

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

PARTIAL CROSSLINKING OF THE HETEROPHASIC ETHYLENE-PROPYLENE COPOLYMER IN THE SOLID PHASE

Nadezda Spisáková^a; Manfred Rätzsch; Norbert Reichelt

^a Department of Plastics and Rubber, Faculty of Chemical Technology, Slovak Technical University, Bratislava, Slovakia

Online publication date: 18 January 2000

To cite this Article Spisáková, Nadezda , Rätzsch, Manfred and Reichelt, Norbert(2000) 'PARTIAL CROSSLINKING OF THE HETEROPHASIC ETHYLENE-PROPYLENE COPOLYMER IN THE SOLID PHASE', *Journal of Macromolecular Science, Part A*, 37: 1, 15 – 35

To link to this Article: DOI: 10.1081/MA-100101078

URL: <http://dx.doi.org/10.1081/MA-100101078>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

PARTIAL CROSSLINKING OF THE HETEROPHASIC ETHYLENE-PROPYLENE COPOLYMER IN THE SOLID PHASE

Nadezda Spisáková*

Department of Plastics and Rubber
Faculty of Chemical Technology
Slovak Technical University
Radlinského 9, 812 37 Bratislava, Slovakia

Manfred Rätzsch and Norbert Reichelt

PCD Polymere G.m.b.H./Borealis
St.-Peter-Str. 25, 4020 Linz, Austria

Key Words: Radical Modification, Polyolefins, Peroxide, Solid Phase, Mechanical Properties

ABSTRACT

The influence of radical modification with peroxides under solid phase conditions on mechanical properties and the morphology of an heterophasic ethylene-propylene copolymer (HECO) were investigated. The extent of crosslinking and degradation was characterized by the melt flow index and extraction data. Influence of modification on dynamic viscoelasticity of HECO was also investigated. The morphology was studied by the transmission electron microscopy (TEM). Tensile and impact tests were performed on samples of the modified HECO. Crosslinking occurred in the dispersed EPR phase of HECO in the investigated peroxide concentration range. The extent of crosslinking and degradation was dependent on the type of per-

* Author to whom correspondence should be addressed.

oxide as a result of the modification in the melt. The modification with higher peroxide concentrations led to the morphology close to the one of the unmodified HECO powder before and also after the extrusion step. The elongation at break of HECO increased at low peroxide concentrations. Improved impact strength at 23°C was attained. Loss of toughness at -20°C was found probably due to slight degradation of PP matrix and due to an inhomogeneous crosslinking of EPR in HECO.

INTRODUCTION

Heterophasic ethylene-propylene copolymers (HECO) were developed to improve poor low temperature impact resistance of PP. Originally, PP homopolymer was melt-blended with a prefabricated elastomer like EPR. Later, HECOs were developed as PP reactor blends made *in situ* by sequential homopolymerization of propylene and copolymerization of propylene and ethylene [1]. In the reactor, a well-dispersed morphology is obtained and there is no need to further mix the components. HECO comprises a hard matrix and a soft dispersed phase, which in general is the morphology of thermoplastic elastomers.

An improvement of mechanical properties of the PP/elastomer blend can be reached by partial or total crosslinking of EPR [2]. Usually, a radical mechanism is used for the chemical modification of blends of saturated polyolefins [3]. The most common crosslinking agents are peroxides and peroxides with a crosslinking coagent.

The modification is usually made in the melt under static or dynamic conditions. The mechanical properties of the product are very dependent on processing conditions or on the grade of preblending in the case of the modification under static conditions. Processing conditions control the reaction conditions, and further, they control the morphology - the size, shape, and interparticle distance of the particles of the dispersed phase. Impact strength and also other mechanical properties of heterophasic systems depend on many factors. The improvement of desired property is thus a complex problem.

If modified with peroxides alone in the melt, improved processability of HECOs is reported only, unless the content of elastomeric component reaches a certain minimum [4]. Not all types of elastomers are curable with peroxides. The crosslinking degree of EPR depends on the content of ethylene units in chains. It is known that PP matrix degrades, since the rate of β -scission of tertiary carbon

radicals of PP is high under conditions of the melt radical modification. This is believed to be the most important reason for the degradation of PP.

HECOs and also PP pure, can be crosslinked easier with peroxide and polyfunctional monomer. Crosslinking of PP has been reported by the modification under static melt conditions [3] and also, in some cases, under dynamic vulcanization [5, 6]. Its degradation degree was found to still be high.

To overcome the problem of the degradation of PP, a special crosslinking system with low activity radicals has been used by the modification in the melt of the blend of EPDM and PP [7]. The presence of unsaturated bonds in EPDM is necessary in this case.

A lower degradation extent of PP matrix could be reached by a radical modification with peroxidic system at low temperatures, i.e. in the solid phase. It was found that the rate of β -scission of macroradicals decreases with the sinking temperature [8]. Moreover, the solid phase modification of polyolefins, especially grafting, has gained attention [8, 9] as a procedure with low costs and high variability. Thus, there would be several advantages if a solid-phase impact modification of a reactor blend were possible.

In the solid phase, the homogeneity of the distribution of the reaction agents cannot be assured by mixing. A composition gradient from the surface to the center of the particle has been reported by grafting in the solid phase [10]. If the requirement on the pore diameter and overall surface of pores in the sponge-like particles is fulfilled, a homogeneous product can be obtained [11].

This report deals with solid phase radical modification of HECO with two peroxides. The influence of the type and concentration of peroxide on the content of crosslinked parts and on mechanical properties of HECO was evaluated. The aim was to acquire material with improved mechanical performance.

EXPERIMENTAL

Materials

A standard type of HECO with 12 mol% content of ethylene units (Daplen KSC12, product of PCD Polymere, Austria) and with 20 mol% of ethylene units (Daplen KSR25) were used for the modification. These types are called "standard block copolymers" [12]. Their actual characteristics are summarized in Table 1. The HECO powders were stored under nitrogen after filling from the plant to avoid the degradation with oxygen.

TABLE 1. Data from the Extraction with Cold Xylene (XCS), Melt Flow Index (MFI) and Mechanical Properties from the Uniaxial Tensile Test and the Impact Test of Raw HECO Used for Modification

Material	Ethylene Content [mol%]	XCS [wt%]	MFI 230/2,16 [g/10min]	Tensile Modulus, E [MPa]	Impact Strength	
					-20°C a_C	+23°C a_{CN}
KSC12	10	12	7.2	1200	53	7.1
KSR25	20	22	6	870	152	21.5

a_C - Charpy impact strength unnotched, a_{CN} - Charpy impact strength notched

HECOs are PP reactor blends prepared in the two-stage polymerization process [1]. Basically, HECO consists of a PP matrix, produced in the first stage in liquid propylene, and of a dispersed EPR phase which is produced in the second reactor in a gas phase. Compared to physical blends of PP and EPR, the morphology of HECO is more homogeneous. EP copolymerization, that takes place in the second stage, leads to a mixture of the crystalline and amorphous phases. This makes an exact quantification of the EPR content difficult. For the characterization of the copolymer, the quantity of ethylene and XCS value—cold xylene extractable fraction (see Extraction data in this chapter)—is used.

The distribution of the EPR particles in the PP matrix of HECO powder is not even, as it is illustrated in Figure 1 (a and b). After extrusion, the EPR inclusions are more homogeneously dispersed, but coalescence occurs (compare Figures 1 and 2).

Two types of peroxide with different decomposition rates were used as radical initiators:

tert-butylperoxybenzoate, $t_{1/2}$ at 120°C = 116.7 min, Akzo AG (TBPB)

and

tert-butylperoxyisobutyrate, $t_{1/2}$ at 120°C = 4.2 min, Akzo AG (TBPIB).

Modification of the HECO in the Solid Phase

Non-stabilized powder of HECO was charged into the reactor and flushed with nitrogen to remove oxygen. A nitrogen atmosphere was assured in the reactor during all operations of the modification. The reactor was a vessel

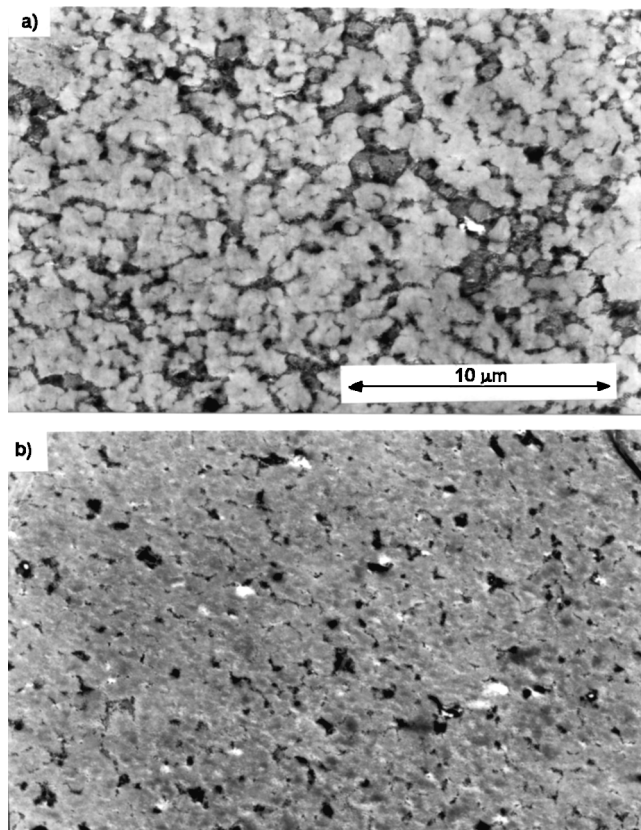


Figure 1. Transmission Electron Micrographs of HECO KSC12: Documentation of the Uneven Distribution of the EPR Particles in the Unmodified HECO Powder a) a High Content of EPR; b) a Low Content of EPR.

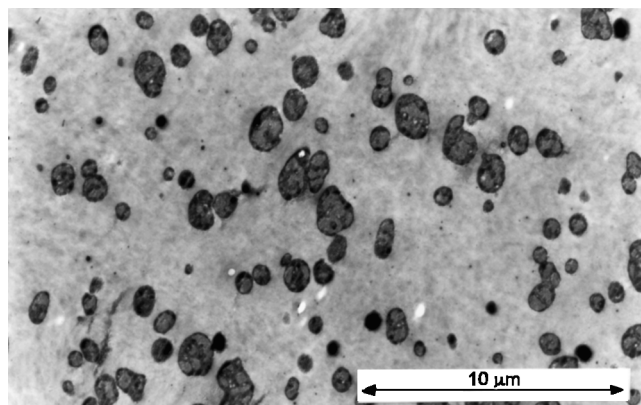


Figure 2. Transmission Electron Micrographs of HECO KSC12: Unmodified Copolymer after Extrusion.

provided with a stirrer, nitrogen inlet and outlet on the top and a thermometer. The temperature was measured in the middle of the reactor. The sorption of the reaction agents was performed from the liquid phase. The reaction agents were first diluted with acetone and then added into the reactor. The sorption was carried out for 20 minutes under vigorous stirring. The reactor was heated up to the reaction temperature using an oil bath. The reaction temperature was a temperature under the melting point of PP phase of HECO, so that HECO stayed the whole reaction time in particulate form. The used reaction time was at least seven times the half time of the peroxide decomposition. After the reaction ended, the reactor was cooled to 30°C and the crude sample was stabilized with a solution of stabilizers (Ionol, Irganox 1010, Irgafos 168; Ciba Geigy Ges.m.b.H.) in acetone and dried at the room temperature.

The stabilized powder samples were extruded on a pilot plant twin-screw extruder (fa.Berstorff). They were characterized both in the form of a powder and an extrudate.

Preparation of Control Samples of HECO in the Melt

Samples of HECO powder were mixed with reaction agents and stabilizers in primarily nitrogen atmosphere. Peroxide TBPIB was not used in the modification in melt because its decomposition rate at the temperature of extrusion is too high. The mixtures were allowed to diffuse for 20 minutes, then fed into the pilot plant twin-screw extruder with good mixing ability. The temperature of extrusion was 180-230°C. The extrudate was cooled down in water bath and pelletized.

Characterization of the Modified HECO Samples

Extraction Data

The content of the EPR phase was determined by extracting polymer in cold xylene (XCS = xylene cold soluble fraction). The sample of polymer was dissolved in hot xylene and allowed to stand for 24 hours at room temperature. Then, the solution was filtered through a medium filter and a very slow sintered-glass filter funnel. The filtrate was dried in vacuum at 110°C to constant weight. The XCS value was the weight of the dried filtrate divided by the weight of the polymer before the extraction. The XCS value is taken as an approximate quantification of the EPR phase in the HECO (a small amount of crystalline parts of EPR phase is not soluble in cold xylene).

For quantification of the crosslinking reaction, the gel content was determined (**XHI** = xylene hot insoluble fraction). The sample of polymer was extracted in Soxhlet apparatus for 48 hours in boiling xylene. XHI value is the weight of the polymer after the extraction, which was dried by 120°C in vacuum to constant weight, divided by the weight of the polymer before the extraction.

MFI: Melt flow index was measured with Zwick 4105 at 230°C, and 2.16 kg according to DIN 53735.

Transmission Electron Microscopy

To study the morphology, the samples of HECO were prepared and investigated as follows: The rubber phase of the samples was selectively stained with ruthenium tetroxide. Thin sections were microtomed and investigated in a TEM (Phillips EM 300).

Mechanical Tests

The mechanical properties of materials were characterized according to following standards: Tensile-testing procedures followed the standard ISO 527. Stress-strain curves were recorded for each sample. Unnotched and notched impact tests were performed according to ISO179 1eU and 1eA at the temperatures of -20°C and +23°C. The specimens were injection-molded. At least six specimens were tested for each sample.

Dynamic Viscoelasticity Test

The specimens, 10×60×1 mm, were tested with a Myrenne ATM3 machine (free oscillation) and the testing followed ISO 6721. The heating rate of 1,5 - 2 K/min was used for tests. Dynamic loss and storage moduli in a broad temperature range were recorded.

RESULTS AND DISCUSSION

Crosslinking and Degradation of HECO in the Solid Phase

Table 2 presents characterized samples of HECO modified in the solid phase with an increasing initiator concentration. Above certain peroxide concentration, “gels” could be isolated from the solid phase modified samples of both HECO types by the extraction with hot xylene. The presence of the gels is evidence of crosslinking. In comparison, no gels were found in the control samples

TABLE 2. Modification of HECO KSC12 with Tert-butylperoxybenzoate (TBPB) in the Melt and in the Solid Phase

Concentration of TBPB [wpph]	Modification in solid phase at 142°C				Modification in melt at 220°C		
	MFI _{pellets} [g/10min]	MFI _{pellets} / MFI _{powder}	XCS [wt%]	XHI [wt%]	MFI [g/10min]	XCS [wt%]	XHI [wt%]
0	6.5	1	12	0	7.7	11.6	0
0.05	12.2	1.1	10	0	21.5	10.5	0
0.1	19.8	1.4	9.2	0.8	33.9	11.2	0
0.165	33.2	2.1	6.9	6.5			
0.2					68.8	11.9	0
1.0	118	1.4	2.4	10			

wpph - weight parts per hundred weight parts of origin HECO

modified with the same reagents in the melt. This difference should rise, mainly due to the influence of the temperature on the rate ratio of degradation, and crosslinking of both PP and EPR. As already mentioned, the relative rate of β -scission of macroradicals was found to decrease with the decreasing temperature.

Generally, even though the HECO samples modified with small peroxide concentration show worse solubility in hot xylene, they do not contain gels. XHI extraction data cannot, therefore, characterize the early stages of the crosslinking.

Due to the reaction with peroxide, the samples of HECO become less soluble in a cold xylene. Xylene cold soluble parts are the equivalent of the amorphous EPR content. XCS sinks gradually already at low peroxide concentrations under the gel point (gel point = appearance of XHI parts). The solubility is expected to be reduced since increasing the molar weight of EPR, and so XCS could characterize early stages of crosslinking and/or branching. In comparison, no such decrease of XCS was found in the control HECO samples modified in the melt.

The influence of two types of peroxides on the extraction data of modified HECO samples are shown in Figures 3 and 4. Only negligible amounts of gels are formed with TBPIB (see Figure 3a) due to the different kinetics of decomposition and other factors. We can observe the effect of the modification with TBPIB only in the decrease of XCS.

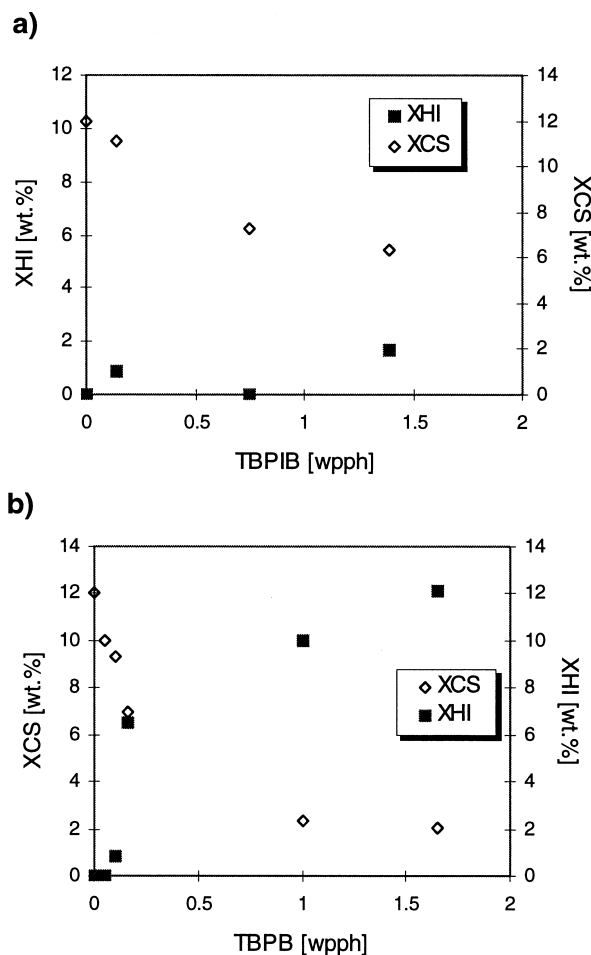


Figure 3. Modification in the Solid Phase at 142°C of HECO KSC12 with Different Types of Peroxide a) Tert-butylperoxyisobutyrate (TBPIB) and b) Tert-butylperoxybenzoate (TBPB)-Extraction Data.

The IR measurement of ethylene-unit content in gels isolated from the modified KSC12 showed that even at the concentration of 1.65 weight parts per hundred weight parts of HECO (wpph) of peroxide TBPB, the composition of gel is similar to the composition of EPR before the modification (ca. 60 mol%). This implies that the gels consist of crosslinked EPR and only at higher concentrations, PP gels appear (over 1.65 wpph TBPB, the gel content exceeds the XCS of the original sample). As the reports on crosslinking of PP homopolymer with

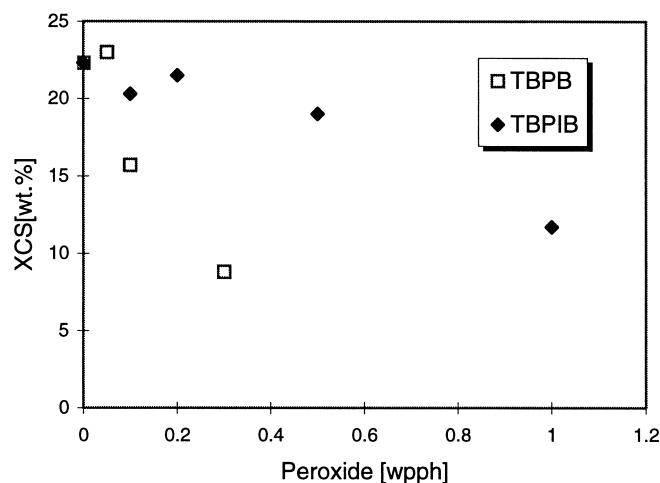


Figure 4. Modification in the Solid Phase of HECO KSR 25 at 142°C with Different Types of Peroxide Tert-butylperoxyisobutyrate (TBPIB) and Tert-butylperoxybenzoate (TBPB) - Extraction Data.

peroxides teach, the high stationary concentration of radicals is needed for the PP gels to appear [13]. We tested a quite narrow peroxide concentration range, for at higher concentrations, the samples are degraded and inhomogeneous in appearance.

Simultaneously, the degradation reaction takes place. The MFI values show, that solid phase modified samples are even after the extrusion and pelletization to some extent less degraded than the melt modified samples (Table 2).

The MFI value can be influenced by a different crosslinking extent of samples and by their morphology. After extrusion of solid phase modified samples, their MFI changes (Table 2). We see two reasons for the change: one is probably a higher residual peroxide or radical concentration when the original peroxide concentration is risen. High shear mixing in the extruder yields then a greater degradation. But since the ratio of MFI value of modified powder and extrudate does not seem to be dependent on peroxide concentration, this change could occur also due to morphological change. When the concentration of the peroxide is risen from 0.165 to 1.0 wpph, the MFI ratio stays in the same range (is even slightly lower). We assume that due to crosslinking in the solid phase, dispersed EPR particles are fixed in a network-like structure, which hinders the flow of the modified copolymer melt under low shear conditions. After extru-

sion, the network-like structure is destroyed and the flow behavior of the polymer melt is determined more by the degraded PP matrix. Support for this is seen also in the TEM micrographs where the EPR inclusions are not isolated from each other in the PP matrix but there are “EPR bridges” between two larger EPR inclusions before the extrusion of the HECO powder.

The degradation extent of the HECO modified in the solid phase depends on the type of initiator and temperature. Tert-butylperoxybenzoate (the initiator with lower decomposition rate) causes a higher extent of degradation of modified HECO than tert-butylperoxyisobutyrate (the initiator with faster decomposition). The difference in the degradation activity of the peroxides is due to the activity of primary radicals for H-abstraction. We can conclude that the use of less active radicals with respect to the H-abstraction in our system is of advantage.

In order to better characterize the changes of the individual phases of HECO due to modification, the dynamic mechanical spectra of samples were recorded. The plot of $\text{tg } \delta$ of HECO KSC12 as a function of the temperature ($^{\circ}\text{C}$) shows shifts of the center of the β -transition peaks of two phases and change of their area due to modification. The β -transition peak of EPR of solid phase modified samples (extraction data in Figure 3) shows an evident shift to higher temperatures and its area increases (details in the Table 3). There is a slight shift of the center of the β -transition peak of PP and its area decreases due to modification significantly. The change of the damping capacity of EPR and PP can be

TABLE 3. Characterization of β Relaxation of PP and EPR in HECO KSC12 from the DMA Spectrum: Changes Due to Solid Phase Modification at 142°C

Type	Peroxide Concentration [wpbh]	Area of peak β EPR arbitrary units	$\text{tg } \delta_{\text{max}}$ of EPR [$^{\circ}\text{C}$]	Area of peak β PP arbitrary units	$\text{tg } \delta_{\text{max}}$ of PP [$^{\circ}\text{C}$]
-	0	16.9	-58.7	68.4	6.2
TBPIB	0.1	22.5	-55.5	55.7	4.2
TBPIB	0.75	24.8	-54	54.7	4.2
TBPB	0.165	27.2	-51.7	52.6	2.1

ascribed to the decrease or increase of their crystallinity mainly. We assume the crystallinity of EPR is lowered due to crosslinking [7]. On the other hand, the crystallinity of PP probably increased and could be caused both by crosslinking and degradation. The shift of the peak can be found in systems in which the compatibility of phases was improved due to the addition of an external compatibilizer [14] or due to a copolymer formed *in situ* by the chemical reaction of the phases at the interface [15]. The shift due to formation of gels has been also proposed [16]. From the results presented in Table 3, we can see that the EPR peak is shifted more at higher peroxide concentrations. With a rising concentration, both more gels and more copolymer can be formed therefore, both structural changes can be employed in the shift of the EPR peak.

Morphology

The differences in the distribution of EPR in the matrix in individual HECO powder grains were already mentioned in the Experimental above (see Figure 1(a, b)).

A coagulation of the dispersed phase occurs by processing an unmodified powder of HECO (Figures 1 and 2). Due to the modification with higher concentration of peroxide, morphology of powder is preserved in the extrudate of HECO (Figures 1 and 6) - its particle size, distance and distribution do not change. Thus, the partial crosslinking of the EPR particles in the solid phase leads to the stabilization of the powder morphology. The original shape of the EPR particles also remained essentially unchanged.

At small concentrations of peroxide, the morphology of extrudate of modified HECO is homogeneous and very close to the morphology of unmodified HECO extrudate. The dispersed EPR phase coagulates during the extrusion.

Tensile Properties

Tensile curves of samples of KSC12 and KSR25 modified with increasing peroxide concentration in the solid phase were recorded. The shape of the tensile curves and the yielding behavior do not change much due to modification when compared with the original values. The curves in Figure 7 that show the results for KSC12 are representative also for the KSR25. The only parameter that changes significantly is the elongation at break. The similarity of shapes of stress-strain curves is apparently the effect of PP being the major component that constitutes the matrix phase.

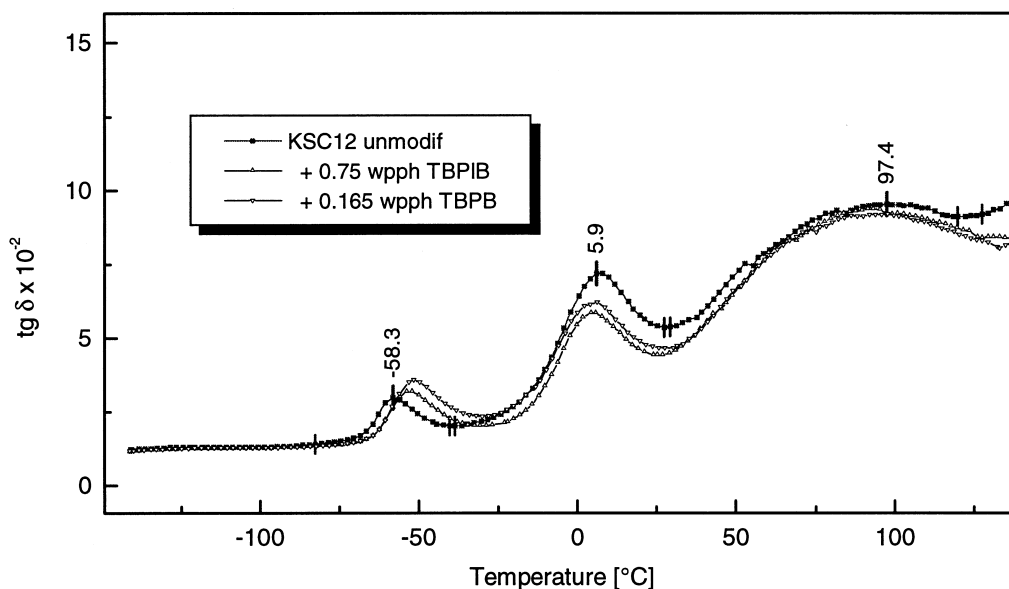


Figure 5. Temperature Dependence of Loss Tangent of HECO KSC12 Unmodified and Modified in the Solid Phase with Peroxide.

In a very narrow range of low peroxide concentration, elongation at break jumps to the maximum and then decreases below the value of the original material (Figure 8 (a, b)). The decrease of the elongation at break after modification with peroxide has been reported in similar blends with PP as a major com-

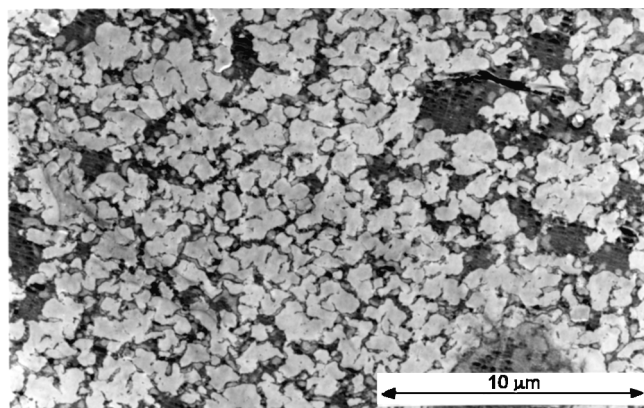


Figure 6. Transmission Electron Micrographs of HECO KSC12: Modified with 0.165 wpph of Tert-butylperoxybenzoate at 142°C, after Extrusion.

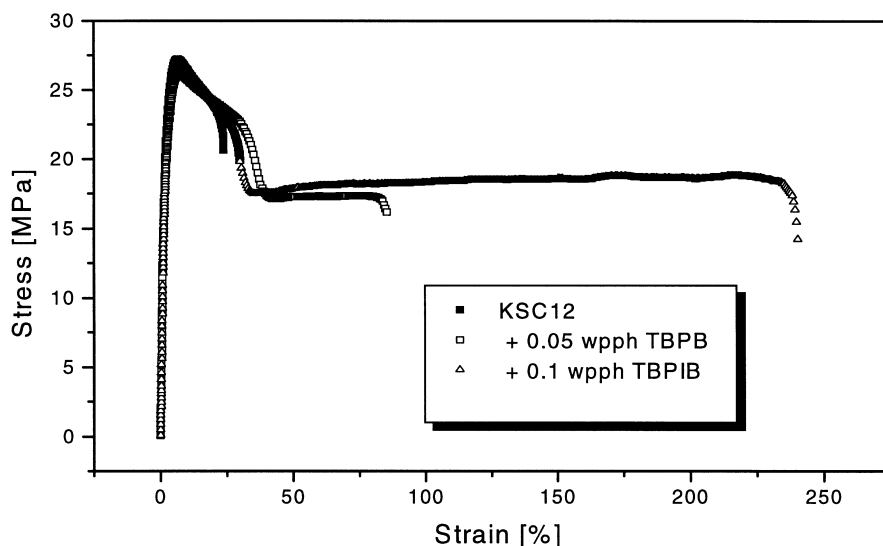


Figure 7. Stress - Strain Curves of HECO KSC12 Modified in the Solid Phase at 142°C with Low Peroxide Concentrations.

ponent due to degradation of PP matrix [17, 18]. Increase of the elongation at break means that more energy is needed to break the sample. The influence of the different peroxide type is also illustrated in Figure 8. For both KSR25 and KSC12, the deterioration sets on later with TBPIB. It is more visible on KSR25, where at 0.5 wpph concentration of TBPIB, the elongation at break is still at the original level, while for KSC12 modified with TBPIB it is already below the starting value.

The increase of ϵ_B at the beginning of investigated peroxide concentration range could be explained as a compatibilization action due to modification [7, 19], probably formation of an interface copolymer. Such an increase was also reported due to advantageous morphological change, but this is not our case as it was shown on the TEM micrographs. The XCS, MFI values together with E-modulus of tested samples are given in the Table 4. As it can be seen, the XCS values decrease slightly. In fact, the decrease in the case of KSC12 is within an experimental error. For KSR25, the change of XCS value rises around 0.5 TBPIB above the experimental error. The decrease of MFI values in some cases serves as a prove of crosslinking or branching even though according to XCS values no chain extension reaction could be found. However, the crosslinking or branch-

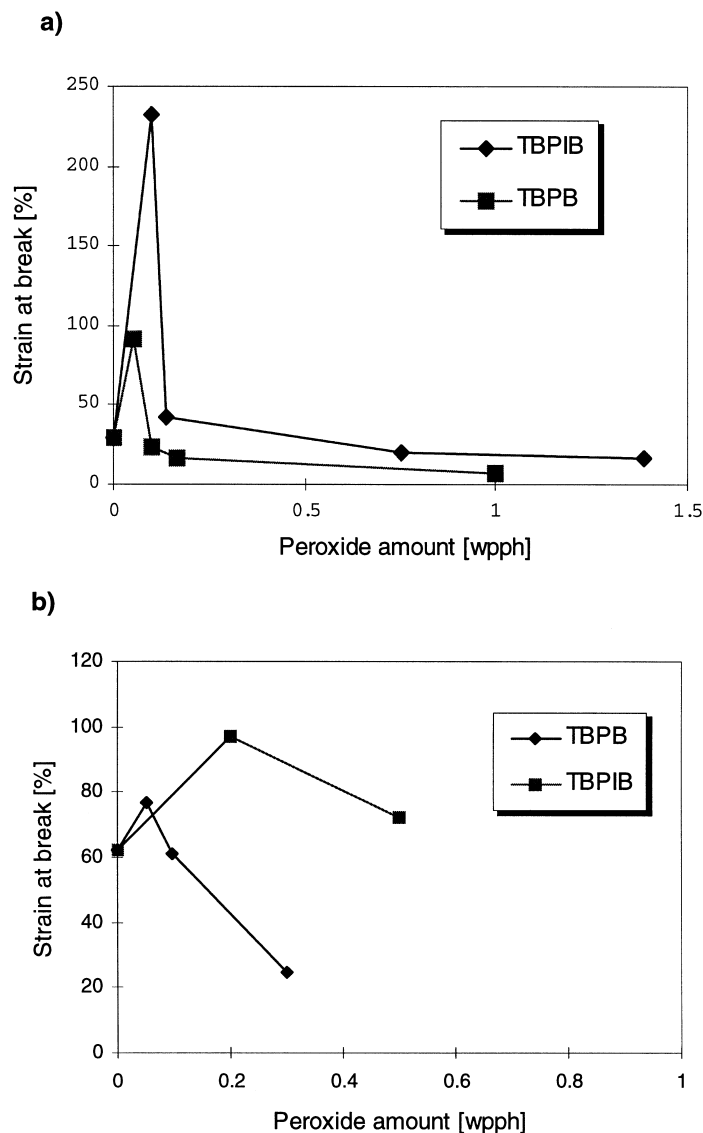


Figure 8. Dependence of the Ultimate Strain on Peroxide Concentration of a) HECO KSC12 and b) HECO KSR25 ; Both Modified in the Solid Phase at 142°C.

ing of EPR itself should not be the source of increased elongation at break. It is suggested that due to combination of macroradicals at the interface, an “in situ” copolymer be created that improves the cooperation between two phases under tensile stress. Since the stress at break is not increased in the samples modified

TABLE 4. Comparison of the Influence of the Modification in the Solid Phase on the Tensile Modulus of KSR12 and KSR25

Material	Type	Peroxide Amount [wpph]	XCS Pellets [%]	MFI Pellets [g/10min]	Tensile test E-Modulus [MPa]
KSR25	-	0	22.5	5.5	865
	TBPIB	0.1	20	7	829
		0.2	21.5	5.4	796
		0.5	19	4.9	762
KSR25	TBPB	0.05	23	6.1	814
		0.1	15.7	6.2	787
		0.3	8.8	15.7	673
KSC12	-	0	12	7.9	1295
	TBPIB	0.1	11	6.3	1203
	TBPB	0.05	12	8	1225

[wpph] - weight parts of peroxide per hundred weight parts of polymer powder

with low peroxide concentrations, it may not indicate an improvement of the impact strength.

The Table 4 shows the E-modulus lowers slightly due to modification along with increasing of strain at break. Its values are slightly lowered already at the lowest peroxide concentration when no chain extension was detected with XCS and XHU. This is probably due to the degradation of the PP, even though the MFI values show no increase. The decrease of E-modulus of samples modified with TBPB is more severe.

The visual homogeneity of the samples of KSR25 with higher ultimate elongation is as was originally and it worsens subsequently with the increase of the used peroxide concentration.

Impact Strength

In spite of the same trends in the change of tensile properties due to modification with peroxides, the impact strength of two investigated materials changes differently. Table 5 shows the influence of the modification with the lowest investigated concentration of two peroxides in the solid phase on the impact strength of HECO KSC12. At these concentrations, the toughness of the modified KSC12 at +23°C remains at the same level. However, the impact strength at -20°C is already decreased with both peroxide types. The samples in

TABLE 5. Influence of the Modification in the Solid Phase at 142°C on Mechanical Properties of HECO KSC12

Material	Peroxide		XCS [wt%]	MFI 230°C/2.16kg [g/10min]	a _{CN} +23°C	a _C -20°C
	Type	Amount [wpph]			work [kJ/m ²]	work [kJ/m ²]
KSC12	-	-	12	7.9	7.1	53
	TBPIB	0.1	11	6.3	7.8	43
	TBPB	0.05	12	8	7.8	42

a_C - Charpy impact strength, a_{CN} - notched Charpy impact strength

the Table 5 can have only a slightly degraded PP-matrix since the MFI value almost did not change. XCS values reveal practically no crosslinking or branching. That means that in the case of modification with 0.1 wpph of TBPIB, crosslinked parts will not influence MFI value to significant extent. Hence, we assume the cause of decrease of impact strength of modified samples at -20°C to be firstly a slight degradation of PP that is not detectable with MFI measurement, and secondly an additional influence such as an inhomogeneous modification. In this case, the higher elongation at break of KSC12 in the low peroxide concentration region did not mean an improvement of the impact strength.

At higher peroxide concentrations than in the Table 5, all properties deteriorate, the tensile modulus being the least influenced, due to strong degradation of the matrix visible in the increase of MFI values and due to strong crosslinking of the dispersed phase (decreased XCS values).

If HECO comprises more EPR (KSR25), an evident improvement of the impact strength at 23°C can be attained (Figure 9). The extent of the improvement depends on the type of peroxide used.

The curves of impact strength of KSR25 at 23°C vs. peroxide concentration are similar to the curves of elongation at break versus peroxide concentration of KSR25, indicating that there could be some correlation. The samples with increased strain at break have also improved impact strength at 23°C. Some correlation of the change of work of yield or elongation at break with the change of the impact strength has already been proposed [7, 20]. The enhancement of these properties was ascribed to the compatibilization of the phases in the blends.

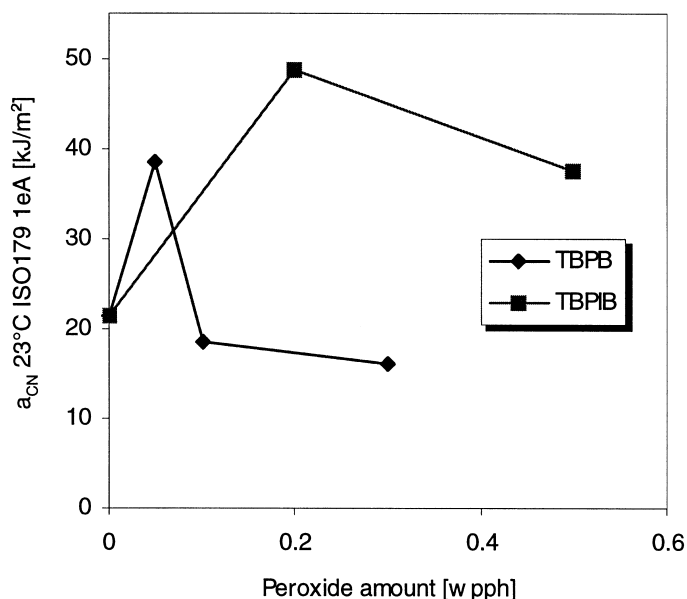


Figure 9. Impact Strength at 23°C of HECO KSR25 Modified in the Solid Phase at 142°C with Different Peroxides; Dependence on the Peroxide Concentration.

In our case, it could be the result of slight crosslinking or branching of EPR, together with an effect of an “in situ” formed interfacial copolymer. Crosslinking or branching of EPR should increase its cohesion energy, that should have a positive effect on impact strength. Interfacial copolymer should decrease interfacial tension in the blend and thus, improve compatibility of the blend. Based on the reported results, we cannot clearly distinguish one influence from another or exclude one of them.

However, a decrease in the impact strength at -20°C appears by HECO KSR25 as well (Figure 10) (extraction data in the Figure 4 or Table 4, 5). Modification with TBPIB causes only a slight decrease. With TBPB, the impact strength decreases substantially. The different tendencies of change of impact strength at different temperatures caused by the modification are possible due to the different mechanisms of fracture above and below the T_g of PP.

At higher peroxide concentrations, a high extent of degradation and coarsening of the morphology are the main reasons for deterioration of the

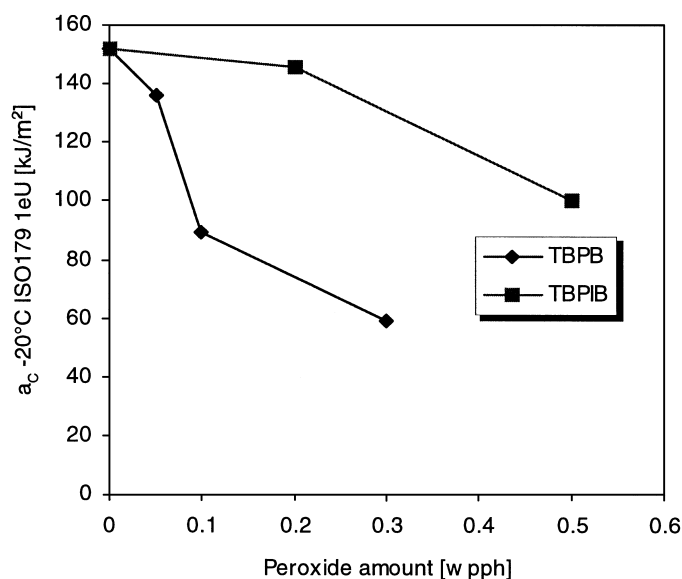


Figure 10. Impact Strength at -20°C of HECO KSR25 Modified in the Solid Phase at 142°C with Different Peroxide; Dependence on the Peroxide Concentration.

impact strength at -20°C by modification of both types of HECO. It is responsible for the deterioration of all other properties as well, as was stated before. The crazing of the PP matrix is considered to be the primary mode of fracture energy absorption below its T_g and thus, the degradation of PP will lower the impact resistance of the blend, especially below the T_g of the matrix. Additionally, coarsening of morphology makes the dissipation of the energy in the material more difficult.

At low peroxide concentrations, morphology of modified samples is fine and similar to the one of unmodified extrudate. It is probable that there is a slight degradation of PP already at these concentrations, even though not noticeable on the MFI values. However, due to its very low extent, it cannot be the only reason for the abrupt decrease of impact strength at -20°C . As for the diffusion of liquids being hindered in the solid phase, it could be due to the concentration gradient, and also to the crosslinking gradient from the surface to the center of the particle. This kind of inhomogeneity can also have a negative influence on the fracture mechanism of the material.

CONCLUSION

Radical modification of two types of HECO with different EPR content in the solid phase with peroxides TBPIB and TBPB was studied. It was found that:

By modification in the solid phase with low peroxide concentrations, only a slight degradation of PP matrix and yet crosslinking or branching of the dispersed EPR particles takes place. Peroxide TBPIB that gives lower activity radicals towards the H-abstraction, causes less degradation of PP matrix, and is of advantage with respect to the achievement of better mechanical properties;

The ultimate elongation of the HECO samples modified under said conditions with low peroxide concentrations - up to 0.1 wpph TBPB and to ca. 0.5 wpph TBPIB - increases substantially. The samples are homogeneous;

At low peroxide concentration also impact strength at 23°C is improved. Improvement can be small or substantial, depending on the type of peroxide used and the amount of EPR in HECO;

An improvement of -20°C was not found at any peroxide concentration with chosen types of peroxide.

The result of the modification of HECOs in the solid phase as a method of preparing new valuable polymers is dependent on the homogeneity of the morphology. It can lead to HECOs with improved impact strength at 23°C, and just slightly decreased impact strength at -20°C. This can be attained with HECO with 25 wt% of EPR. An improvement of impact strength at -20°C was not achieved. These effects cannot be achieved by the modification in the melt without a crosslinking agent in employed polymer blends. A more even distribution of the EPR in HECO is expected to result in a more positive effect.

ACKNOWLEDGEMENT

The authors thank Dr. Elisabeth Ingolic, ZFE Graz, Austria for preparing the transmission electron micrographs. We thank PCD Polymere Ges.m.b.H. Linz, Austria for the support of this research.

REFERENCES

- [1] D. Del Duca, in *Proceedings of Conference Aufbereiten von Polymeren mit neuartigen Eigenschaften*, Baden-Baden, VDI-Ed. Düsseldorf, 1995.

- [2] E. Borsig, M. Lazár, and M. Rado, *Chemical Letters*, 85, 30 (1991).
- [3] S. B. Brown, in *Review of Reactive Extrusion Processes, Reactive Extrusion, Principles and Practice*, M. Xanthos, Ed., Hanser Publishers, New York, 1992, p. 170.
- [4] USP 4 535 125, J. D. McCullough, Shell Oil Co. (1985).
USP 4 508 872, J. D. McCullough, Shell Oil Co. (1985).
- [5] EP 0 469 153 A1, Y. M. Otawa, K. Okamoto, M. Kioka, T. Ueda, Mitsui Petrochemical Industries, Ltd. (1991).
- [6] M. Rätzsch, *Makromol. Chem., Macromol. Symp.*, 28, 11 (1989).
- [7] T. Inoue, *J. Appl. Polym. Sci.*, 54, 709 (1994); T. Inoue, *J. Appl. Polym. Sci.*, 54, 723 (1994); T. Inoue and T. Suzuki, *J. Appl. Polym. Sci.*, 59, 1443 (1996).
- [8] M. Rätzsch, H. Bucka, A. Hesse, and M. Arnold, *J. Macromol. Sci.-Chem.*, A33 (7), 913 (1996).
- [9] R. Rengarajan, M. Vicic, and S. Lee, *J. Appl. Polym. Sci.*, 39, 1783 (1990).
- [10] V. Verney, E. Koerper and A. Michel, *Makromol. Symp.*, 25, 187 (1989).
- [11] EP 519 341 A1, A. De Nicola, Himont Inc. (1991).
- [12] K.-D. Rümpler, J. F. R. Jaggard, and R. A. Werner, *Kunststoffe*, 78, 602 (1988).
- [13] E. Borsig, A. Fiedlerová, and M. Lazár, *J. Macromol. Sci.-Chem.*, A21, 514 (1981).
- [14] K. Kalfoglou, *J. Macromol. Sci.-Phys.*, B22(3), 343 (1983).
- [15] Y. D. Lee and M. L. Chen, *J. Chinese Institute of Chemical Engineers*, 14, 367 (1983).
- [16] K.-Y. Chiu and S.-J. Fang, *J. Appl. Polym. Sci.*, 30, 1473 (1985).
- [17] D. W. Yu, M. Xanthos, and C. G. Gogos, *J. Appl. Polym. Sci.*, 52, 99 (1994).
- [18] Ch. S. Ha and S. Ch. Kim, *J. Appl. Polym. Sci.*, 37, 317 (1989).
- [19] E. Robertson and D. R. Paul, *J. Appl. Polym. Sci.*, 17, 2579 (1973).
- [20] K. Gupta and S. N. Purwar, *J. Appl. Polym. Sci.*, 30, 1799 (1985).

Received May 20, 1999

Revision received August 20, 1999