Crosslinking of Polypropylene–Polyethylene Blends by Peroxide and the Effect of Pentaerythritol Tetrallyl Ether

EBERHARD BORSIG, AGNESA FIEDLEROVÁ, LYDA RYCHLÁ, and MILAN LAZÁR, *Polymer Institute, Centre of Chemical Research, Slovak Academy of Sciences, 842 36 Bratislava, Dúbravská cesta 9, Czechoslovakia* and MANFRED RÄTZSCH and GOTTFRIED HAUDEL, *Institute of Polymer Technology, Academy of German Democratic Republic, 8010 Dresden, Hohe Strasse 6, German Democratic Republic*

Synopsis

Crosslinking of polypropylene–polyethylene (PP-PE) blends involving 10, 20, 30, 40, 50, 60, 70, 80, and 90% of PP with dicumylperoxide (DCP) or tert-butyl perbenzoate (TBPB) and in the presence of coagent pentaerythritol tetrallyl ether (PETA) was investigated at 180°C. It was found that at lower concentrations of peroxide alone (e.g., 2.5% of DCP) only PE component is crosslinked in all compositions of PP-PE blends. In the crosslinking of PP-PE 50:50 with 4% of TBPB, insoluble gel was obtained, which contained 13% PP and 87% PE. If 2% PETA was also used, the portion of PP in gel increased to 39%; the total yield of gel in PP-PE blend increased from 50 to 70%. The lower crosslinking efficiency of coagent PETA in the PP-PE blends compared with PP alone is associated with better solubility of the coagent in the PE phase in contrast to the PP phase. The coagent does not particularly raise the crosslinking efficiency of peroxide in PE, but increases it in the PP phase. A remarkable decrease in melting temperature and temperature of crystallization of both polymer components depending on peroxide concentration was found by calorimetric measurements.

INTRODUCTION

Polyolefin mixtures have been shown great interest in the last decade, particularly with regard to the possibilities of the inexpensive combinations of the properties of individual components of blends. A wide spectrum of their properties, which makes possible preparation of "tailored" polymers[1] led to a tenfold increase in application of these blends in the European automobile industry from 1976 to 1980.[1,2]

Initial reports dealing with these problems appeared in the latter half of the 1960s.[3-5] Polypropylene and polyethylene are mutually incompatible and the blend prepared from the melt of the mixture of both polymers is, to a certain extent, heterogeneous. Polyethylene acts here as an impact modifier. The more finely it is dispersed in the blend, the better are the resulting mechanical properties. From this point of view, polypropylene affecting the interface properties also plays an important role.[6]

This article is submitted in honor of the 60th birthday of Professor Otto Vogl.

The aim of the present article was to evaluate the possibilities of the use of the peroxide-multifunctional monomer (coagent) system. The system showed good efficiency in the crosslinking of polypropylene alone.[7] Because of the low miscibility of PP with PE and consequent inhomogeneity of the prepared blends a physical effect of the unequal distribution of the components of the crosslinking system in polymeric systems and a corresponding influence on the crosslinking is to be expected.

EXPERIMENTAL

Polymers

Isotactic polypropylene, type Mosten 58412 (Czechoslovakia), density $\rho = 0.90–0.92$ g/cm^3, melting index MFI$_{2.16}$ (230°C) = 2.5–4.0 g/10 min.

Polyethylene, type Mirathen AL13 (of GDR provenance) density $\rho = 0.91–0.92$ g/cm^3, melting index MFI$_{2.16}$ (190°C) = 1.1–3.0 g/10 min. Both polymers contained from 0.1 to 0.3% antioxidants. Granulates of both polymers were first thoroughly mixed and homogenized at temperatures up to 220°C in a twin-screw extruder ZDSK 28 of Werner Pfleiderer with the screw length 24D and with n = 150 rpm. Granulate prepared from this melt was pulverized in a ball mill to give powdered polymer with the particle size ranging from 50 to 300 μm.

Chemicals

Dicumyl peroxide (DCP) was recrystallized twice from dry methanol, di-tert-butyl perbenzoate (TBPB) (from Luperox) was used without purification. Pentaerythritol tetrallyl ether (PETA) was prepared from pentaerythritol and allyl bromide as has been described earlier.[7]

Preparation of Samples, Their Crosslinking, and Extraction

About 1 g of polymers (PP or PE) or their blends (PP-PE) in powdered form, containing 10, 20, 30, 40, 50, 60, 70, 80, and 90% PP was impregnated in chloroform solution of peroxide (DCP or TBPB) an coagent PETA ($-$ 20 cm^3) for 2 h at 40°C. Chloroform was then evaporated from the polymer sample in a rotary evaporator and the polymer sample was dried in vacuum at 25°C. The polymer sample or the polymer (PP-PE) blend was sealed into a glass ampoule in a nitrogen atmosphere and annealed at 180°C for 20 min (at 170°C for 30 min) to perform the crosslinking reaction.

The gel content was determined measuring the weight of polymer after extraction in boiling cyclohexane for 8 h and then in boiling xylene for 14 h with admixture of a small amount of hydroquinone. The solvent in an extraction vessel was exchanged every 2 h. The samples were dried to constant weight in vacuum at 40°C.

Cyclohexane and xylene extracts from individual samples of PP-PE blends, which represented uncrosslinked component of the polymer blend, were precipitated into the threefold amount of ethanol and thin foils pressed at 180°C were obtained from the dried precipitate.

Infrared Analysis of the Soluble Part of Crosslinked PP-PE Blends (Extracts)

Infrared (IR) analysis of the foils from cyclohexane and xylene extracts was done on a Specord 71 IR spectrometer. A calibration graph was used for determining the composition of the foil. The graph consisted of the plot of the ratio between deformation vibrations γ (CH_2) at 710 cm^{-1} (corresponding to PE) and deformation vibrations $\gamma_s(CH_3)$ at 1160 cm^{-1} (corresponding to PP) against the composition of PP-PE blend. The ratio of PE/PP peaks at the mentioned vibrations was determined for each foil and the blend composition was obtained from the graph.

DSC Measurements

Melting and crystallization temperatures of the PP–PE blends were measured on a DSC-2M apparatus (Made in the USSR). Samples weighing (4–5 mg) were placed in aluminum pans and heated from 330 K at a rate of 8°/min to 470 K. At this temperature, the samples were thermostatted 5 min and then cooled to 330 K. Endotherms of melting and exotherms of crystallizations were recorded as a function $d\Delta H/dt$ of temperature T for both polypropylene and polyethylene.

RESULTS AND DISCUSSION

Gel Yield and the Composition of a Blend

As expected, the dependence of the gel yield on the increasing polypropylene content in a blend obtained experimentally by crosslinking with dicumyl peroxide alone has decreasing tendency. It is interesting that at low polypropylene content from 0 to 10% in the blend the gel content changes slightly and does not decrease as with higher contents of polypropylene (Fig. 1, curve 1). Since at the peroxide concentration used and under the given reaction conditions, we cannot assume crosslinking of polypropylene alone, this may be explained by binding long polypropylene chains to polyethylene network.

At 90% polypropylene content in the blend and 4% of PETA, the amount of the gel formed is more than 50% higher when compared with the same system without PETA (Fig. 1). As may be deduced from curves 2 and 3 in Figure 1, other factors come into play when using this crosslinking procedure. If this were not so, the gel should decrease linearly from pure polyethylene to pure polypropylene. The decrease in the gel content, however, is not directly proportional to the increase of the PP content in the blend and some minimum is observed at higher PP weight fraction.

Around the minimum (i.e., at 80–90% of polypropylene in a blend), the gel yield is about 10% lower than in polypropylene alone. This declination may be explained, assuming that PETA and probably also peroxide, are more soluble in the polyethylene phase of a blend.

Examination of the solubility of PETA in PE and PP foils at 100°C showed that the amount of PETA dissolved in the former polymer is five times greater (i.e., about 25 and 5%, respectively).[8]
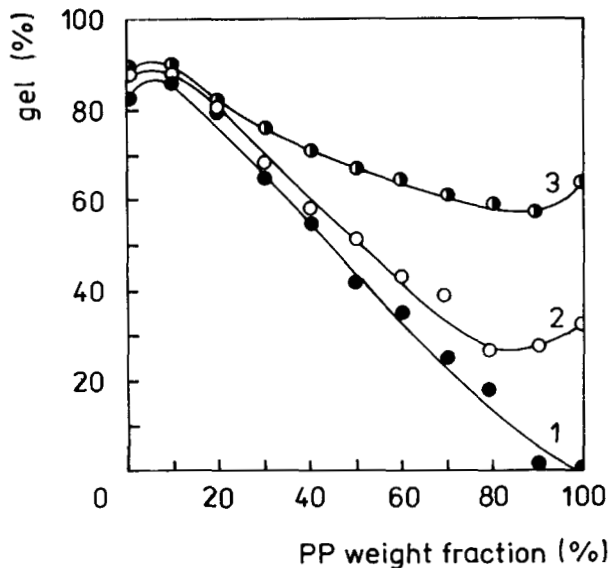
Fig. 1. A plot of gel formation during crosslinking of PP–PE blends vs. their composition in the absence and in the presence of PETA coagent (conc. DCP = 2.5 = const., t = 180°C, reaction time = 20 min): 1—without PETA, 2—with 2% PETA, 3—4% PETA.

Results obtained from the determination of the gel point when using various peroxides have also pointed to unequal dispersion of peroxide in the PP-PE blend. At the ratio of PP/PE = 60 : 40, using certain peroxides, the gel point was achieved at lower peroxide concentration than for polyethylene alone.[8] This is also accounted for by better peroxide solubility in the polyethylene component.
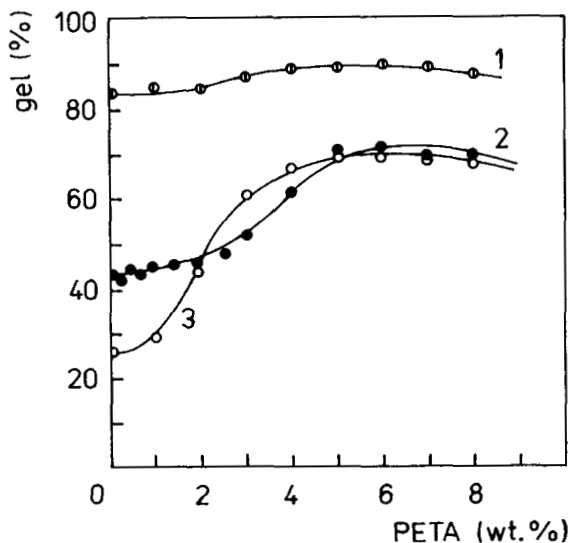

Fig. 2. A plot of gel formation during crosslinking of PP–PE blends with various contents of polymers vs. PETA concentration (conc. DCP = 2.5%, t = 180°C, reaction time = 20 min): 1—PP : PE = 20 : 80, 2—PP : PE = 50 : 50, 3—PP : PE = 70 : 30.
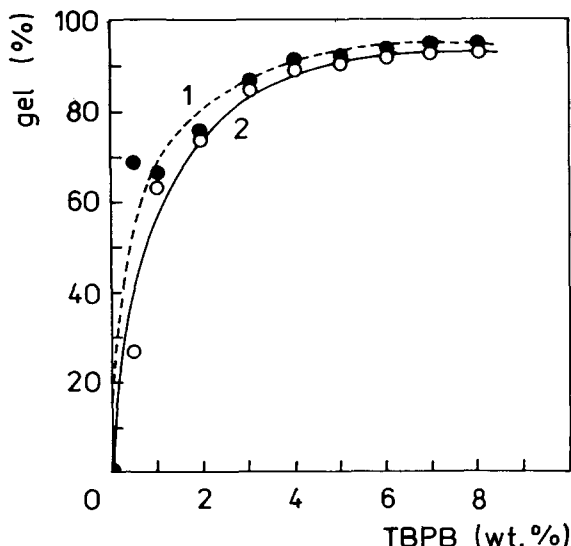
Fig. 3. A plot of insoluble part and gel, respectively, during crosslinking of PE alone vs. TBPB concentration in the presence of PETA (conc. PETA = 2% = const., t = 180°C, reaction time = 20 min). Insoluble part and gel, respectively, were determined by extraction with cyclohexane or with xylene: 1—determined by extraction with cyclohexane, 2—determined by extraction with xylene.

In the blend containing 20% PP in the presence of PETA coagent, no remarkable increase in gel content is observed (Fig. 2). PETA exerts a greater effect on the gel yields in blends containing 50 and 70% of PP, the maximum value of the gel being reached at 5–6% of PETA. Comparison of the blends with 50 and 70% content of PP shows a more intense rise in gel yields even at low concentrations of the coagent for blends richer in PP.

Extraction of Polypropylene and Polyethylene

Boiling xylene was used as solvent for the extraction of crosslinked PP-PE blends (Figs. 1 and 2). The uncrosslinked parts of both components, PE and PP were extracted simultaneously under such conditions. In an effort to successively extract polymers from the blend (at first the main part of PE and then the main part of PP) we have chosen a procedure, where the crosslinked sample of PP-PE blend was extracted first with boiling cyclohexane and then with boiling xylene. The successive extraction with cyclohexane and xylene was verified on crosslinked PE alone and i-PP alone.

Figure 3 shows that when PE crosslinked with tert-butyl perbenzoate (TBPB) was extracted in cyclohexane almost all uncrosslinked polymer was removed except for the sample crosslinked with 0.5% TBPB where some difference between cyclohexane and xylene extract was observed.

As expected, in the case of crosslinked PP great differences between cyclo-hexane and xylene extract were observed (Fig. 4). However, the relatively high solubility of polypropylene in cyclohexane is surprising. This is probably associated with the degradation effect of peroxide on PP. The minimum on plot 1—the highest solubility of uncrosslinked PP—is therefore observed for the sample crosslinked with 3% TBPB, where the concentration of radicals is
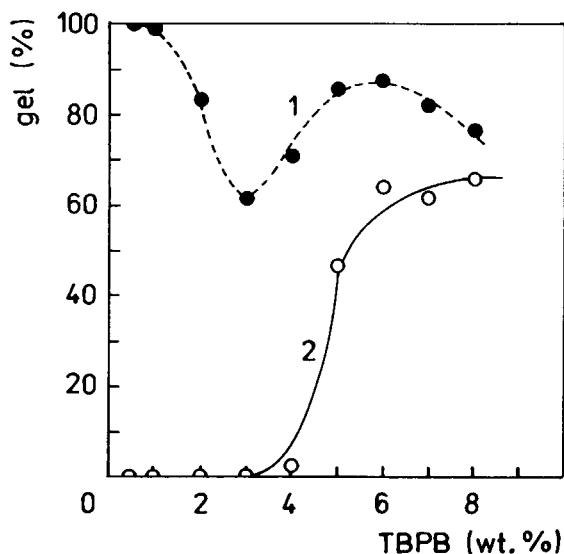
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Fig. 4. A plot of insoluble part and gel, respectively, during crosslinking of PP alone vs. TBPB concentration—without PETA (t = 180°C, reaction time = 20 min): 1—determined by extraction with cyclohexane, 2—determined by extraction with xylene.

higher but still low enough to give rise to a crosslinking reaction in order to achieve the gel point of the polymer; then mainly degradation occurs.[7] We cannot exclude partial modification of the PP chain due to mutual recombination of polymer radicals with the radical segments of the initiator and with the polymer fragments which reduce crystallinity of the polymer and thus increase its solubility. At the TBPB content of 4% and higher, the crosslinking
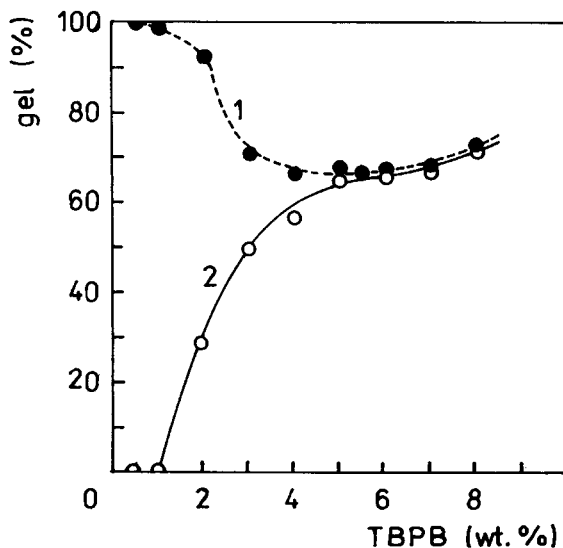

Fig. 5. Variations of insoluble part and gel, respectively, during crosslinking of PP alone with TBPB concentration in the presence of PETA (conc. PETA = 2%, t = 180°C, reaction time = 20 min): 1—determined by extraction with cyclohexane, 2—determined by extraction with xylene.

starts to compete with degradation and the solubility of isotactic polypropy-
lene decreases.

The greatest difference in the solubility in cyclohexane and in xylene for PP
crosslinked with TBPB in the presence of 2% PETA (Fig. 5, curve 1) occurs,
similarly as in Figure 4, curve 2, at low peroxide concentrations (the solubility
of uncrosslinked PP in cyclohexane being negligible). The solubility in cyclo-
hexane increases here, however, with the increasing degree of the polymer
crosslinking. This may be due to groups stemming from the crosslinking agent
grafted to the part of uncrosslinked isotactic PP. This may also account for
the minimal difference in cyclohexane and xylene extract obtained—during
crosslinking with TBPB amount higher than 5% as well as for the difference
between the plots in Figure 4 and Figure 5 in this region.

Effect of Peroxide and Coagent–PETA Concentrations on Gel Formation

Extraction analysis of the crosslinked blend. Discussion about Figures
3, 4, and 5 showed that successive use of cyclohexane and xylene for the
extraction of the uncrosslinked part of polyethylene and polypropylene does
not lead to complete separation of both polymers from the blend. On the other
hand, previous experiments showed that cyclohexane extract reflects the
chemical and possibly also physical changes in the uncrosslinked part of
polypropylene. We therefore tried to make use of these properties of cyclohe-
xane for the study of the crosslinking of PP/PE blend of the ratio 70/30.

Figure 6 shows the dependence of the polymer amount extracted with
xylene and cyclohexane on the peroxide content of TBPB without PETA used
for the crosslinking of the blend PP/PE = 70/30 (curves 1, 4).

A similar course is also observed in the presence of polyfunctional monomer
PETA (Fig. 6, curves 2, 4) up to 4% TBPB content. During extraction of the
crosslinked blend PP/PE = 70/30 with higher peroxide content, the course of
cyclohexane extraction is close to xylene extraction and apparently does not
depend on the presence of PETA. The course of the cyclohexane extraction
without PETA should be similar to that for the crosslinking of PP alone
(Fig. 4), if we assume that the PE part of the blend is crosslinked. On the
other hand, the higher solubility of PP (Fig. 6, curve 3) cannot be attributed
to greater degradation of the PP part of the blend, since in both cases (Fig. 4,
curve 1 and Fig. 6, curve 3), the dependences of the amount of extracted
polymer on the peroxide content are comparable within the same peroxide
concentration range. Participation of polyethylene, mainly by the chemical
binding to PP chains (via recombination reactions of polymer radicals) and
thus also the lowering of its crystallinity may be expected, leading to its
better solubility in cyclohexane.

Relatively high gel content in the blend PP/PE = 50 : 50 is obtained under
the effect of tert-butyl perbenzoate (TBPB) alone even at low peroxide
content. For instance, at 1% peroxide content, as much as 30% of gel is formed
(Fig. 7, curve 1). With increased peroxide content, the increase in gel content is
much slower. The initial rapid increase of the gel at low peroxide content may
be understood as a preferential dissolution of peroxide in polyethylene do-
mains. Further increase in the peroxide content leads to greater diffusion into
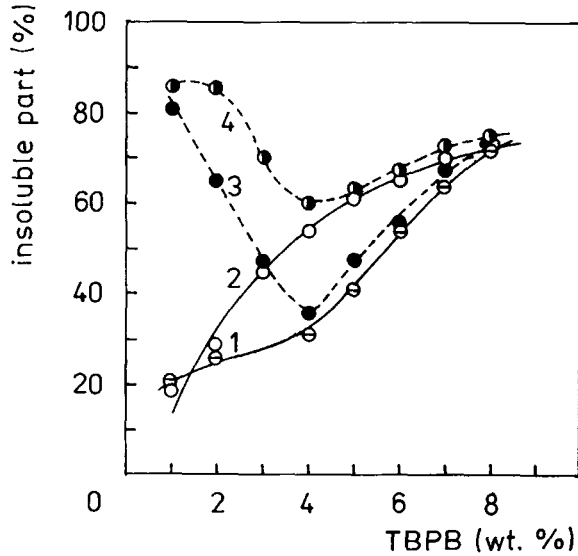
Fig. 6. Variations of insoluble part and gel, respectively, during crosslinking of the blend
PP : PE = 70 : 30 in the presence and in the absence of PETA with TBPB concentration
(t = 180°C, reaction time = 20 min): 1—without PETA, determined by extraction with xylene,
2—with 2% PETA, determined by extraction with xylene, 3—without PETA, determined by
extraction with cyclohexane, 4—with 2% PETA, determined by extraction with cyclohexane.
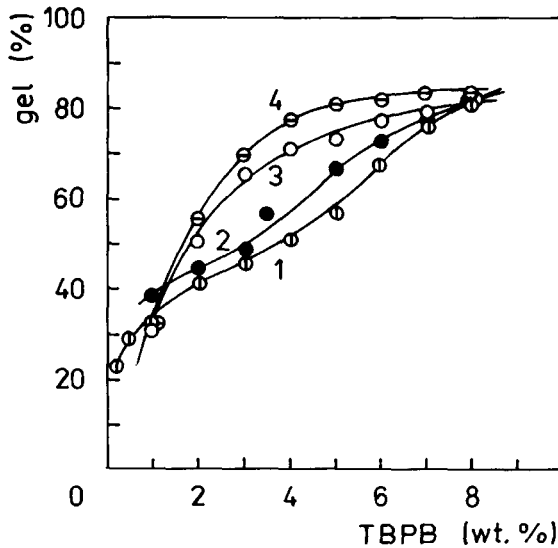

Fig. 7. Variations of gel formation during crosslinking of the blend PP : PE = 50 : 50 with
TBPB concentration in the presence and in the absence of PETA (t = 180°C, reaction time = 20
min) determined by extraction with xylene: 1—without PETA, 2—with 1% PETA, 3—with 2%
PETA, 4—with 4% PETA.

the polypropylene component, where the crosslinking efficiency will be minimal at the beginning. A more remarkable increase of the gel content occurs at 5% of peroxide, which is above the gel point of tert-butyl perbenzoate for pure polypropylene,[7] that is more intense crosslinking occurs in PP inhomogeneities of the blend above this concentration.

The coagent PETA (1, 2, and 4%) (Fig. 7) shows slight retardation effect in gel formation at very low peroxide concentrations (1%). This results from some consumption of primary radicals by the coagent at the overall low rate of the formation of macroradicals and also of the gel.

One can assume that under these conditions grafting of the polypropylene chain with the coagent PETA also takes place to some extent to the detriment of the crosslinking.

As the concentration of peroxide and thus also the rate of radical formation increases, PETA starts to function as a coagent of the crosslinking of the polypropylene or of polypropylene with polyethylene (Fig. 7, curves 2, 3, and 4). In comparison with the crosslinking with peroxide alone (Fig. 7, curve 1) the presence of PETA leads to an increase of the overall crosslinking efficiency of the blend. The higher the PETA content in a polymer blend, the more marked is the gel increase with the increasing peroxide content for the region of 2 to 7% of peroxide.

As Figure 7 shows, all curves intersect at the peroxide content of about 8%. At such a high peroxide content, the coagent is probably rapidly consumed in the initial stage of reaction (crosslinking + reactions between coagent and peroxide) and the gel yield depends only on the crosslinking initiated by peroxide alone. The peroxide content is high enough to obtain about 60% of gel in pure polypropylene.[7]

Relatively small amounts of cyclohexane extract (26%) containing 46% uncrosslinked polyethylene (Table I) were obtained in a PP/PE = 50 : 50 blend crosslinked with 1% tert-butyl perbenzoate at 180°C (Fig. 8). Polypropylene was found almost exclusively in the additional xylene extract (40% of

TABLE I
Composition of cyclohexane and xylene extracts of crosslinked PP/PE = 50 : 50 as a function of tert-butyl perbenzoate and coagent PETA at 180°C

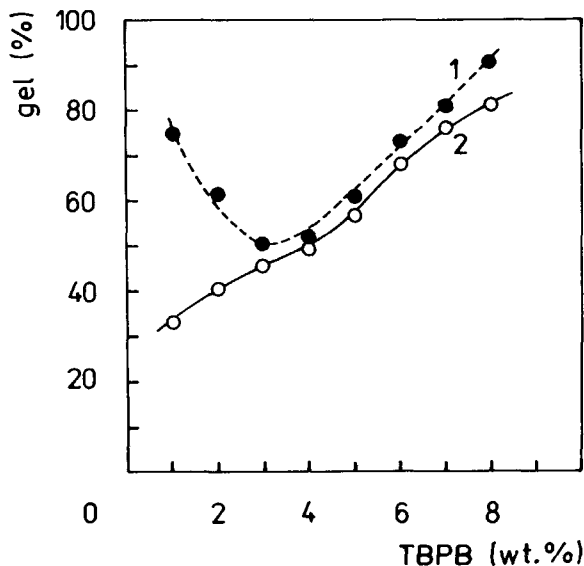| Crosslinking coagents | | Extraction of crosslinked PP/PE blend with cyclohexane | | | | Extraction of cyclohexane-insoluble part of PP/PE blend with xylene | | | |
			Soluble part				Soluble part		
		Insoluble part (%)	%	Extract (%) composition		Gel content (%)	%	Extract (%) composition	
TBPB (%)	PETA			PP	PE			PP	PE
1	—	74	26	54	46	34	40	92	8
4	—	52	48	89	11	48	4	83	17
8	—	91	9	35	65	82	9	84	16
1	2	81	19	29	71	39	42	90	10
4	2	74	26	80	20	70	4	87	13
8	2	84	16	89	11	81	3	91	9

Fig. 8. A plot of insoluble part and gel, respectively, during crosslinking of the blend
PP : PE = 50 : 50 vs. TBPB concentration (t = 180°C, reaction time = 20 min), insoluble part and
gel, respectively, were determined by extraction: 1—with cyclohexane, 2—with xylene.

the sample). Both extractions (Table I) show that polyethylene crosslinking
takes place almost exclusively (34% of gel was obtained under such conditions).
In the crosslinking of PP-PE blend 50 : 50 with 4% TBPB, the amount of
cyclohexane extract (48%) increases and the amount of the subsequent xylene
extract is reduced by only 4%. The total amount of the extracted PE decreases
and from the amount of extracted polymers we may deduce that the cross-
linked sample should contain 87% of PE and 13% of PP; this means that
polypropylene component also starts to crosslink, mainly at the contact of
interfaces of the dispersion. Further increase of TBPB content (8%) in PP-PE
blend leads to an increase of the gel, but it contains more than 40% of the
total amount of PP which was in the original PP-PE blend. With respect to
the results from the crosslinking of PP alone, where the gel point reaches
about 4% with TBPB, this course seems to be obvious.[7]

A similar examination of cyclohexane and xylene extracts of PP-PE blend
(50 : 50) crosslinked in the presence of 2% PETA and at 180°C yielded higher
gel contents as a result of the effect of the crosslinking coagent PETA (Fig. 9).
Table I shows that even at 1% TBPB content and 2% PETA in PP-PE blend
(50 : 50), crosslinking of the PP component occurs. The crosslinked
blend contained 13% of PP. At 4% TBPB content (Fig. 9), the crosslinked
blend contains as much as 61% of PE and 39% PP. The result contradicts the
data for the crosslinking of polypropylene alone under similar reaction condi-
tions, where about 60% of gel was obtained as earlier.[7] This finding supports
the conclusion put forward, that nonuniform dissolution of the crosslinking
coagents occurs in inhomogeneities of the PP-PE blend. Better solubility of
coagents in polyethylene causes lower efficiency of the crosslinking of
polypropylene. At 8% TBPB, the content of PP rises only to 42%. But only a
negligible amount of uncrosslinked polyethylene (about 1%) was extracted. On
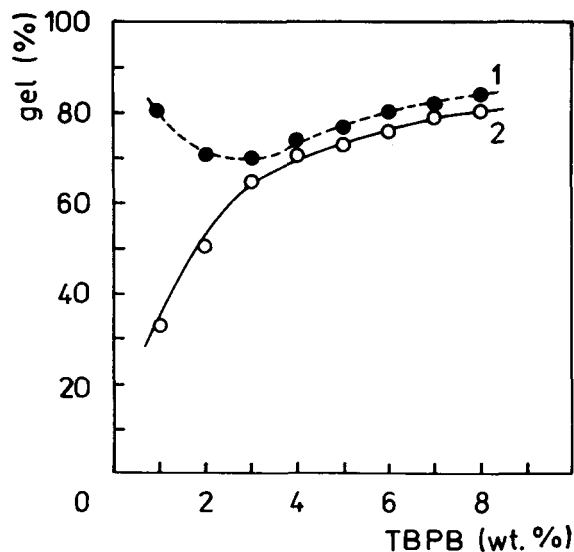the other hand, one can assume that because of the nonuniform solubility in

Fig. 9. A plot of insoluble part and gel, respectively, during crosslinking of PP : PE = 50 : 50 vs. TBPB concentration in the presence of 2% PETA (t = 180°C, reaction time 20 min), insoluble part and gel, respectively, were determined by extraction: 1—with cyclohexane, 2—with xylene.

both polymeric phases, the crosslinking density of the polyethylene component increases to the detriment of the polypropylene component.

Influence of radical reactions on the crystallinity and melting temperatures of PP-PE blends. In the PP-PE blend (50:50), the gel content increases with increasing TBPB concentration (at constant PETA concentration = 4%) only in the range up to 5% of TBPB at 180°C and attains a
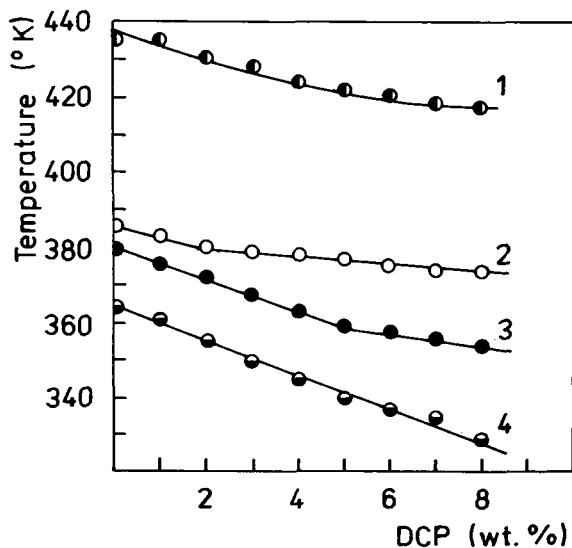

Fig. 10. Variations of melting temperatures T_m and crystallization temperatures T_{cryst} of both components of PP–PE blends with DCP concentration (t = 180°C, reaction time 20 min): 1—T_m for PP, 2—T_{cryst} for PP, 3—T_m for PE, 4—T_{cryst} for PE.

constant level as follows:

TBPB%	1	2	3	4	5	6	7	8
gel%	33.5	53.5	70.0	77.6	80.6	81.8	82.8	82.3

Melting temperatures T_m and crystallization temperature T_{cryst} of both components decrease with the increase of polymer branching. The reduction is more marked for PE (by 20°C) while for PP T_m it decreased by 15°C. At higher TBPB concentrations, when the gel content remains practically constant, a still less intense reduction of T_m is observable for both PP and for PE (Fig. 10).[9]

The plot of the crystallization temperature against the gel or peroxide content decreases more rapidly in the case of PE than for PP over the whole concentration region (Fig. 10). The greater influence of the peroxide decomposition on the lowering the PE crystallinity than that of PP crystallinity documents the idea of higher solubility of peroxide in PE. This is in agreement with the description of Figures 8 and 9. The reduction of T_{cryst} and T_m for PE above 5% TBPB may be assigned mainly to the density increase of crosslinks.[10]

CONCLUSIONS

1. Relatively small amounts of PP incorporate into the polymer network on crosslinking PP/PE blends with small amounts (up to 4%) of peroxide.

2. Since the crosslinking coagent PETA leads to an increase in the crosslinking efficiency of peroxide in polypropylene only, its effect becomes distinct only in blends with higher content of polypropylene.

3. The crosslinking efficiency of PETA coagent in PP/PE blends is somewhat lower than that for PP alone. This discrepancy is due to a higher solubility of PETA in PE compared with the PP phase of the blend. The crosslinking of PP part than occurs with the lower initial PETA concentration as it corresponds to the initial amount of PETA added to the mixture.

4. The decrease of T_m and T_{cryst} of both PP and PE phases with increasing peroxide concentration cannot be ascribed to the increasing amount of crosslinks only, but, particularly, to other reactions of macromolecules (branching, binding of peroxide radicals to polymer chain, and degradation).

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