the blend is irradiated which should result in controlled chain scission of one of the phases and, preferably, in crosslinking of the other one. A porous material will be achieved upon subsequent extraction of the degraded phase in a suitable solvent. Scission will enhance the extraction process and crosslinking will yield a material with better temperature and chemical resistance.

Results concerning the model system of crosslinkable PE and degradable PIB will be discussed.

8.2.2 Experimental

Blends of LLDPE (Stamylex 1026, DSM) and PIB (Oppanol B150, BASF) were prepared in various weigth ratios on a two roll mill (Schwabentahn) at a temperature of 200 °C. Subsequently the blends were compression moulded (Fontijne press) into plates with a thickness of approximately 1 mm. These plates were irradiated with a dose of 100 kGy, as described in paragraph 8.1.2.

Subsequently the samples were extracted in n-hexane for 96 hours. The permeability of nitrogen gas was determined according to ASTM D-1434. Morphologies of the extracted blends were characterized with SEM.

8.2.3 Results

Investigation of the morphologies of the various blends revealed that at a concentration of 60 wt% LLDPE and 40 wt% PIB a co-continuous structure was achieved [23]. Comparison of the extracted PIB amount in the irradiated and unirradiated blend clearly shows the effect of irradiation, see table 8.2. In the irradiated blend the PIB phase is removed completely, within the experimental error, whereas in the unirradiated blend only 50 % is removed. The differences are also clearly demonstrated in the morphology of the extracted blends, see

Figure 8.3. A very porous structure can be observed for the irradiated blend (8.3b) whereas only a few pores can be discerned in the unirradiated blend (8.3a).

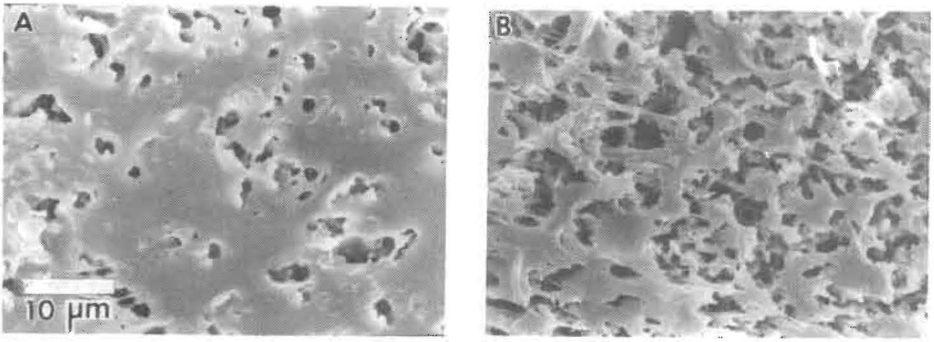

Figure 8.3 Morphologies of extracted LDPE/PIB 60/40 blends: solvent: n-hexane, time 96 hours, T = 20 C. a) 0 kGy, b) 100 kGy.

The porosity of the structure shown in Figure 8.3b is reflected in the permeability for nitrogen which is $1.3 \cdot 10^{-7}$ Barrer compared to typical values of 10^{-13} Barrer for non porous polymers (1 Barrer = 1 $cm^3/(cm^2 s Pa)$). Commercially available support layers possess permeabilities in the order of magnitude of $2 \cdot 10^{-6}$ to $1.5 \cdot 10^{-2}$ Barrer. This implies that some optimization is nescessary for this system.

Table 8.2 Extracted PIB percentage in a LDPE/PIB 60/40 (w/w%) blend. Solvent: n-hexane, time 96 hours, T = 20 °C.

dose (kGy)	PIB extracted (%)
0	48.7
100	96.7

Discussion

The results shown above indicate that preparation of porous polymer materials can, in principle, be generated via the blending/irradiation technique. More extensive experiments indicated that a droplet in matrix morphology does not meet the requirements: a co-continuous structure, or even better a fibrillar structure with the fibrils perpendicular to the filmsurface, is a requirement for a permeable structure [23].

In principle a flexible method to prepare porous materials is achieved. Flexible, since many combinations of polymers (and copolymers) with various miscibilities exist, which implies that the pore sizes can be varied easily. This offers the possibility to generate asymmetric membranes. Different blends with a gradual decrease in particle size can be positioned onto each other. Subsequently, the layers can be 'glued' (via melting), whilst keeping the different layers intact. After irradiation and extraction a porous structure results, with a gradual increasing pore size. The pore volume can be varied by simultaneously changing the volume fractions and viscosity ratio. Good processability of the blend before extraction/irradiation offers the possibility to generate porous structures in simple as well as in complex geometries. However, care has to be taken concerning the viscosity ratio of the two polymers if different processing methods are used [23].

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CHAPTER 9

OUTSTANDING PROBLEMS IN THE IRRADIATION OF POLYMER BLENDS

Publications in the open literature on irradiation of polymer blends were mainly focussed on overall crosslinking of the blends or on diminishing the negative effects of irradiation on the major component of a blend [1].

The possibilities of using irradiation as a tool to induce a controlled amount of crosslinking and/or chain scission in either of the two phases or to induce reactions at the interface, aimed at obtaining unique properties, were discussed in this thesis.

In this chapter, some of the outstanding problems or interesting aspects will be addressed.

1) Crosslinking of the dispersed phase

The primary aim of using EB irradiation was to retain any morphology, i.e. a structured blend during subsequent processing steps [2,3,4]. It was shown, however, that in the model system PS/LDPE, fixation of a highly non-equilibrium morphology is not possible, due to the limitations in the crosslinking of the dispersed LDPE phase [2], although an enhanced stability was observed compared to the unmodified blend. It should still be investigated whether complete fixation can be obtained when the degree of crosslinking approaches 100% which may, for example, be obtained by the addition of crosslink enhancers or by irradiation at a higher temperature. In the absence of external flow, thread break-up and coalescence might be prohibited, whereas in the presence of flow the acting stresses are much larger and, consequently, deformation and break-up will continue. A direct micro-rheological study is required for these investigations. It was not possible to perform these experiments within the timeframe of this thesis.

For the unique blend of PP and EPDM sufficient stabilization of the morphology was obtained, resulting in an easy processable material with a high impact strength. However, the detailed rheological behaviour of irradiated PP/EPDM blends is rather complicated. At low shear rates, the irradiated blends show pronounced network behaviour and the viscosity may even exceed that of the unirradiated blends. The rheology proves to be dependent on the inter particle distance and degree of crosslinking of the dispersed EPDM phase.

The study of the rheology of immiscible polymer blends is generally hampered by the continuously changing morphology during measurements. As a result, much confusion exists in the literature on rheology of blends, see e.g. [5,6]. Stabilization of morphologies via compatibilizers, added to the blend or formed in situ, does not yield unambiguous results, because the interfacial tension, and consequently the morphology itself, changes by these modifications. If a suitable system is chosen, it is possible to stabilize a morphology via irradiation without changing the interface properties and the particle size. For the PP/EPDM blends used in this thesis, the interesting relation between inter particle distance and rheological behaviour at low frequencies could be revealed via the independently induced stability [7]. In general, radiation-induced crosslinking of the dispersed phase could be a valuable tool for the study of the rheology of polymer blends.

2) Improved adhesion at the interface

In a PS/EPDM blend, with SB added as a compatibilizer, irradiation increases the impact strength with a factor up to 3 as a result of grafting of the SB onto the EPDM [8]. Irradiation of these types of materials can be of interest since an optimum morphology for controlled craze initiation can be induced and subsequently, the adhesion can be increased in order to retard craze propagation.

In compatibilized blends several requirements exist for optimum performance of the compatibilizer. A high rate of diffusion requires a low molecular weight, equal blocklenghts are needed to prevent micel formation and long chains are desirable for good adhesion [9,10]. Using EB irradiation, the effect of these parameters can be investigated seperately and influenced after blending, in function of the molar mass of the (diblock) copolymers or the ratio of their blocklengths. For this purpose samples with well defined fracture surfaces should be used, see Brown et al. [11-13].

3) Specific use of scission

Controlled scission of the dispersed phase has only been subject of a preliminary study but yields a unique method to change the ratio of the moduli of the dispersed phase and the matrix, independently of the morphology. As an example may serve the introduction of small, liquid (low viscous), PIB particles in a PA-6 matrix, to study the relation between cavitation stress of the PIB phase and impact properties of the blend [14]. The use of degradable block copolymers offers the possibility to generate even smaller dispersed liquid particles in a polymer matrix.

The fabrication of porous polymer films is another application of controlled scission. Via the appropriate choice of the constituents of the blends, compatibilizers, volume fraction, viscosity ratios and processing parameters, cocontinuous morphologies can be induced. In LLDPE/PIB blends, with a cocontinuous morphology, the PIB phase was easily extracted after irradiation [14]. As discussed in chapter 8, preparation of asymmetric membranes via this method is worthwhile to investigate, because of the flexible and well controlled production possibilities.

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13\. Chapter 8

Appendix

Some Details of Mechanical and Rheological Properties of Irradiated Blends

In this appendix, additional information is presented on the mechanical and rheological behaviour of PP/EPDM and PS/EPDM blends.

PP/EPDM blends

The characteristics of the PP and EPDM grades used are listed in table A1.

Table A1 Characteristics of the materials used, as supplied by the manufacturer.

Polypropylene	M_n kg/mole	M_w kg/mole	MFI dg/min
13E10, (DSM)	62	330	1.1
15M10, (DSM)	37	250	3.0
112Mn40, (DSM)	29	112	45

EPDM-rubber	M_n kg/mole	M_w kg/mole	Mooney *(1+4)/125*	diene mole %	ethylene mole (%)
Keltan 312, (DSM)	45	135	33	4 *	55
Keltan 512, (DSM)	55	185	46	4 *	55
Keltan 514, (DSM)	45	180	46	8 *	52
Keltan 740, (DSM)	70	200	63	1**	60
Vistalon 808, (Exxon)	74		36		77

* *ethylidene norbornene*
** *dicyclopentadiene*

Rheological characterizations were performed via 3 different methods: melt index (MFI) determination (ASTM D1268-65T), dynamic mechanical analysis (DMA, Rheometrics RDS II) and capillary viscosimetry (Gottfert HKR 200). Rheological properties of blends and homopolymers, in an order of increasing MFI, as well as their Izod values are listed in table A2.

Table a2 Rheological characterization vs impact properties
PP/EPDM, 70/30 (wt%) blends.

Material	MFI	DMA *		Capillary **		Izod
frequency =		10^{-1} (s^{-1})	10^{2} (s^{-1})	10^{2} (s^{-1})	10^{3} (s^{-1})	
	dg/min	Pas	Pas	Pas	Pas	kJ/m^2
13E10/K512, 0 kGy	0.64					79.6
13E10/K514, 0 kGy	0.69					79.3
13E10/K740, 0 kGy	0.91	13000	800	961	172	88.6
13E10/V808, 0 kGy	1.19	16000	1205	887	182	75.9
13E10/K514, 44 kGy	2.1					64.7
13E10/K514, 88 kGy	2.19					61.9
13E10/V808, 100 kGy	2.26	93000	805	382	107	72.3
13E10/K512, 44 kGy	2.74					64.7
15M10/K512, 0 kGy	3.03			571	125	14.4
112Mn40/K514, 0 kGy	8.2					9.3
112Mn40/K740, 0 kGy	16.2	2100	398	261	76	5.0
15M10/k512, 75 kGy	22			210	60	36.4
13E10/K740, 100 kGy	28.6	16000	191	218	70	58.6
15M10/K312, 75 kGy	52.3	9000	141	127	48	11.4
13E10, 0 kGy	1.16			802	644	3.6
15M10, 0 kGy	3.55	4100	495	548	120	7.2
13E10, 100 kGy	135			50	25	1.5
15M10, 75 kGy	141	249	58	59	25	6.1

Viscosities as obtained from:
* DMA: dynamic mechanical analysis. Complex viscosity at frequency = 10^{-1} and 10^{2} rad/s

** Capillary Viscosimetry. Apparent viscosity shear rate at 10^{2} and 10^{3} s^{-1}

From table A2 it can be inferred that, in principle, a blend with a low viscosity at high shear rates and good impact properties can be obtained via irradiation, for example, 13E10/K740, 100 kGy.

Table A2 also shows that the MFI, which is frequently being used for industrial purposes, does not only result in wrong predictions of the processability at high shear rates, but especially underestimates the viscosity of irradiated blends at low shear rates. A more detailed discussion about the rheological behaviour of irradiated PP/EPDM blends is presented in chapter 5.

In table A3 the elongation at break is shown for two blends as a function of irradiation dose. It can be inferred from this table that the elongation at break for irradiated blends with, initially, a high molecular weight PP as a matrix remains high compared to the elongation at break of a blend with a low molecular weight PP as a matrix (reference sample).

Upon irradiation, the sensitivity towards orientation drastically decreases.

Table A3 Elongation at break for some PP/EPDM 70/30 (wt%) blends.

Material	elongation at break (%) perpendicular	 parallel
13E10/K740, 0 kGy	776	260
13E10/K740, 50 kGy	599	464
13E10/K740, 100 kGy	549	497
112Mn40/K740, 0 kGy (reference sample)	232	336

PS/EPDM blends

In table A4 some characteristic properties as obtained from stress strain measurements are shown for irradiated PS/EPDM/SB blends. It can be inferred that the yield stress (σ_y) as well as the elongation at break (ε_b) increase upon irradiation, whereas the modulus (E) remains relatively constant.

An increase in yield stress implies a decrease in craze initiation ability and is normally accompanied with even a stronger decrease in elongation at break, which implies a decreased total energy at break. In the irradiated PS/EPDM/SB blends, however, also the elongation at break strongly increases, which results in an increase in the total energy at break. Evidently, both, the delay in craze initiation and the reduction in craze growth rate, have a positive effect on the ultimate impact properties.

Table A4 *Mechanical properties of PS/EPDM/SB blends. SB/h-PS is used. Irradiated after injection moulding. (Styron 638 was used).*

	σ_y (MPa)	ε_b (%)	E (MPa)
PS/EPDM/SB, 0 kGy	11.6	2.3	1100
PS/EPDM/SB, 40 kGy	16.9	6.1	1400
PS/EPDM/SB, 100 kGy	16.3	13.0	1200
PS/EPDM/SB, 180 kGy	16.4	14	1200

SUMMARY

Blending of two or more polymers offers a possibility to generate materials with unique properties in a relatively easy way. Since most polymers are immiscible on a molecular scale, blending normally results in a heterogeneous mixture. The morphology, the characteristic size and shape of the distribution, as well as the adhesion between the phases determine, to a large extent, the ultimate properties of these blends. This thesis presents results concerning the modification of immiscible polymer blends via Electron Beam (EB) irradiation.

In principle, a tailor-made morphology which in many cases can be induced during mixing, e.g. a droplet-in-matrix structure for rubber toughened brittle polymers or a layered structure in a barrier blend, is required for each application. However, such a morphology represents a non-equilibrium situation in the melt, depending on shear or elongational stress and rate, viscosity ratio, volume fraction and temperature and adapts continuously to changes in these processing conditions.

It was shown that an enhanced stability of a highly non-equilibrium morphology could be achieved via irradiation in the model system of relatively inert polystyrene (PS) and crosslinkable polyethylene (PE), resulting from selective crosslinking of the dispersed PE phase. Complete fixation was expected, because dynamic rheological measurements in the melt revealed that the radiation-crosslinked PE possesses a yield stress. However, micro-rheological processes like thread break-up and coalescence of particles were, although retarded considerably, not prevented. Further, slow-down of these processes proved less pronounced than expected from calculations performed with equations derived for these processes for Newtonian systems. The

observations can be explained by the fact that via EB irradiation, an uncomplete network is formed in the PE phase in this model system (an intrinsic limitation of radiation crosslinking of PE, possibly enhanced by shielding of the PS matrix).

A second, unique and consequently more interesting possibility for EB irradiation is in toughening of polypropylene (PP) with EPDM-rubber. In the choice of the constituents for this blend, a contradiction exists between two essential requirements in the development of an injection moulding grade: the blend should be easy processable and possess high impact strength. A high impact strength can only be obtained when small EPDM particles are homogeneously distributed in the PP matrix. Since dispersive mixing is most efficient when the viscosities of the polymers are matched, a highly viscous PP as a matrix is required, due to the intrinsicly high viscosity of EPDM-rubber. This results, however, in a blend which is difficult to process via injection moulding. On the other hand, the use of an easy processable PP (low viscosity) as a matrix results in coarse morphologies and poor impact properties in the final product.

An optimum morphology could be introduced during compounding, using a highly viscous PP, and subsequent irradiation of the blend combined a controlled scission of the PP matrix resulting in a lower viscosity and a stabilization of the morphology, via crosslinking of the EPDM-particles. Coalescence of the EPDM particles in the typical timescale of the injection moulding process was prevented.

A more detailed rheological analysis over large shear rate intervals of the PP/EPDM blends revealed that irradiation resulted in a decrease in viscosity at high shear rates (i.e. easy processable via injection moulding). At low shear rates, however, the irradiated blends behaved like a network and the viscosity could even exceed that of the unirradiated blends. The rheological behaviour proves to depend both on the extent of crosslinking of the EPDM phase and the inter particle distance. This behaviour is attributed mainly to the aggregation of the dispersed, crosslinked EPDM particles.

Ternary PP/EPDM/HDPE blends possessed a morphology containing composite dispersed particles: a HDPE core and an EPDM shell which was frequently perforated with HDPE lammelae. Irradiation before injection moulding fixed relatively large particles (induced via a non-optimized extrusion step), resulting in a decrease in impact properties compared to the unirradiated blend.

A third application of the irradiation of blends can be found in the improvement of the interfacial properties. Irradiation of a PS/EPDM blend, with a styrene-butadiene (SB) diblock copolymer added as a compatibilizer, did not lead to a fixation of the morphology during injection moulding. However, upon irradiation, the Izod value could be raised up to a factor 3. Due to the abundance of double bonds in the butadiene part, the SB copolymer grafted onto the EPDM phase, resulting in an increased adhesion between PS and EPDM. Evidence from FT-IR and Solid State NMR affirmed a radiation induced change in interaction at the interface in these blends. When the less reactive SEP copolymer was used, neither the adhesion nor the impact strength increased upon irradiation.

Finally, preliminary experiments have been performed, studying the effects of controlled scission of the dispersed phase of the blend.

In polyamide-6/polyisobutylene (PA-6/PIB) blends an appropriate morphology for impact toughening could be obtained when the viscosity ratio of the components and processing conditions are well-tuned. Subsequent irradiation resulted in controlled scission of the dispersed PIB phase. This method offers the possibility to study, independently, the relation between a controlled cavitation stress of the PIB phase and impact strength of the blend.

An additional application of chain scission can be found in the fabrication of porous films. Through the appropriate choice of processing parameters, a co-continuous morphology could be induced in LLDPE/PIB blends. Controlled scission via EB irradiation resulted in an easily extractable PIB phase and a highly porous material could be obtained.

Samenvatting

Polymere materialen met unieke eigenschappen kunnen, in principe, eenvoudig vervaardigd worden door 2 of meer polymeren te mengen. Omdat de meeste polymeren niet (homogeen) mengbaar zijn op moleculaire schaal, wordt veelal een heterogeen mengsel verkregen. De morfologie, d.w.z. de karakteristieke afmetingen en vorm van de verkregen verdeling, alsmede de hechting tussen de verschillende fasen bepalen in grote mate de uiteindelijke eigenschappen van een dergelijk mengsel.

In dit proefschrift worden de resultaten beschreven betreffende de modificatie van deze niet-mengbare polymere mengsels met elektronen bestraling (EB).

In principe is voor iedere toepassing een specifieke morfologie vereist, die in veel gevallen ook vervaardigd kan worden, bijvoorbeeld een bolletjes-in-matrix morfologie voor slagvastheidsverbetering van brosse polymeren of een gelaagde structuur in barriere systemen. In de smelt is zo'n morfologie echter niet in evenwicht. Omdat de morfologie afhangt van verwerkingscondities zoals afschuif- en rekspanning, afschuif- en reksnelheid, viskositeitsverhouding, volumefractie en temperatuur vindt een continue aanpassing plaats aan lokale veranderingen in deze condities.

Via EB kon een verbeterde morfologiestabiliteit gerealiseerd worden in een model systeem van inert polystyreen (PS) en vernetbaar polyetheen (PE), door specifieke vernetting van de disperse PE fase. Complete fixatie van de morfologie werd verwacht omdat dynamisch mechanische metingen in de smelt het bestaan van een zwichtspanning in de vernette PE fase aantoonden. Micro-rheologische processen, die van belang zijn bij het mengproces, zoals het opbreken van draden via Rayleigh verstoringen en coalescentie, verliepen weliswaar trager bij toenemende bestralingsdosis maar konden niet voorkomen worden. Bovendien verliepen ze zelfs sneller, dan verwacht werd op grond van berekeningen gebaseerd op zuiver Newtonse systemen.

De waarnemingen kunnen verklaard worden doordat via EB geen compleet netwerk wordt gevormd in de PE fase van dit model systeem (een intrinsieke beperking van vernetting van PE via bestraling, mogelijkerwijs versterkt door een afschermende werking van de PS matrix).

Een tweede, unieke en daarom interessantere mogelijkheid voor EB betreft de slagvastheidsverbetering van polypropeen (PP) met EPDM-rubber. Bij de keuze van de componenten ontstaat er een tegenstelling tussen twee essentiële vereisten bij de ontwikkeling van een spuitgietbaar mengsel: een goede verwerkbaarheid en een hoge slagvastheid. Een hoge slagvastheid kan slechts verkregen worden indien kleine EPDM deeltjes homogeen over de matrix verdeeld zijn. Omdat dispersief mengen het meest effectief is als de viskositeiten ongeveer aan elkaar gelijk zijn, moet vanwege de intrinsiek hoge viskositeit van EPDM-rubber, een hoog viskeus type PP als matrix gebruikt worden. Dit resulteert echter in een moeilijk verwerkbaar mengsel. Daarentegen leidt het gebruik van een makkelijk verwerkbaar PP (lage viskositeit) tot grove morfologieën en een slechte slagvastheid in het uiteindelijke product.

Door nu gebruik te maken van een hoog viskeus PP kon een optimale morfologie voor slagvastheid worden gerealiseerd. Daarna kon, m.b.v. EB, gecontroleerde ketenbreuk van de PP matrix, resulterend in een lagere viskositeit, en een stabiliteit van de optimale morfologie, via vernetting van de EPDM deeltjes, gerealiseerd worden.

Via een meer gedetailleerde rheologische analyse van PP/EPDM blends, over een groot afschuifsnelheidsgebied, kon aangetoond worden dat het rheologisch gedrag van bestraalde blends vrij complex is. Bij hoge afschuifsnelheden resulteerde bestraling in een afname van de viskositeit (d.w.z. goed verwerkbaar via spuitgieten), terwijl bij lage afschuifsnelheden een netwerkgedrag werd gemeten, waarbij de viskositeit van bestraalde blends die van onbestraalde zelfs kon overschrijden. Het rheologisch gedrag blijkt af te hangen van de mate van vernetting van de EPDM deeltjes en de afstand tussen de deeltjes. Aggregatie van de disperse, vernette, deeltjes is de voornaamste verklaring.

In ternaire PP/EPDM/HDPE blends werd de disperse fase gevormd door een hoge-dichtheids polyetheen (HDPE) kern en een schil van EPDM, welke geregeld werd gepenetreerd door HDPE lamellen. Door bestraling vóór spuitgieten werden relatief grote deeltjes (vanwege een niet geoptimalizeerd extrusieproces) gefixeerd, wat leidde tot een afname van de slagvastheid in vergelijking met de onbestraalde blends.

Een derde toepassing van het bestralen van mengsels betreft de verbetering van grensvlak eigenschappen. Bestraling van PS/EPDM blends, waaraan een styreen/butadieen (SB) diblokcopolymeer is toegevoegd als compatibilizer, resulteerde niet in een fixatie van de morfologie bij spuitgieten. De slagvastheid nam echter toe met een factor 3. Door de grote hoeveelheid dubbele banden in het butadieen gedeelte, entte het SB copolymeer op de EPDM fase, resulterend in een toename van de hechting tussen PS en EPDM. Bewijs voor de toegenomen hechting bij bestraling van PS/EPDM/SB mengsels werd verkregen via FT-IR en vaste stof NMR. Bij gebruik van het minder reactieve styreen/etheen-propeen diblok copolymeer als compatibilizer, nam noch de hechting noch de slagvastheid toe bij bestraling.

Tot slot zijn er enige inleidende experimenten verricht om de mogelijkheden van gecontroleerde ketenbreuk van de disperse fase van de blend te bestuderen.

In polyamide-6/polyisobuteen (PA-6/PIB) mengsels kon een geschikte morfologie voor slagvastheidsverbetering gerealiseerd worden door een optimale keuze van de viskositeitsverhouding en verwerkingscondities. EB resulteerde in gecontroleerde ketenbreuk van de gedispergeerde PIB fase. De methode biedt de mogelijkheid om, onafhankelijk van andere parameters, de relatie tussen een gecontroleerde cavitatie van de PIB fase en slagvastheid van de blend te bestuderen.

Vervaardiging van poreuze films is een andere mogelijke toepassing voor gecontroleerde ketenbreuk. Via de geschikte keuze van verwerkingscondities kon een co-continue morfologie verkregen worden in lineair lage-dichtheids polyetheen / polyisobuteen (LLDPE/PIB) blends. Gecontroleerde ketenbreuk via EB resulteerde in een gemakkelijk extraheerbare PIB fase, waardoor een zeer poreus materiaal kon worden verkregen.

Nawoord

Het in dit proefschrift beschreven onderzoek is zeker niet de verdienste van slechts één persoon. Iedereen, van binnen en buiten de Technische Universiteit, die mij met raad en daad heeft bijgestaan wil ik daarvoor bedanken. Speciaal de medewerkers en studenten van de vakgroep kunststoftechnologie, bij wie ik niet alleen met wetenschappelijke vragen terecht kon, maar die mij ook voldoende gelegenheid boden om stoom af te blazen.

Grote gedeelten van het experimentele werk zijn uitgevoerd door de afstudeerders Henk Benthem, Chris Borgmans, Jan-Willem Goedmakers, Wilfred Hoeben, Jelmen Meijerink, Marco van der Sanden, Irene Tauber, Frits Verheesen (TU Eindhoven), Luc Van Camp, Ann De Vos (Industriele Hogeschool Mechelen), Marc Verstraete (Hogeschool Eindhoven) en Mariet Vanaken (Groep T, Leuven).

De enthousiaste samenwerking met de vakgroep stralingschemie van het inter universitair reactor instituut (IRI, Delft), werd ten zeerste geapprecieerd. Ondanks de "geweldige massa's" die wij te bestralen hadden, werd altijd goedgemutst de 'Van de Graaff' versneller voor ons bediend en was er gelegenheid voor stimulerende discussies.

Dit onderzoek werd mogelijk gemaakt door financiële steun van TNO (Delft), waarvoor grote erkentelijkheid.

Tot slot, maar niet op de laatste plaats, wil ik Anita, mijn ouders en andere familieleden bedanken voor hun steun, geduld en belangstelling, vooral toen veel extra tijd gestoken moest worden in de afronding van dit proefschrift.

Curriculum Vitae

De auteur van dit proefschrift werd op 8 juli 1964 geboren te Hooge Mierde. Van 1976 tot en met 1982 heeft hij het gymnasium ß doorlopen aan het St. Odulphus Lyceum te Tilburg. Hierop aansluitend werd in september 1982 met de studie scheikundige technologie aan de Technische Universiteit Eindhoven begonnen. Het propedeutisch diploma werd in juli 1983 behaald en in december 1986 het ingenieursdiploma, cum laude, na een afstudeerproject binnen de (sub)vakgroep kunststoftechnologie. Bij dezelfde vakgroep is hij sinds februari 1987 werkzaam als 4-jarige AIO'er. Per 1 maart 1991 zal hij in dienst treden bij General Electric Plastics in Bergen op Zoom.

Stellingen

1. Verkeerde verwachtingen over micro-rheologische processen ontstaan uit op zich juiste macroscopische rheologische gegevens, verkregen uit dynamisch mechanische analyse.

   Dit proefschrift, hoofdstuk 3

2. Een vertraagde initiatie van crazes hoeft niet automatisch een afname in slagvastheid tot gevolg te hebben.

   Dit proefschrift, hoofdstuk 7 en appendix

3. De "melt-flow-index", die in de industrie gebruikt wordt als maat voor het vloeigedrag, geeft bij blends niet alleen een volkomen verkeerd beeld van het vloeigedrag bij hoge afschuifsnelheden (spuitgietcondities), maar kan vooral de viskositeit bij lage afschuifsnelheden onderschatten.

   ASTM norm, D 1268-65T
   Dit proefschrift, hoofdstuk 5 en appendix

4. Bestraling van polymere blends kan een stralende toekomst tegemoet gaan indien afgeweken wordt van het idee "overall vernetting" en er specifiek gebruik gemaakt gaat worden van het verschil in bestralingsgevoeligheid van de diverse polymeren.

   Dit proefschrift, hoofdstuk 2 vs. hoofdstuk 3 t/m 9

5. Uit de door Stehling et al. gepubliceerde gegevens over slagvastheid, modulus en morfologie van ternaire PP/EPDM/HPDE blends kan niet zondermeer geconcludeerd worden dat de struktuur van de disperse fase, "core-shell" of "inter-penetrating", uitsluitend van invloed is op de modulus van de blend en geen invloed zou hebben op de slagvastheid.

   Stehling, F.C., Huff, T., Speed, C.S. and Wissler, G., J. Appl. Polym. Sci., 1981, ***26****, 2693*

6. In de "lattice fluid" theorie van Sanchez, Lacombe en Balasz voor polymeersystemen met specifieke interacties, worden die interacties alleen in rekening gebracht in het ontmenggedrag en niet in de toestandsvergelijking. De theorie is dus inconsistent.

   Macromolecules, 1989, 22, 2325