

# Peroxy-Initiated Chain Degradation, Crosslinking, and Grafting in PP–PE Blends

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**ABSTRACT:** Polyolefines are frequently functionalized with polar monomers via peroxide-initiated grafting that starts at macroradicals. However, polyolefine macroradicals also undergo undesired secondary reactions. Polypropylene (PP) is degraded, while polyethylene (PE) is crosslinked. Mechanistically, PP radicals are split by  $\beta$  scission while PE radicals recombine to clusters. If these opposed tendencies can be balanced in PP–PE blends was investigated in this study. In principle, coupling of PP and PE radicals can lead to graft copolymers PE-*g*-PP. But the chances for graft reactions are good only in homogenous PP–PE blend melts. It is difficult to decide whether these blends are, in fact, in the melt one-phase or two-phase systems because molten PP and PE are too similar in all respects. PP–PE blends were processed with peroxide in the melt and, for comparison, also in solution. According to viscosity and gel permeation chromatography and differential scanning calorimetry results, graft reactions occurred only in the (presumably homogeneous) blend solutions in which degradation was subdued and crosslinking prevented. In PP–PE blend melts, on the contrary, the two polymers reacted fairly independently of each other. PP was degraded, and PE crosslinked. Apparently, these blend melts, although transparent, are two-phase systems.

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## INTRODUCTION

When attacked by the aggressive oxy radicals of peroxides, polyolefines form macroradicals. Industrially, this is exploited for functionalizing polypropylene (PP), polyethylene (PE), and ethylene propylene rubbers (EP) with polar monomers as maleic anhydride by radical grafting, commonly via reactive processing in the melt.<sup>3,4</sup> Problems are caused by the tendency of polyolefine macroradicals towards secondary reactions that can alter the molecular weight consid-

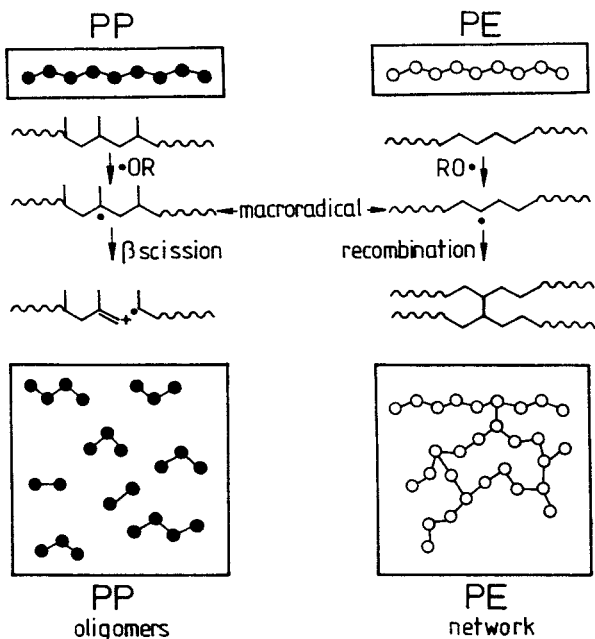
erably. This article deals with these macroradical reactions.

PP and PE respond in opposite ways to oxy radicals (Scheme 1), as follows: PP is degraded, due to chain scission in  $\beta$  position to the macroradical site,<sup>5–10</sup> while PE is crosslinked, due to macroradical recombination.<sup>11–13</sup> Both processes are usually undesired since short-chained PP and crosslinked PE exhibit inferior properties. Exceptions in which deliberate use is made of macroradical reactions are “visbreaking” of PP, where the chains are subjected to controlled degradation to optimize the melt viscosity<sup>5–10</sup> and crosslinking of PE to enhance the durability.<sup>12</sup>

A seemingly straightforward way to prevent the reactions in Scheme 1 is indicated in Scheme 2, as follows: the chain decay of PP and the chain

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**Scheme 1** Macroradical reactions after the attack of oxy radicals ( $\cdot\text{OR}$ ) from a peroxide: chain degradation of PP via  $\beta$  scission and crosslinking of PE via radical recombination.

buildup of PE should be balanced in PP–PE blends,<sup>14–29</sup> where coupling of PP and PE macroradicals can lead to graft copolymer chains PE-*g*-PP. Short PP oligomers are tied to PE chains which, thereby, are kept from crosslinking.

But this interchain coupling is favored only in one-phase blends where the components are in intimate molecular contact. In two-phase blends, the components can react only in the interfaces between phase domains so grafting is severely hindered.

One-phase and two-phase blends are usually easily distinguished by turbidity, scattering, microscopy, or relaxation analysis. But these methods fail with PP–PE blend melts. Molten PP and PE are practically isorefractive, and their blend melts are transparent. Moreover, the two polymers have no X-ray contrast, which invalidates static scattering techniques, and are dynamically too similar to be distinguished by relaxation spectroscopy and dynamic scattering techniques. It is thus hard to decide, in fact, whether PP–PE blends are in the melt, at temperatures  $T > 160^\circ\text{C}$ , one-phase or two-phase systems.<sup>20–29</sup> At room temperature, of course, PP and PE do not mix because both are crystalline.<sup>18,20,28</sup>

This study deals with polymer reactions that

occur after oxy radical attack (1) in PP–PE blend melts and, for comparison, (2) in homogeneous PP–PE solutions. It will be confirmed that PP–PE blend melts are indeed two-phase systems.

## EXPERIMENTAL

### Polymers

The polyolefines Daplen PP and Daplen HDPE (PCD Polymere GmbH, Linz, Austria), both powders made by heterogeneous ZN polymerization, are characterized in Table I. They are long-chained with a broad chain length distribution. The refractive indices  $n_D$  and the densities  $\rho$  of amorphous PP and PE are obviously too similar to cause turbidity or excess scattering in two-phase PP–PE blends.

### Melt Reactions

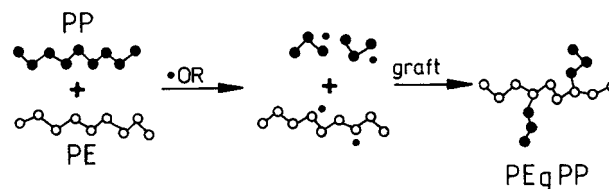
PP, PE, and PP–PE blends were processed for 5 min at  $180^\circ\text{C}$  in a kneader (Brabender Plastograph, 30 mL chamber, 60 rpm), with and, for comparison, without peroxide. For the PP–PE blends, PP and PE powders were premixed in a ball mill prior to processing.

The peroxide was Luperox 101 (2,5-di-*tert*-butylperoxy-2,5-dimethylhexan, Elf Atochem). Producers provide conflicting data on the bond scission of this initiator. A differential scanning calorimetry (DSC) run of the pure peroxide yielded, for the thermal decomposition, the Arrhenius law, as follows:

$$\ln \tau_{1/2}/\tau_{1/2}^* = (E^*/R)(1/T - 1/T^*) \quad \tau_{1/2}^* = 1 \text{ min}$$

$$T^* = T(\tau_{1/2}^*) = 177^\circ\text{C}, \quad E^* = 116 \text{ kJ/mol} \quad (1)$$

where  $\tau_{1/2}$  is the half-life time,  $T^*$  is the temperature for 1 min, and  $E^*$  is the activation energy.



**Scheme 2** Coupling of PP and PE macroradicals to a graft copolymer PE-*g*-PP with a PE backbone and PP grafts.

**Table I** Weight-Average Molecular Weight  $M_w$ , Polydispersity  $M_w/M_n$ , Melting Point  $T_m$ , Density  $\rho$ , and Refractive Index  $n_D$  of the Polymers PP and PE

	$10^{-3}M_w$	$M_w/M_n$	$T_m$ (°C)	$\rho$ (g/cm <sup>3</sup> )		$n_D$
				25°C <sup>1</sup>	Amorph <sup>2</sup>	Amorph <sup>2</sup>
PP	612	3.6	163	0.91	≈0.85	≈1.474
PE	309	15.6	130	0.945	≈0.855	≈1.479

The half-life time  $\tau_{1/2}$  of the peroxide at the processing temperature of 180°C is thus slightly less than 1 min.

Two series of melt reactions with PP, PE, and PP–PE blends were studied.

### Method I

The system was processed without gas protection, in contact with air. First, the polymers were plastified in the kneader, then the peroxide was injected into the molten blend, after 2 min.

### Method II

The system was protected throughout with inert gases. The polymers were first impregnated with the peroxide by dispersing the polymer powder in an acetone solution of the peroxide, stirring, and drying under nitrogen. Then, the polymer–initiator mixtures were plastified and processed in the kneader under argon. The initiator is better dispersed from the start than in method I, and oxygen is kept away from the melt.

### Reactions in Solution

PP, PE, and PP–PE blends, without or with peroxide (injected as in the above method I), were dissolved at 180°C in trichlorobenzene (TCB), at a total concentration of 10 wt %. The solution was degassed and then stirred for 15 min at 180°C under nitrogen. The solvent was evaporated off at 120°C.

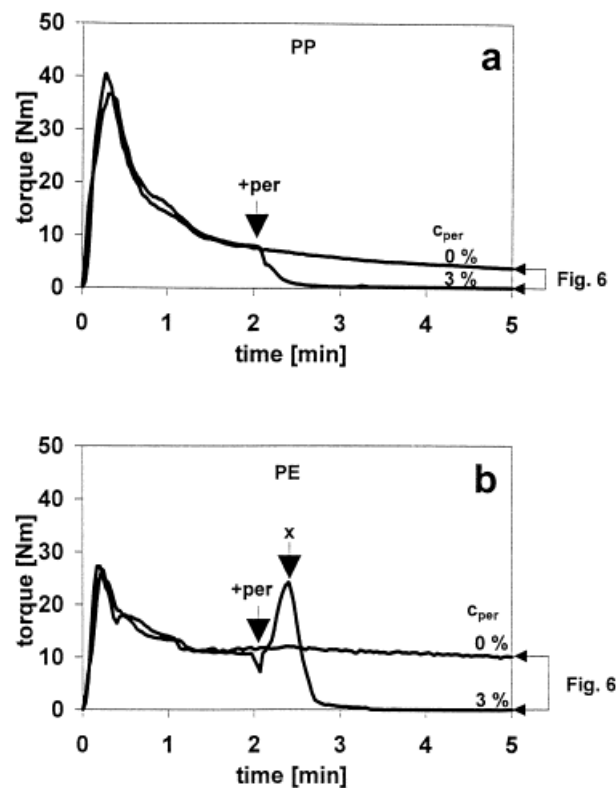
### Analytics

During processing in the kneader, the torque–time curve was monitored. The molecular weight distribution was measured by high-temperature gel permeation chromatography (GPC) in TCB (PS calibration). The crystallinity was studied in

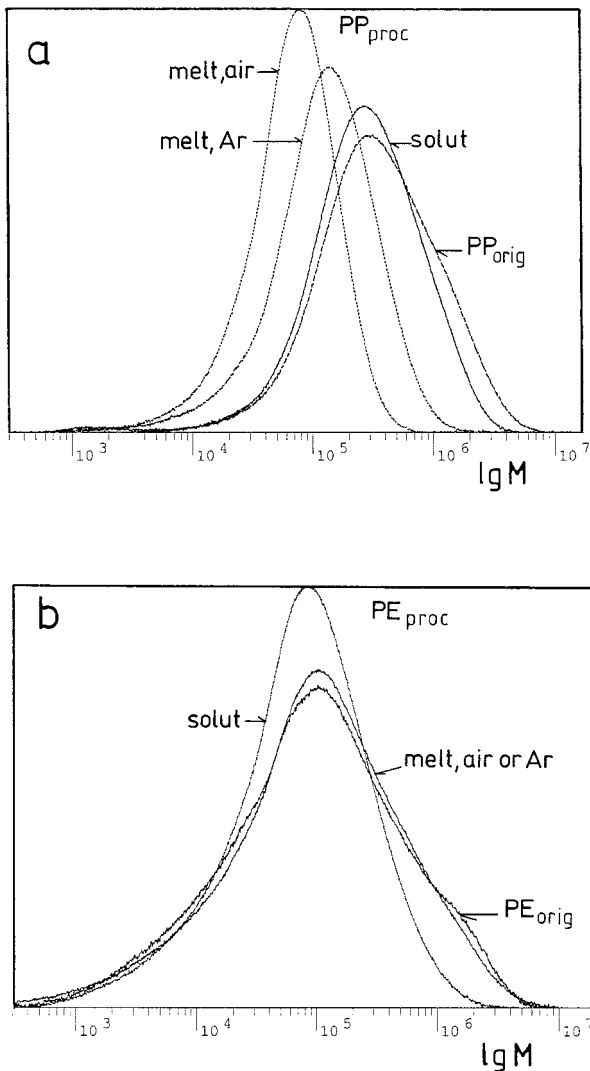
melt-processed samples after cooling in air. The crystal morphology was characterized by transmission electron microscopy (TEM) (cryocut ultrathin sections), and the melting behavior by DSC (heating rate 10 K/min).

## RESULTS

PP, PE, and PP–PE blends were processed 5 min in a kneader, which is comparable to 2 min of processing in a twin-screw extruder. Uncommonly



**Figure 1** Torque–time curves of (a) PP and (b) PE melts, without and with 3 wt % peroxide (added after 2 min, “+per”). “X” in (b): peak due to crosslinking.



**Figure 2** Effect of oxygen: GPC curves of (a) PP and (b) PE, original samples (orig), and samples processed (proc) without peroxide in the melt (in air or under argon) or in solution.

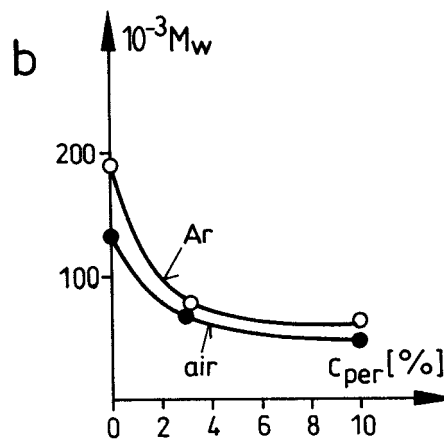
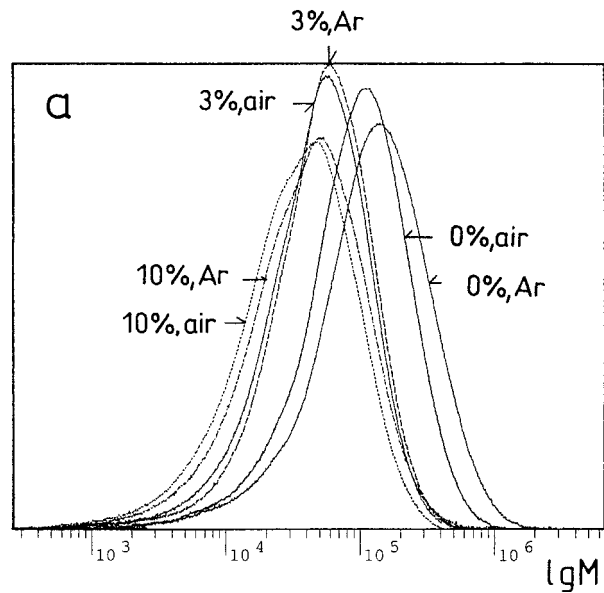
high concentrations of the peroxide were added, 3 and 10 wt %, to accentuate the effects. Tests with lower peroxide concentrations yielded basically the same effect, only weaker.

**PP and PE Melts and Solutions**

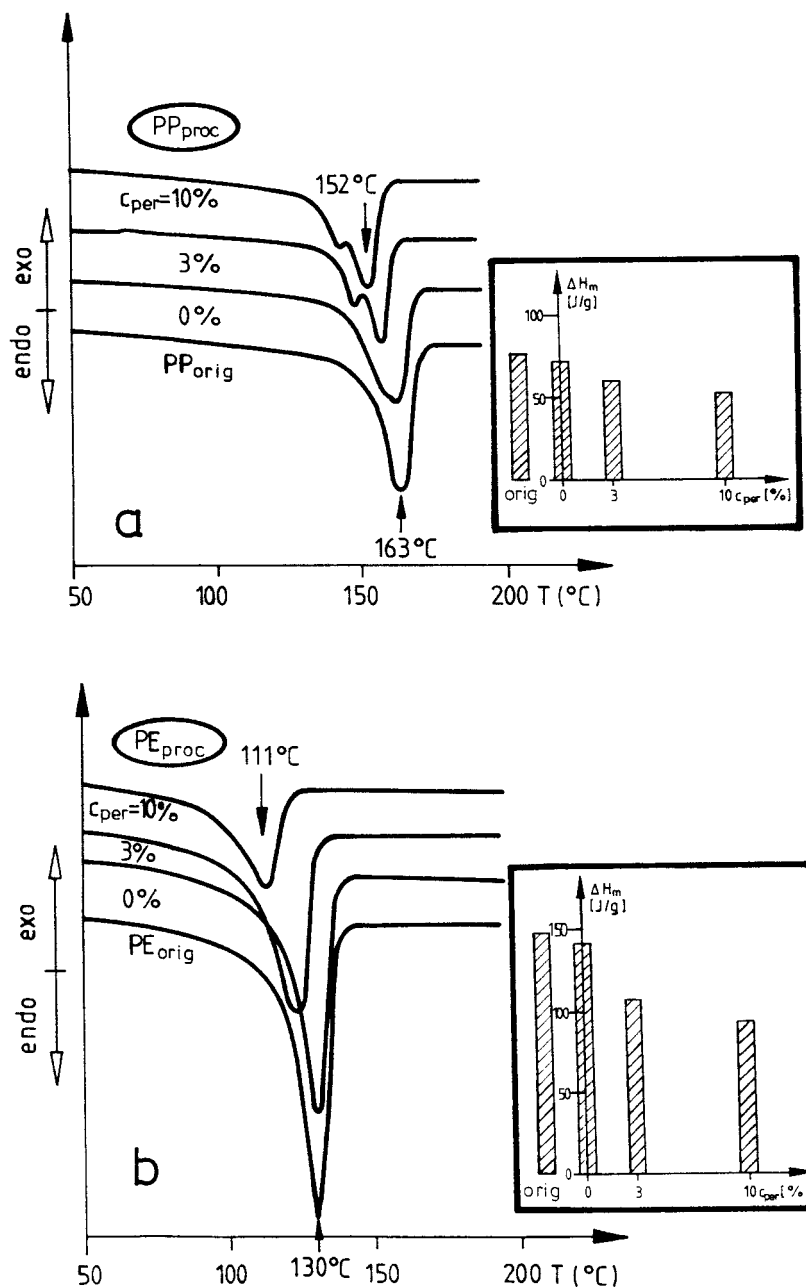
Torque–time curves of PP and PE without and with 3 wt % peroxide are shown in Figure 1. After the plastification peak, the curves without peroxide reach at 2 min a fairly constant level. But when peroxide was added, at 2 min, the torque dropped drastically, both in PP and PE, however,

for very different reasons: PP was degraded and formed a very fluid melt; on the contrary, PE was crosslinked. This caused first a peak, but then the torque vanished completely: the PE melt broke up into a soft, incoherent solid of crosslinked gelled bits.

The GPC analysis revealed a mixed chemistry of peroxide and air. The GPC curves in Figure 2 demonstrate the effect of oxygen on PP and PE in the absence of peroxide. PP was strongly de-



**Figure 3** Effect of the peroxide on PP: PP processed in the melt (in air or under argon) with different amounts  $c_{per}$  of the peroxide. (a) GPC curves; (b) weight-average molecular weights  $M_w$ .

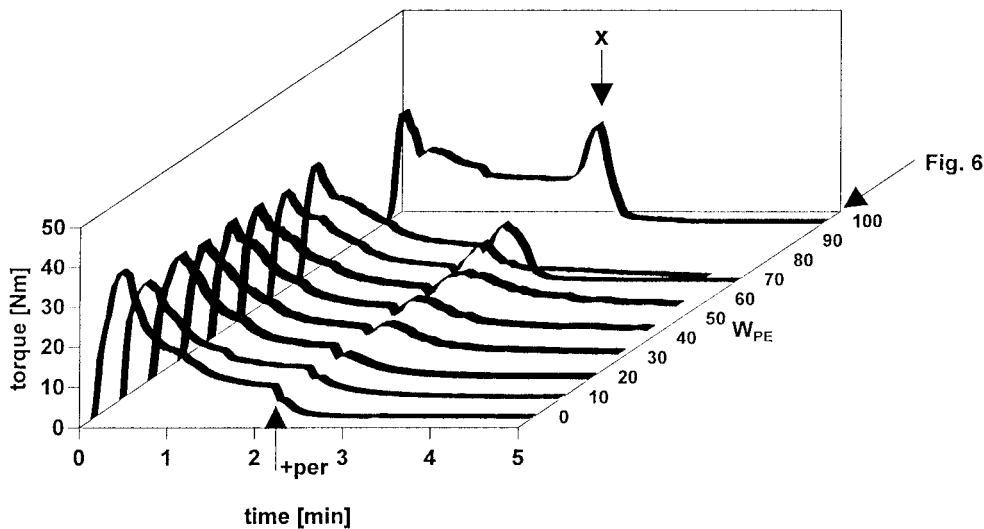


**Figure 4** DSC traces with melting peaks and heat of melting ( $\Delta H_m$ ) of (a) PP and (b) PE, processed with varying amounts ( $c_{per}$ ) of the peroxide.

graded, more in air (method I), less but still considerably under argon (method II). Only in the degassed TCB solution, PP remained practically unaltered [Fig. 2(a)]. PE reacted much less to oxygen than PP. It was not at all affected in the melt and slightly degraded in TCB solution [Fig. 2(b)].

The peroxide had the effects predicted by Scheme 1, as follows: it crosslinked PE and shortened the PP chains, in air and under argon to similar degrees, as shown in Figure 3. The crosslinking of PE was so efficient that no sol fraction could be extracted for a GPC analysis.

The DSC data in Figure 4 demonstrate how



**Figure 5** Torque–time curves of PP–PE blends ( $w_{PE}$  PE weight fraction) with 3 wt % peroxide; addition of the peroxide (“+per”) at 2 min causes a down-peak, while clustering, and crosslinking causes an up-peak (x).

the melt reactions lowered the temperatures and heats of melting successively.

#### PP–PE Blend Melts

Torque–time curves of PP–PE blend melts with 3 wt % peroxide (prepared with method I) are collected in Figure 5. The injection of the (cold) peroxide caused a negative peak. After this down peak, an up peak is observed at intermediate and high PE weight fractions  $w_{PE}$ , indicating chain buildup reactions. Up to  $w_{PE} = 60$  wt %, the curves end, after 5 min, in a finite plateau. Thermoplastic melts were obtained, which were transparent at low  $w_{PE}$  and turbid in the range  $40 < w_{PE} < 70$  wt %. Above  $w_{PE} = 70$  wt %, on the contrary, a pronounced peak is observed that ends at zero torque. Incoherent crosslinked solids had been formed.

Figure 6 shows the final torque values, after 5 min, of PP–PE blends that were processed without or with peroxide. The torque can be taken as a value of the blend viscosity. In the reference blends processed without peroxide, the torque increases steadily with  $w_{PE}$ , on a high level. But processing with peroxide, 3 wt % (from Fig. 5) or 10 wt %, yields quite different curves: these curves start at a very low torque, due to the strong chain degradation in pure PP. Then, added PE increases the torque rapidly. Finally, the curve breaks off, down to zero, at a critical PE content  $w_{crit}$ , from

where on, the products are crosslinked. The critical limit  $w_{crit}$  decreases as the peroxide concentration increases.

It is tempting to interpret these torque curves in terms of Scheme 2, which seems to provide the following compelling interpretation: at  $w_{PE} < w_{crit}$ , the torque is raised because short-chained macroradicals of PP are tied to PE chains, whereby graft copolymer chains PE-*g*-PP are formed. Thereby, crosslinking is prevented too. Only at high PE contents, at  $w_{PE} > w_{crit}$ , the crosslinking finally takes over.

Unfortunately, this “compelling” interpretation had to be dismissed, because all blends processed with peroxides were insoluble in TCB and yielded only turbid dispersions containing crosslinked gel particles.

The DSC traces of the PP–PE blend melts processed with 3 wt % peroxide are collected in Figure 7. The temperatures and heats of melting behave as expected. To analyze the gel particles, TCP dispersions of the blends were separated by filtering off the gel, and the separate fractions were analyzed by DSC. In Figure 8, the melting endotherm of the blend with  $w_{PE} = 30$  wt % is compared with the endotherms of the gel and the sol fraction. The two traces in Figure 8(b), when added together, reproduce the original trace in Figure 8(a) well.

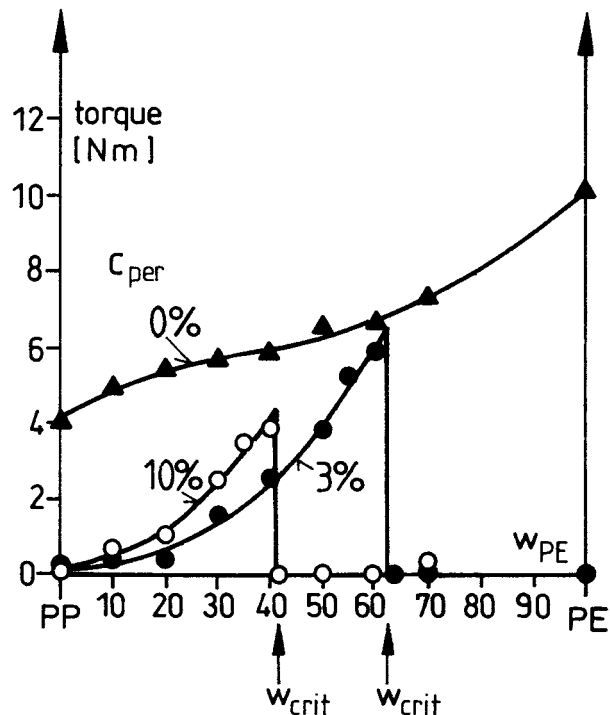
The peaks in Figure 8(b) prove that the soluble sol fraction consists exclusively of PP while the

insoluble gel fraction contains both polymers. In the sol fraction, the PP chains were almost exactly as strongly degraded as in pure PP, as is demonstrated in Figure 9. This means that the presence of PE in the blend did not hinder the  $\beta$  scission of PP macroradicals noticeably.

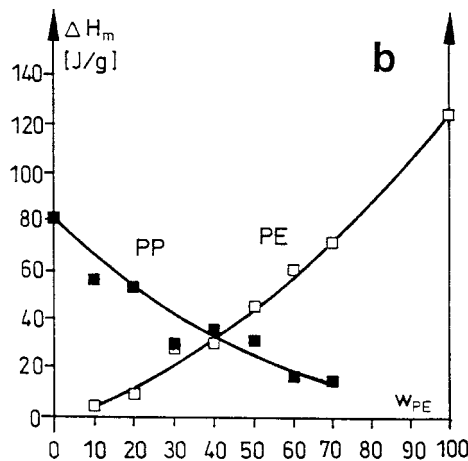
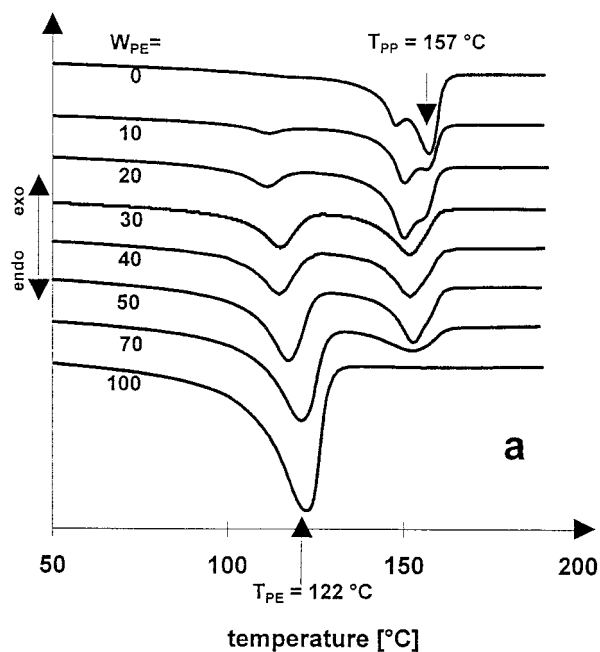
In the gel fraction, the crosslinked PE is dominant. The heats of melting of the PP and PE peak of this fraction in Figure 8(b), normalized to the heats in Figure 8(a), lead to a gel composition of PP-to-PE = 38 : 62 by weight. The PE gel thus contains a fair amount of PP.

This PP is possibly grafted. If so, approximately  $\frac{1}{4}$  of all PP is incorporated in graft copolymer chains PE-*g*-PP (Scheme 2) while  $\frac{3}{4}$  of the PP are free. This is not satisfactory. Moreover, this disappointing grafting efficiency might even be overestimated: part of the PP in the gel fraction was perhaps just physically confined in the PE network, during the hot filtering of the swollen gel (which is hampered by filter clogging).

To conclude, it must thus be suspected that grafting is only a minor reaction in these PP-



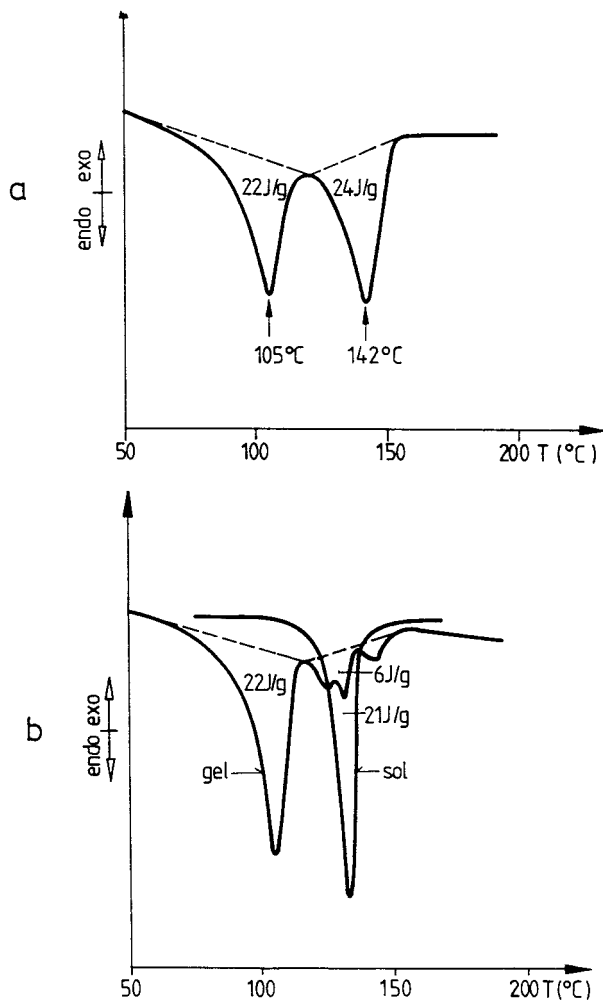
**Figure 6** Torque after 5 min in the kneader: PP-PE blends without peroxide and with 3 wt % (from Fig. 5) or 10 wt % peroxide, as a function of the PE content  $w_{PE}$ ; above the critical limit  $w_{crit}$ , blends with peroxide are cross-linked.



**Figure 7** (a) DSC traces and (b) heats of melting of PP-PE blends.

PE blends. The dominating processes are still PP degradation and PE crosslinking. The two polymers react quite independently from each other. Particularly annoying is that the crosslinking of PE could not be prevented by efficient grafting.

In summary, the observations in Figures 6-9 suggest strongly that the PP-PE blend melts, although transparent, are two-phase systems: in demixed PP-PE blends, in which PP is the major component, crosslinked PE forms dispersed phase

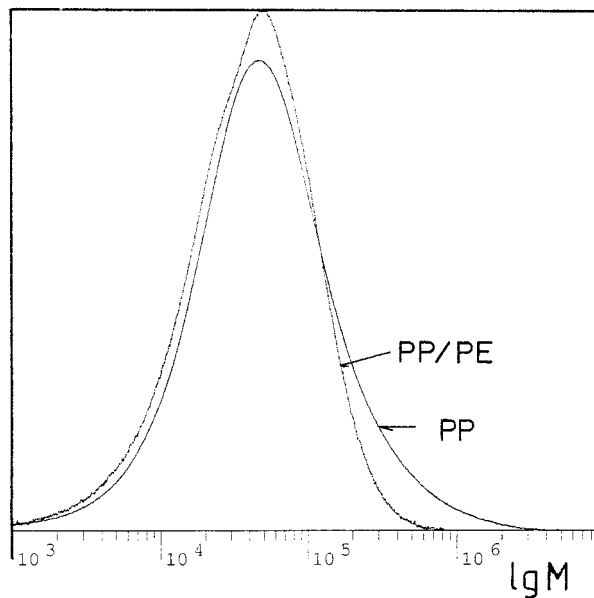


**Figure 8** Melting endotherms of the PP-PE blend with  $w_{PE} = 30$  wt % (a) before and (b) after filtering.

domains which, floating in the matrix of degraded PP, act as filler particles that raise the torque. Since the PP matrix is not crosslinked, these blend melts are still thermoplastic. But at higher PE contents, above  $w_{crit}$ , where the crosslinked PE network takes over the matrix, the whole system behaves like a crosslinked network.

Consequently,  $w_{crit}$  has the significance of a percolation threshold: it indicates from where on PE forms the matrix. The matrix inversion occurs earlier with 10 wt % than with 3 wt % peroxide, due to stronger crosslinking (Fig. 6).

The morphology of a PP-PE blend just below the critical limit  $w_{crit}$  is illustrated by Figure 10. Crosslinked PE forms extended clusters which are, however, not yet interconnected. The system is in this situation very close to a crosslinked net-

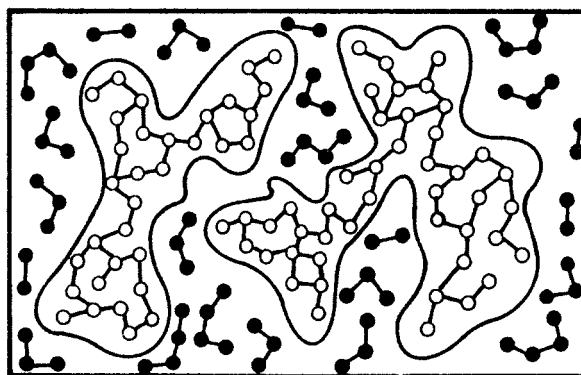


**Figure 9** GPC curves of PP processed with 3 wt % peroxide: (a) pure PP and (b) sol fraction of the PP-PE blend with  $w_{PE} = 30$  wt %.

work. Therefore, a slight increase of the PE content should increase the torque drastically before the PE clusters grow together, and a PE network immobilizes the system.

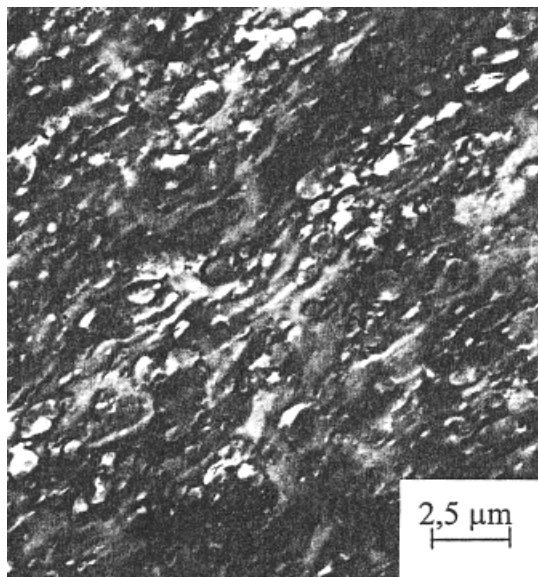
This effect was tested. However, crosslinking came about too rapidly: when 1 wt % more PE was added to the blends with the maximum torque in Figure 6, that is,  $w_{PE} = 60$  wt % and  $w_{PE} = 40$  wt % (with 3 and 10 wt % peroxide, respectively), the melts were already crosslinked.

Attempts to visualize the two-phase structure of the demixed PP-PE blends by electron micros-



**Figure 10** Extended crosslinked PE domains, dispersed inside the PP matrix in a PP-PE blend just below the critical limit  $w_{crit}$ .





**Figure 11** Transmission electron micrograph of the PP-PE blend with  $w_{PE} = 30$  wt %, processed with 3 wt % peroxide; the darker PP phase consists of spherulites.

copy failed. Figure 11 shows, in the blend with  $w_{PE} = 30$  wt % (3 wt % peroxide), two continuous phases, one of which is built up by PP spherulites. This is certainly not the original morphology in the melt. Similar pictures are published in the literature,<sup>14,21,23</sup> but all of them show morphologies that are controlled by the crystallization of PP and PE and do not reflect the morphology as it is in the melt.

### Reactions in Solution

Since degradation and crosslinking could not be prevented by grafting, in the apparently demixed PP-PE blend melts, the effect of the peroxide was studied, for comparison, in TCB solution. Since TCB is a good solvent for molten PP and PE, it is safe to assume that PP-PE blends are homogeneous when dissolved in hot TCB, above the melting points.

PP, PE, and PP-PE blends were annealed for 15 min at 180°C in TCB solution. The peroxide was added in high concentration, 10 wt %, because all effects were smaller than in the melt. Reactions due to oxygen did not interfere (Fig. 2).

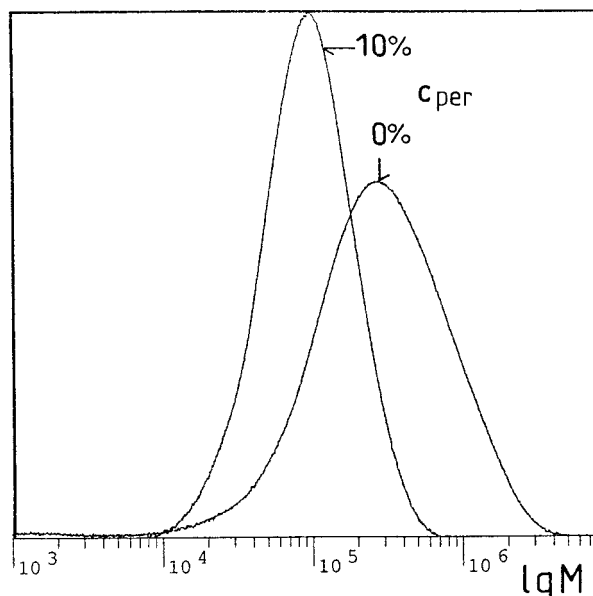
PP and PE responded as in the melt. PP was degraded, as shown in Figure 12, while PE was crosslinked. But contrary to the blend melts, none of the dissolved PP-PE blends contained a crosslinked gel fraction. All blends could be

analyzed by GPC. The GPC curves were fairly similar at all  $w_{PE}$ . Comparison of these blends (“proc”) with reference blends without peroxide (“orig”) in Figure 13 reveals a satisfactory pattern: the peroxide degrades the PP only moderately and does not noticeably build up or crosslink the PE.

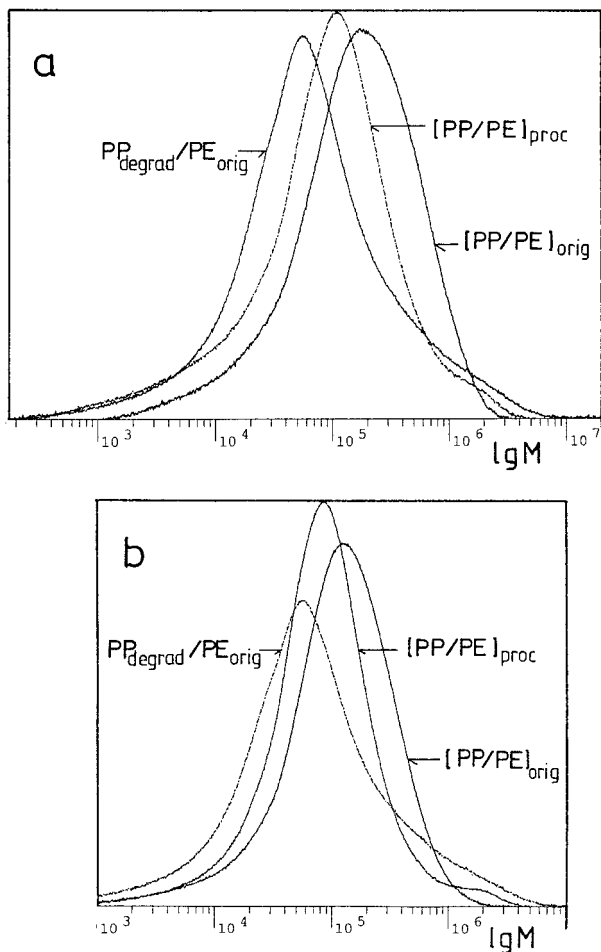
PP is indeed much less degraded, in these blends, than in pure PP (Fig. 12). To demonstrate this, GPC curves were simulated that correspond to the following assumption: the peroxide (1) degrades PP exactly as in pure PP and (2) does not alter PE at all. Blends  $PP_{degrad}/PE_{orig}$  corresponding to this situation were prepared by mixing degraded PP (Fig. 12) with original PE. Their GPC curves in Fig. 13 have a peak much lower than that of the PP-PE blends that were actually obtained by solution processing.

To summarize, PP is in dissolved PP-PE blends not much degraded, and PE is not crosslinked. This suggests graft copolymerization, as proposed by Scheme 2. While graft copolymers PE-*g*-PP are, naturally, difficult to determine directly, the fact that the extreme degradation and crosslinking processes in Scheme 1 are subdued or prevented in these dissolved PP-PE blends is compelling evidence for coupling reactions between PP and PE.

The conclusion from this study is that graft copolymers PE-*g*-PP are evidently formed in PP-



**Figure 12** GPC curves of PP, processed in TCB solution without and with 10 wt % peroxide ( $PP_{degrad}$ ).



**Figure 13** GPC curves of blends PP-PE, with a PE content of (a)  $w_{PE} = 30$  wt % and (b)  $w_{PE} = 70$  wt %, processed in TCB solution without and with 10 wt % peroxide, as well as simulated blends  $PP_{degrad}/PE_{orig}$ .

PE blend solutions because these are homogeneous, but not in PP-PE blend melts because these are demixed.

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