CROSSLINKED POLYOLEFINS AS MATRICES FOR   TWO-PHASE
MATERIALS

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This paper gives a review of the results of investigation
of the effect of crosslinking on the properties of
LDPE/PP[a] blends and LDPE filled with particulate silica.
Tensile and impact properties, crystallization beha-
viour, crosslinked portion formation and crack growth
rate have been investigated.
Crosslinking results in an increased compatibility of
originally incompatible LDPE/PP blends apparently due
to an *in situ* formation of a compatibilizer, leading to
improved deformability and better impact resistance.
Changes in the morphology as revealed by crystalliza-
tion behaviour, and the increased number of tie mole-
cules in amorphous region due to crosslinking result in
better impact resistance of LDPE/silica mixtures, as
well as to the improvement of other properties of
two-phase materials, so as resistance to grack growth.

Crosslinking of polyolefins is a rather broadly used mode of
modification of these polymers. Especially if polyethylene is
considered, many applications of crosslinked materials have
been commercialized, e.g. shrinkable products or cable insula-
tion. The crosslinking is usually initiated by thermal de-
composition of peroxides or by high energy radiation, less
often by UV irradiation (Ref. 1). Crosslinking initiated by
moisture introduces more complicated chemistry including
a grafting of silane groups on the polyethylene chain (Ref.
1). Higher thermal resistance is the main advantage of cross-
linking in all these cases. Crosslinking of poly(propylene) is
much more difficult because of extensive fragmentation of
macroradicals formed leading to decrease of molecular weight
and inferior mechanical properties (Ref. 2). Efficient poly-
(propylene) crosslinking can be reached by addition of another
component to initiating system. Polyfunctional monomers are
the most common coagents of poly(propylene) crosslinking (Ref.
3) and the system based on addition of hydroquinone or benzo-
quinone was shown to be most eficient (Ref. 4).

[a] LDPE: Low-density polyethylene; PP: poly(propylene).

Although only marginal change of chemical nature of the poly-
olefine is introduced by crosslinking initiated by thermal de-
composition of organic peroxides, some properties do change
significantly. Certain number of defects of crystalline struc-
ture is formed due to crosslinking resulting in decrease of
melting temperature and heat of fusion (Ref. 5) indicating
lower crystalline portion. Obvious consequence is a decrease
of Young's modulus with the increase of the crosslinking
degree as seen in Fig. 1. On the other hand, an increase of
tensile strength with increasing crosslinking was observed
while yield strength did not change at all. This behaviour can
be explained by increasing number of tie molecules between the
crystallites. Generally, the effect of crosslinking is more
pronounced at higher temperature and significant difference
between properties of crosslinked and uncrosslinked samples is
observed near melting temperature as seen from Fig. 2, where
the dependence of elongation at break vs. crosslinking degree
is shown at 20, 80 and 110 ^{O}C.

This work describes the results of the investigation of the
effect of crosslinking on the properties of two-phase mate-
rials, namely the blends of low-density polyethylene with
poly(propylene)and the composite LDPE with silica. The lecture
is a review of our results in this field, part of those having
been published, therefore only selected data are shown here.
In some cases only the tendencies of the observed dependences
are described without showing all data.

Special features of crosslinking of two-phase systems

Crosslinking of the LDPE/PP blend is complicated by the pre-
sence of poly(propylene). If peroxide only is used for the
crosslinking initiation, the gel content decreases linearly
with rising PP content as seen in Fig. 3. In the presence of
hydroquinone, gel content is almost independent on composition
of the blend, indicating benefitial effect of the coagent on
PP crosslinking.

The presence of inorganic filler does not influence the gel
content significantly, although certain differences indicate
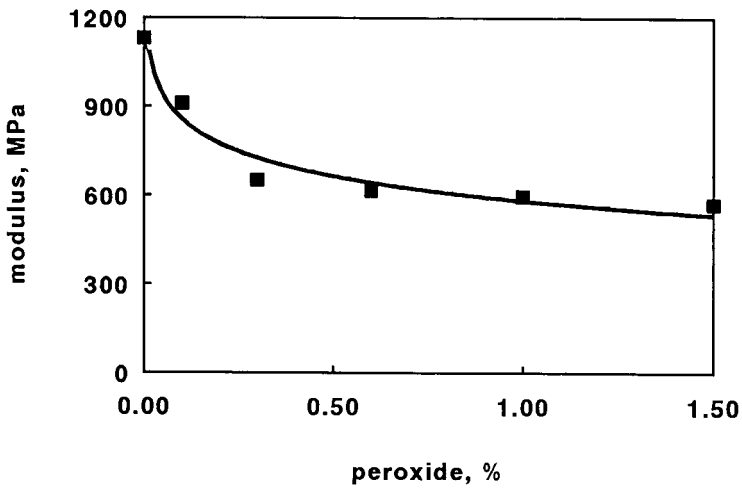that the peroxide is adsorbed at the filler surface. The exent

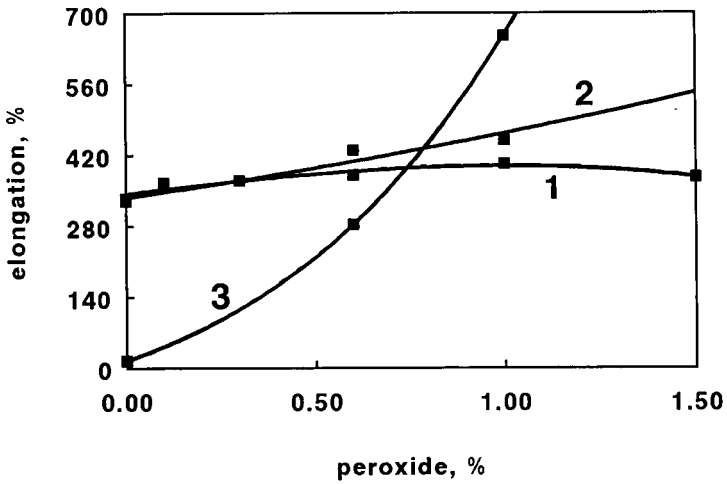Fig. 1 : The dependence of Young's modulus of LDPE on the concentration of initiator of crosslinking.

Fig. 2 : The dependence of elongation at break of LDPE on the concentration of peroxide (1 : 20 ^{O}C, 2 : 80 ^{O}C, 3 : 110 ^{O}C).

of adsorption depends on the filler surface area. It is of interest that significant portion of unsoluble portion is formed even if no peroxide is present. This is ascribed to a formation of so called "bound polymer", formed preferentially due to physical or physico-chemical interactions between filler surface and polymer. Obviously, the bound polymer formation depends primarily on the surface area as is illustrated in the Fig. 4.

The polymer/filler interaction can be evaluated also from the data of equilibrium swelling according to the equation (Ref. 6)

$$V_{ro}/V_r = 1 - [3c \ (1 - V_{ro}^{1/3}) + V_{ro} - 1] \ \Phi/(\Phi - 1)$$

V_{ro} being a degree of swelling of unfilled crosslinked polymer, V_r is swelling of filled polymer crosslinked to the same extent, Φ is the volume portion of the filler and c is the parameter related to the polymer/filler interaction. In our experiments the c was found to be 1.33 and 2.26 for the filler with lower and higher surface area, respectively.

Tensile properties

Tensile behaviour of uncrosslinked two-phase systems investigated is characterized by a decrease of deformability after addition of rather low amount of more rigid component (filler or polypropylene) in the ductile matrix (LDPE). Yielding, observed in virgin homopolymer, dissapears and the fracture becomes to be more or less brittle.

As seen in Fig. 5, crosslinking leads to an increase of elongation at break at filler content between 5 to 20 wt. %. The increase due to crosslinking is dramatic if tensile measurement is performed at 110 $^{\circ}$C.

Similar dependence was found also for the blend of LDPE/PP (Fig. 6). With increasing PP content the elongation at break value is diminishing. In uncrosslinked blend the decrease is steep and the addition of 10 wt. % of PP leads to deterioration of deformability of the blend unlike in crosslinked system where the drop of elongation is much smoother,
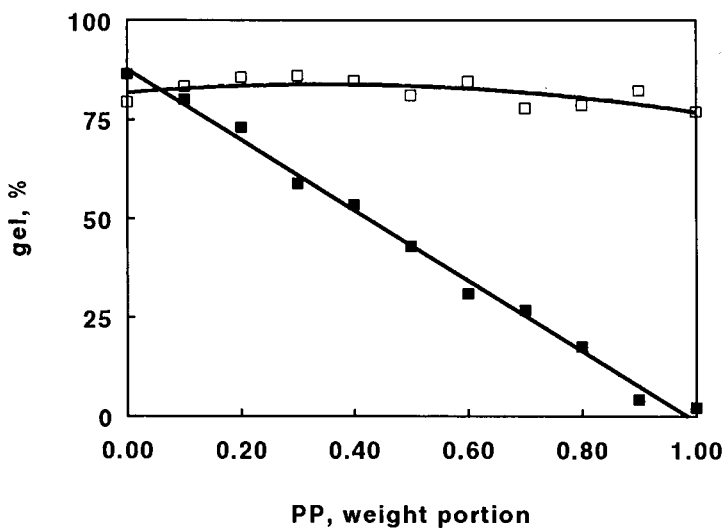
Fig. 3 : Gel formation in the blend LDPE/PP vs. PP content.
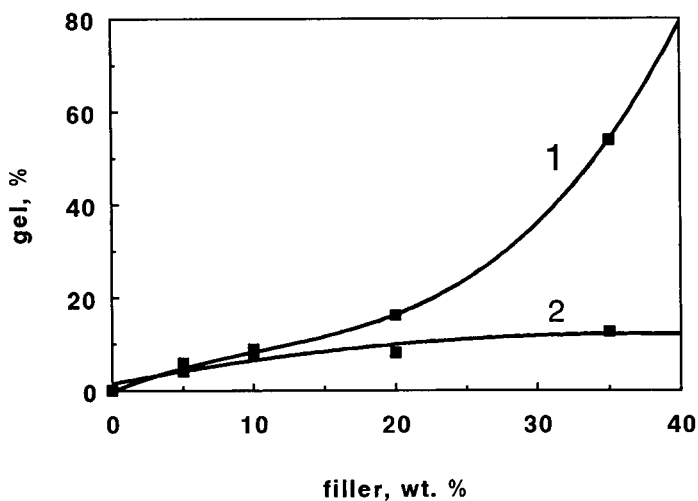■ 3 wt. % of peroxide, ▢ 3 wt. % of peroxide and 0.5 wt.% of hydroquinone.

Fig. 4 : The formation of bound polymer in the blend of LDPE with silica. Filler surface 139 m^2/g (curve 1) or 21 m^2/g (2).

since the elongation of the mixture containing 25 wt. % of PP
is only by one half lower than that of virgin LDPE. Some
doubts about low elongation of virgin polypropylene may be ex-
plained by rather high deformation rate of tensile experiments
(100 mm/minute). Of some importance may be also possible
thermal degradation of the unstabilized poly(propylene) during
the sample preparation in Brabender Plasticorder mixing
chamber.

Impact properties

The presence of the second phase, either polypropylene or
inorganic filler silica results in substantial decrease of
impact strenght of LDPE. Crosslinking has, on the other hand,
benefitial effect, as seen from Table 1.

Table 1 : Impact strength (W) of the uncrosslinked (0) and
crosslinked (XL) blends of LDPE/PP measured at − 20 °C depen-
ding on the composition of the blend and concentration of
additives peroxide (P) and hydroquinone (HQ). The gel content
(g) is shown for crosslinked samples.

LDPE/PP	P wt.%	HQ wt.%	W kJ/m^2		g %
			0	XL	
100/ 0	3	0.5	76	>110	80
75/25	3	0.5	75	>110	83
50/50	3	0.5	13	>110	77
25/75	3	0.5	15	>110	78
0/100	3	0.5	24	27	76
50/50	3	0	13	3	42
50/50	1	0.25	13	13	22

It is seen that the dependence of impact strength on composi-
tion has a minimum at about 50:50 wt. ratio of both polymers
in uncrosslinked blend. This is obvious consequence of low
compatibility of the components resulting in insufficient
interfacial adhesion. Crosslinking leads to an increase of
interactions on the interface apparently due to a formation of
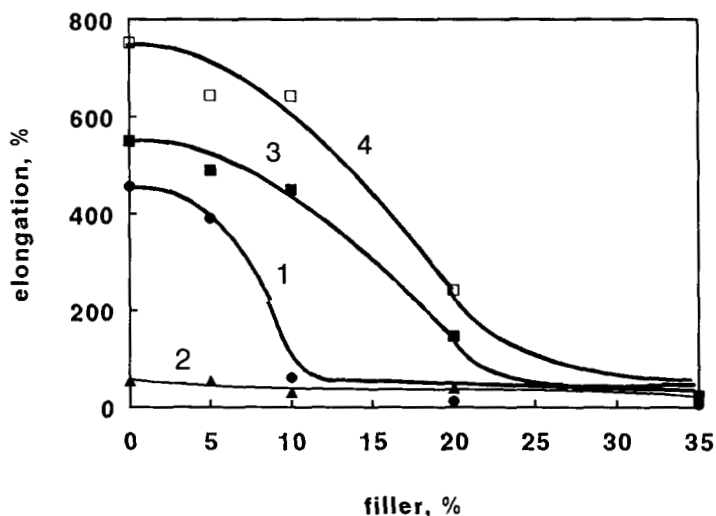
filler, %

Fig. 5 : The effect of crosslinking on elongation at break of LDPE in dependence on the filler content (wt. %). The crosslinking initiated by 0.8 wt. % of the peroxide. Uncrosslinked mixtures measured at 20 ^{O}C (curve 1), or 110 ^{O}C (2), crosslinked mixtures at 20 ^{O}C (3) or 110 ^{O}C (4).
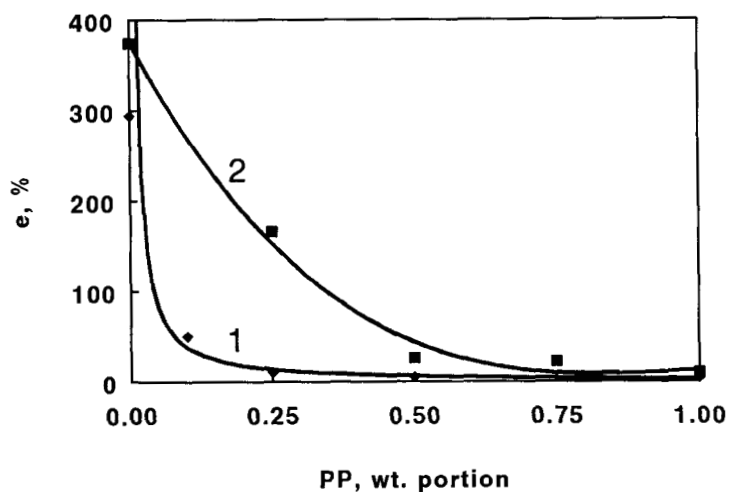

PP, wt. portion

Fig. 6 : Elongation at break of the mixture LDPE/PP vs. PP content in uncrosslinked (1) or crosslinked (2) blends. Crosslinking initiated by 3 wt.% of peroxide and 0.5 wt. % of hydroquinone.
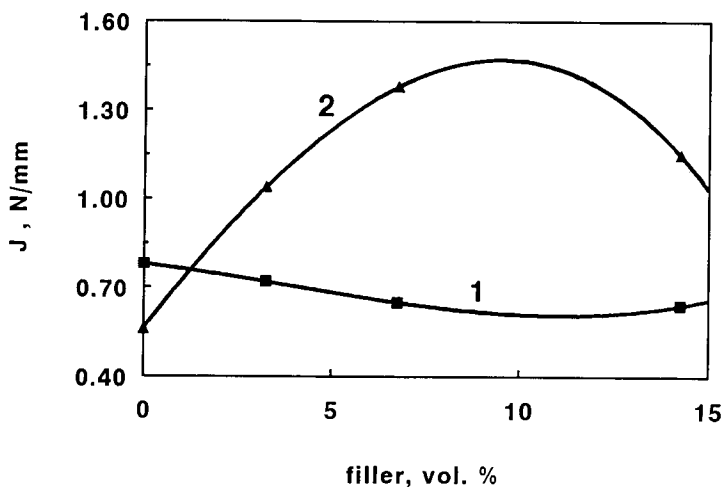
Fig. 7 : Toughness of the mixtures LDPE/silica evaluated by J-integral in dependence on the filler content. Uncrosslinked samples - 1, crosslinked samples (0.8 wt. % of peroxide) - 2.
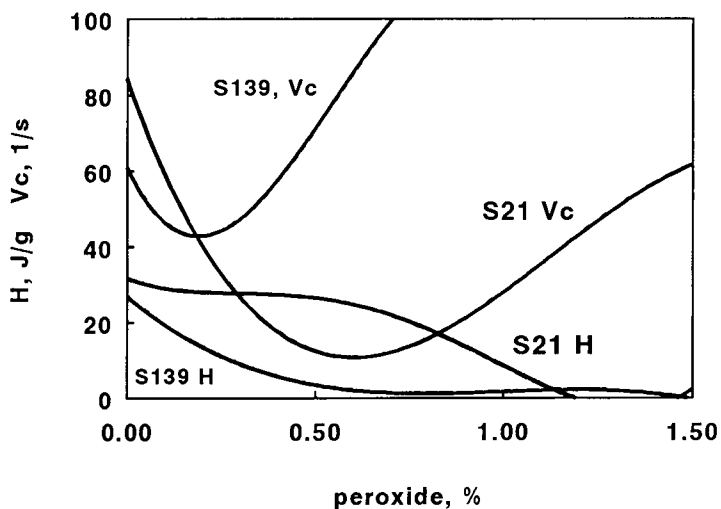

Fig. 8 : The changes of the heat of fusion H and relative crystallization rate V_c for LDPE filled with 20 wt. % of silica with the surface area 21 (S_{21}) or 139 m^2/g (S_{139}) in dependence on degree of crosslinking.

interlinks between polyethylene and poly(propylene) macromole-
cules. Some kind of copolymer is formed *in situ* during cross-
linking acting as compatibilizers on the phase boundary. If
the concentration of additives is decreased, the impact resis-
tance drops down substantially and is approximately equal to
that of uncrosslinked blend. It means that the concentration
of *in situ* formed compatibilizer is not high enough to affect
the toughness of the blend. The absence of the coagent results
in very brittle material with inferior impact strength, al-
though the gel content is higher than in the sample where
1 % of peroxide is added together with 0.25 % of the coagent.
It means that in the absence of the coagent the degradation of
poly(propylene)partof the blend proceeds to rather high extent
and crosslinking takes place almost exclusively in polyethy-
lene part. The last conclusion can be made also from the
dependence of gel content on composition of the blend as given
in Fig. 3.

Similar benefitial effect of crosslinking has been observed in
mixture of LDPE with silica. Toughnesss was expressed in this
case by a value of J-integral according to Sumpter and Turner
(Ref. 7). Change of toughness in dependence on filler content
for uncrosslinked and crosslinked samples is shown in Fig. 7.
A decrease of J-value with increasing filler content has been
found for uncrosslinked samples. Crosslinking results in
a substantial toughness increase of samples with lower filler
content. This is explained by increased deformability of
crosslinked materials confirmed also by impact experiments
(Ref. 8). Benefitial effect of low content of the filler
consists in an intiation of crazing, confirmed by SEM observa-
tion (Ref. 8), leading to an energy consumption by craze
formation without developing a crack of critical size.

Crystallization of two-phase crosslinked systems

DSC measurements reveal a two-phase character of the blends
LDPE/PP. The effect of crosslinking on thermal characteristics
of individual phases is qualitatively the same as in virgin
homopolymers, i.e. a decrease of both melting temperature and
heat of fusion with rising crosslinking degree is observed.

Mutual influence of the components is more detectable in LDPE phase compared to PP part and in crosslinked samples than in uncrosslinked ones. Detailed study of crystallization and melting of crosslinked LDPE/PP blends by dynamical DSC method was made in Ref. 9 .

Isothermal crystallization parameters have been determined for the samples of LDPE filled with two silica grades differing in the surface area value. The changes of the heat of fusion and relative crystallization rate of LDPE filled with 20 wt. % of silica in dependence on the crosslinking degree determined by the peroxide content is given in the Fig. 8. The decrease of the heat of fusion values was observed with rising peroxide content as expected, because of increased number of defects of the structure introduced by crosslinking. The relative crys- tallization rate dependence shows a minimum depending on the filler quality. This rather complicated and unexpected course is explained by a superposition of several parallel effects of filler presence and crosslinking on the crystallization. The crosslinking primarily leads to a decrease of the mobility of the polymer segments. The effect of the filler consists in a nucleation leading to enhanced crystallization rate on one hand and to adsorption of the polymer chains on the filler surface resulting in a decreased mobility on the other hand. The minimum on the dependence rate vs. peroxide content is ex- plained by a formation of some "pre-ordered structure" during the peroxide-initiated crosslinking of LDPE in the melt in the filler presence. Random disordered structure is formed in a short time in the absence of the filler. In the presence of the filler, the random structure formation takes more time. This time is longer with higher extent of immobilization of polymer chains on the filler surface, i.e. with increasing surface area of the filler. If the peroxide is present, the crosslinking may take place before random structure is formed and a structure with some remnants of crystalline morphology is fixed by permanent crosslinks to a network. It is reason- able to assume that the crystallization rate of these "pre-ordered" chains is higher than that of the randomly oriented ones (Ref. 10).

Crack growth rate in crosslinked two-phase materials

The crack growth rate was measured by three-point bending in-
vestigation of the notched samples of LDPE/PP or LDPE/silica.
Two parameters were evaluated, namely the deformation when the
notch starts to grow and subsequent rate of the notch growth.
The determined values for uncrosslinked and crosslinked
samples of different composition are given in the Table 2.

Table 2 : The effect of crosslinking on the deformation of be-
ginning of the crack growth (D_{st}) and the relative crack
growth rate (V_{rel}) for LDPE filled with silica S_{139} or blended
with poly(propylene).

additive	uncrosslinked		crosslinked	
	D_{st} mm	V_{rel} mm/s	D_{st} mm	V_{rel} mm/s
no	3.0	0.014	6.7	0.012
7 wt% S_{139}	1.9	0.40	4.7	0.052
14 wt% S_{139}	1.8	1.40	6.0	0.24
30 wt% PP	1.8	0.68-1.08	7.8	0.029
50 wt% PP	1.4-1.7	0.95-1.50	6.3-10.0	0.11-0.21

The benefitial effect of crosslinking on both parameters is
obvious. Substantial suppression of crack initiation as well
as crack growth rate may be explained by the increased number
of tie molecules in amorphous region comparable to the effect
of higher molecular weight on the crack growth rate in HDPE
(Ref. 11). A detailed study of the effect of crosslinking is
given in (Ref. 12).

CONCLUSIONS

In two-phase polymer blends usually a low compatibility of
components is a reason for inferior properties in the absence
of compatibilizing additive. The polymer/particulate filler
composites usually suffer from an increased brittleness with
increasing filler content.
Crosslinking results in an increased compatibility of origi-
nally incompatible LDPE/PP blends apparently due to an *in situ*

formation of a compatibilizer, leading to improved deform-
ability and better impact resistance. Changes in the morpho-
logy as revealed by crystallization behaviour, and the in-
creased number of tie molecules in amorphous region due to
crosslinking result in better impact resistance of
LDPE/silica mixtures, as well as to the improvement of other
properties of two-phase materials, so as resistance to grack
growth.

EXPERIMENTAL

Both low-density polyethylene (Bralen RA 2-19, MFI = 2 g/ 10
minutes) and poly(propylene)(Tatren HPF, MFI = 8 g/10 minutes)
were products of Slovnaft, Bratislava. Two different grades of
silica were used, namely Ultrasil (Degussa, Germany) with sur-
face area 139 m^2/g and Komsil (Mnišek, Czech Republic) with
low surface area 21 m^2/g. (2,5-dimethyl 2,5-ditertbutyl per-
oxy) hexyne (Luperox 130, Luperox GmbH, Germany) was used as
as initiator of crosslinking. The samples were mixed in
a chamber of Plastograph Brabender at 150 $^{\circ}$C and compression
moulded at 180 $^{\circ}$C during 20 minutes. Almost all peroxide added
is decomposed under these conditions. The unsoluble portion
was determined by weight difference after 14 h extraction in
boiling xylene.
The samples were tested regarding the tensile and three-point
bending properties (Instron 4301), crystallization behaviour
(Perkin Elmer DSC II), impact resistance (Charpy type fracto-
scope enabling to record the stress - strain curve in ultra-
short time range).

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