Mechanical properties of crosslinked polyolefin-based materials

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SUMMARY: The effect of crosslinking on mechanical properties of various polyethylene-based materials is compared. In virgin polyethylene, higher strength results from formation of spatial network, especially at increased temperatures. On the other hand, decreased crystalline portion leads to lower Young's modulus values compared with the uncrosslinked polymer. Crosslinking of LDPE/PP blends leads to a dramatic increase in elongation at break and impact resistance. The reason is seen in an in situ formation of very efficient compatibilizers via co-crosslinking on the phase boundary. In LDPE filled with silica, the main effect consists in higher elongation at break and increased toughness, although the effect is lower than that in LDPE/PP blends. Increased resistance to the crack growth rate was demonstrated to be a reason for the observed behaviour. In LDPE filled with organic fillers, formation of direct covalent bonds on the interface and a significant increase in adhesion is suggested to be the reason for the enormous increase in Young's modulus and tensile strength observed.

Introduction

Crosslinking of polyethylene is a generally known industrially used process for certain special applications, e.g., in cable industry or for production of shrinkable materials(1). The process has been broadly studied and its mechanism is generally well understood although certain aspects are still open. The crosslinking is usually initiated by thermal decomposition of peroxides or by high-energy irradiation, less often by UV irradiation(2). Silane crosslinking is another option for crosslinking of polyolefins consisting in grafting a suitable silane onto polymer backbone followed by condensation of silanol groups(2). Increased thermal resistance is usually the main reason for crosslinking the material in all these cases, although other effects associated with modification of various properties can be reached, too.

Crosslinking of polypropylene is much more difficult because of extensive fragmentation of macroradicals formed. The fragmentation process results in a decrease in molecular weight and in inferior mechanical properties(3). An increase in the efficiency of polypropylene crosslinking can be reached by addition of another component, so-called coagent, to the peroxidic initiator. Polyfunctional monomers are the most investigated and used coagents(4), the systems based on an addition of hydroquinone or benzoquinone have been shown to be the most effective(5).

CCC 1022-1360/99/$ 17.50+.50/0

Crosslinking of multiphase materials with polymeric matrix has been investigated from various points of view. Among the desired effects, stabilization of two-phase morphology⁶⁾, improved compatibility of blends via an in situ formation of compatibilizers as a result of co-crosslinking⁷⁾, and increased thermal stability are mentioned. In this paper, the effect of crosslinking on mechanical properties is compared for three multiphase systems with polyolefin matrix, a blend of low-density polyethylene (LDPE) with isotactic polypropylene (PP), an LDPE mixture filled with silica, and LDPE filled with an organic cellulose-based filler. In all the cases, polyethylene was used as a crosslinkable matrix since the mechanism of the process is relatively simple and the effect of side processes should be negligible.

Experimental

Materials: Low-density polyethylene Bralen RA 2-19 (Slovnaft, Bratislava, MFI 2 g/10 min, 190 °C, 21.6 N), isotactic polypropylene 19 (Slovnaft, Bratislava, MFI 2 g/10 min, 190 °C, 21.6 N), silicas Ultrasil VN3 (Degussa, Germany, surface area 139 m^2/g) and Komsil (Kovohute Mnisek, Czech Republic, surface area 21 m^2/g), and wood particles (beech, particle size 0.2 - 1.0 mm) have been used. A crosslinking initiator, 2,5-di(*tert*-butylperoxy)-2,5-dimethylhexyne (Luperox 130, Luperox GmbH, Germany, 95 % of active compound) was used as received.

Sample preparation: Mixtures of the materials were prepared in the mixing chamber of a Plastograph Brabender PLE 330 (Brabender, Duisburg) at 140 °C at 30 rpm for 10 min if LDPE was mixed with the fillers or at 180 °C if also PP was present. In the latter case, the polymers were mixed first for 10 min, then the peroxide was added and the mixing was interrupted 1.5 min after peroxide addition, i.e., at the moment when the torque value began to rise, indicating an increase in viscosity due to the crosslinking onset. Crosslinking proceeded in a laboratory press (Fontijne 200, Netherlands) by compression moulding for 20 min at 180 °C. Dynamic crosslinking of the LDPE/PP blends was done in the mixing chamber at 180 °C for 20 min so that the peroxide decomposed during processing. Mechanical properties were tested with a universal tester Instron 4301 at the deformation speed 10 mm/min using dog-bone specimens with the working part 30 x 3.6 x 1 mm.

Results and Discussion

The effect of crosslinking on mechanical properties of LDPE can be seen in Figs. 1a-d. The crosslinking to a low degree with a low amount of peroxide results in a certain increase in tensile strength at break while the yield strength does not change. A small increase and further a steady decrease with increasing peroxide content have been observed for elongation at break as a result of the balance of a crystallinity decrease and decreased mobility of crosslinked chains. The decrease in Young's modulus values results from a decrease in crystallinity due to introduction of defects represented by network junctions[1].

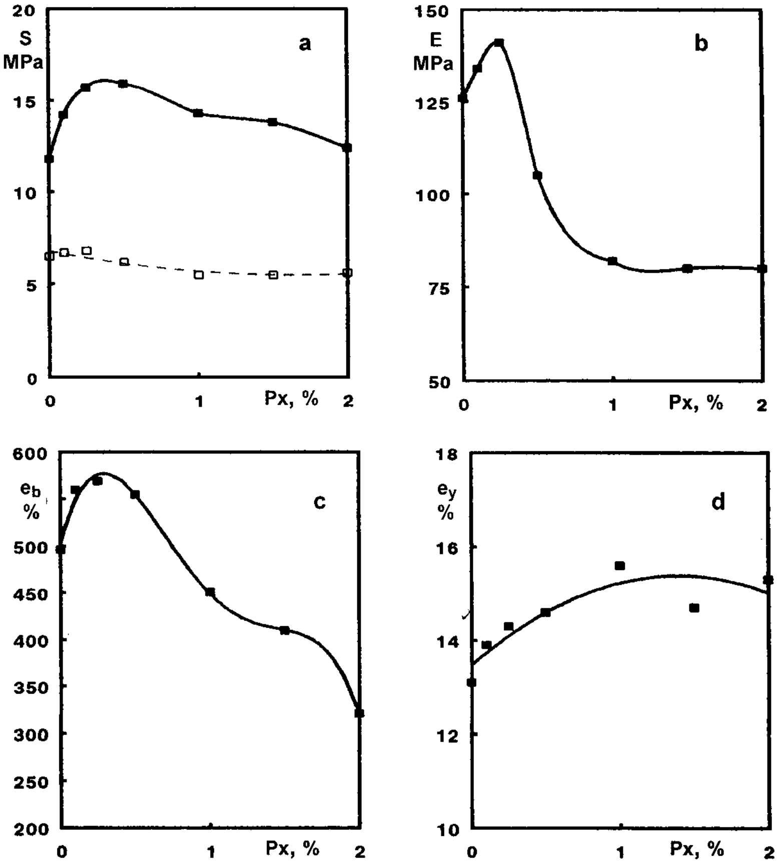

Fig. 1: The effect of the peroxide content (Px, wt.-%) on mechanical properties of LDPE. a tensile strength at break (full squares) and at yield (open squares), b Young's modulus, c elongation at break, d elongation at yield

Crosslinking of LDPE/PP blends is complicated by the presence of polypropylene. If the process is initiated by thermal decomposition of the organic peroxide in the absence of a coagent of PP crosslinking, PE part is only crosslinked as indicated by a linear decrease of the crosslinked portion with increasing PP content in the blend[8]. In the presence of hydroquinone as a coagent, the gel content (relative to the insoluble crosslinked portion of the material) is constant in the whole range of the component concentration. In spite of this, the crosslinking density as well as the crosslinkng efficiency in the PP portion is lower compared with that in the LDPE portion. This means that even in the presence of a very efficient coagent, the fragmentation reaction of polypropylene is not suppressed to zero.

When investigating mechanical properties, an extreme increase in elongation at break is the most important phenomenon observed, as seen in Fig. 2. Young's modulus data are lower for crosslinked blends because of a lower crystallinity due to defects introduced by crosslinking into the crystalline structure, similar to crosslinking of individual polymers. Tensile strength at break of the crosslinked blends is higher than that of the uncrosslinked ones mainly because a substantial orientation strengthening occurs during drawing at high deformation after complete development of the neck.

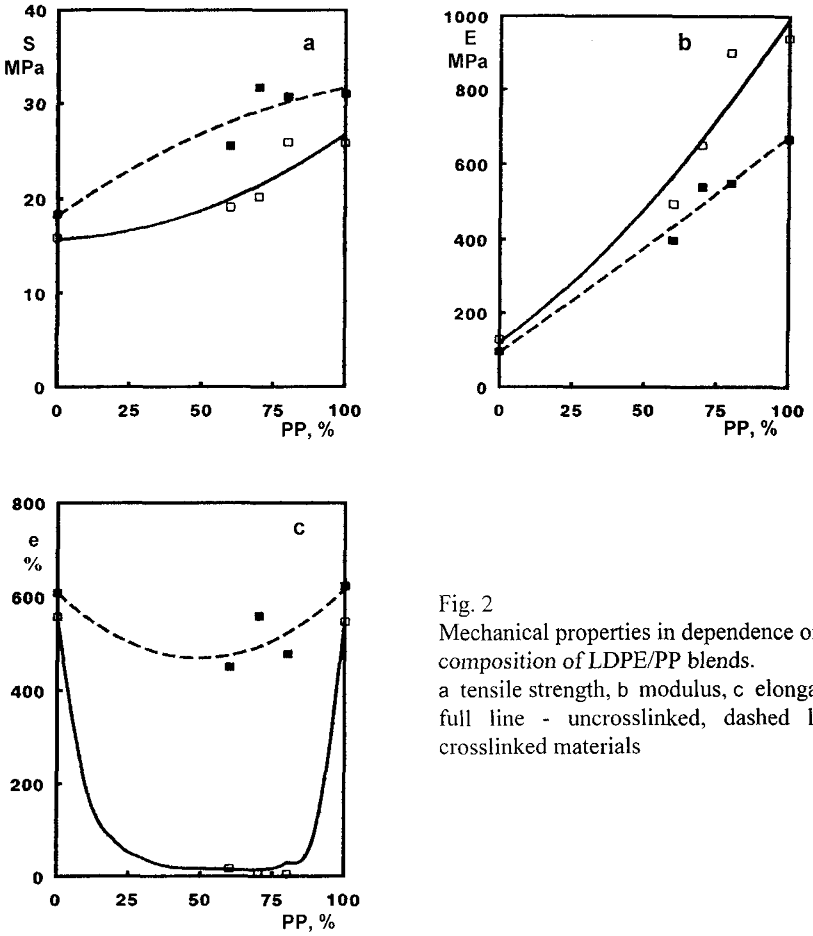

Fig. 2
Mechanical properties in dependence on the composition of LDPE/PP blends.
a tensile strength, b modulus, c elongation, full line - uncrosslinked, dashed line - crosslinked materials

The effect similar to crosslinking by compression moulding can be reached also by dynamic crosslinking during mixing in the chamber of a Brabender Plasticorder. The mechanical properties of the LDPE/PP blend (50:50) are shown in Table 1. The effect of various coagents is compared.

Table 1 Mechanical properties and the gel content of the 50:50 LDPE/PP blend dynamically crosslinked with 3 wt.-% of peroxide in the presence of optimum concentrations of additives

Additive (coagent)	c (%)	Tensile strength at break (MPa)	Elongation at break (%)	Young's modulus (MPa)	Gel content (%)
Hydroquinone	0.5	26.6	515	500	43
Santonox RSX*	1.5	27.0	586	480	48
Bisphenol A	1.0	25.7	626	460	39
Triallyl cyanurate	1.0	18.8	391	250	25
Oligobutadiene	1.0	20.4	408	340	37
	10.0	21.6	212	510	67
Oligobutadiene OH-terminated	3.0	21.6	303	320	61

* A bifunctional phenolic antioxidant

It can be seen that the crosslinking with different coagents results in different properties although the peroxide used for crosslinking is the same in all the cases. The lowest mechanical properties have been obtained with triallyl cyanurate as a coagent. Hydroquinone is similar to the other two phenolic coagents while with oligomeric polybutadienes, lower tensile strength was observed. In any case, it is interesting that very good properties can be reached via dynamic crosslinking. In that case, the material is processable even after crosslinking. Obviously, thermal resistance is not reached, i.e., the material flows if heated above the melting temperature of polypropylene.

An important practical consequence of higher deformation consists in a high impact resistance9). The presence of polypropylene in LDPE results in inferior impact behaviour which is enormously improved by crosslinking so that even 25 % of LDPE in PP leads to an impact resistance comparable with the virgin LDPE.

It is apparent that the process of crosslinking has beneficial effect on the properties of LDPE/PP blends. The reason for this is seen in a co-crosslinking on the phase boundaries and the in situ formation of a compatibilizer9). The effect may be considered to be used in compatibilization of mixtures of waste plastics consisting mainly of PE and PP.

A positive effect of the matrix crosslinking was also demonstrated for mixtures of LDPE with various grades of silica. Regarding mechanical properties, the tensile strength at break does not change with the rising crosslinking degree, i.e., with an increasing concentration of the peroxide initiator, while deformation at break is much higher and

Young's modulus lower for crosslinked samples compared with uncrosslinked materials with the same filler contents$^{9)}$. The toughness of the crosslinked material, expressed by J integral values, is influenced in the same way as deformation at break$^{10)}$. Since with silica as a dispersed phase, no formation of covalent bonds at phase boundaries can be expected, the reason for higher toughness is seen in improved resistance to crack formation and crack growth as demonstrated in our experiments described in$^{11)}$.

The third group of materials where crosslinking of the matrix was investigated is LDPE filled with organic fillers. In this case, the dispersed phase is hard and is not deformed during mixing, similarly to silica, but the organic nature of the surface enables radical reactions initiated with an organic peroxide to proceed not only in the bulk of the matrix but also on the filler surface.

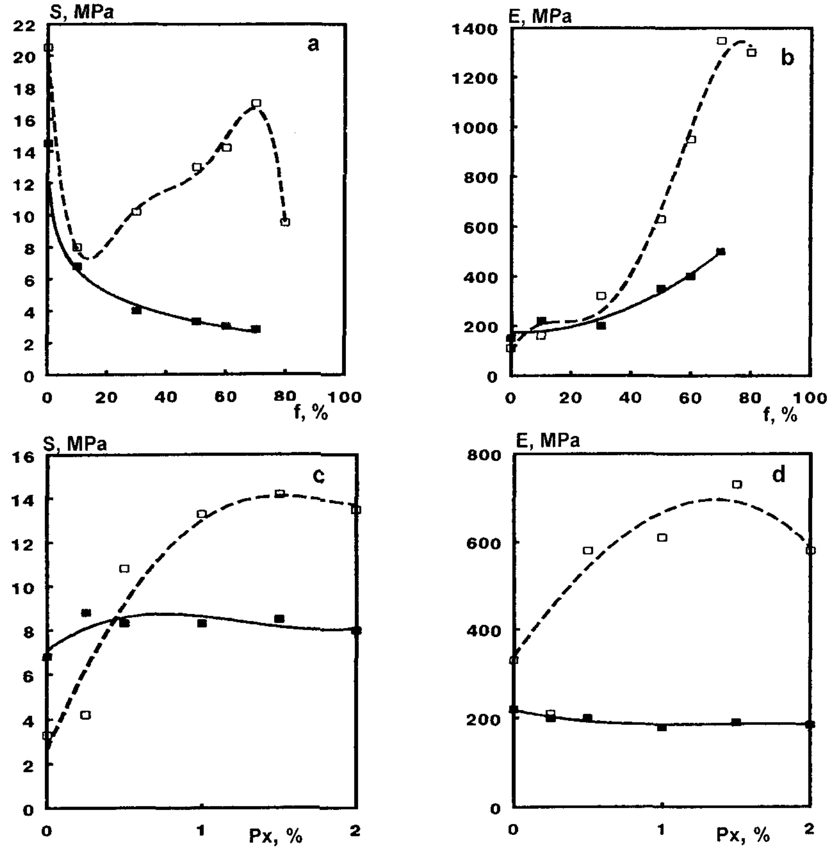

Fig. 3: The effect of the peroxide content (Px, wt.-%) on tensile strength (a,c) and of the filler content (f, wt.-%) on Young's modulus (b,d) in LDPE filled with wood particles. a,b: full lines - uncrosslinked, dashed lines - crosslinked with 1 % of the peroxide, c,d: full lines - 10 %, dashed lines - 50 % of the filler

The effect of crosslinking on tensile strength and Young's modulus of LDPE/wood flour composites in dependence on the filler content is seen in Figs. 3a and 3b.
With increasing filler content, a decrease in tensile strength is observed for uncrosslinked composites, indicating low polymer/filler interactions in the mixture of a nonpolar matrix and polar filler with unmodified surface. Crosslinking results in the reverse course of the dependence since the values of tensile strength at break grow with rising the filler content. A modest increase in Young's modulus values was observed with rising the filler amount. Much steeper increase was found if the material was crosslinked. This fact is rather surprising since the decrease in crystallinity due to crosslinking usually leads to a substantial decrease in Young's modulus due to the decrease in crystallinity, as demonstrated for LDPE as well as for LDPE filled with silica. The crystallinity decrease was also observed for LDPE/wood particle composites$^{12)}$. It is worth noting that tensile tests could be performed for crosslinked composites containing 80 wt.-% of the filler while the uncrosslinked material with the same filler content was not compact any longer. Apparently, some voids due to insufficient amount of matrix also appear in crosslinked composites resulting in a drop of both tensile strength and Young's modulus as seen in Figs. 3a and 3b.

Dependences of tensile properties on the peroxide concentration are given in Figs. 3c and 3d. The increase in both tensile strength at break and Young's modulus is quite significant for the composite with 50 wt.-% of the filler while the change in strength for the material containing 10 wt.-% of the filler is almost negligible, a drop of Young's modulus being observed for this filler concentration.

The observed results are explained in terms of formation of direct covalent bonds between the polymer matrix and filler surface, resulting in grafting of LDPE onto the filler surface. Thus, a better wetting of the surface and improved polymer/filler interactions may be the reason for the observed behaviour. Regarding the dependence of Young's modulus on the peroxide content, 10 % of the filler leads to a modest effect of the filler on properties; thus, the behaviour is mainly influenced by the decreased crystallinity of the matrix due to crosslinking. Fifty % of the filler in LDPE has a pronounced effect; therefore, the modulus increase is quite significant, overlapping the influence of the crystallinity decrease.

Conclusions

Crosslinking has a significant effect on mechanical properties of various polyethylene-based materials. In virgin polyethylene, formation of a spatial network results in higher strength, especially at increased temperatures. On the other hand, decreased crystalline portion leads to lower Young's modulus values compared with the uncrosslinked polymer. Crosslinking of LDPE/PP blends leads to a dramatic increase in elongation at break and impact resistance. The reason is seen in in-situ formation of very efficient compatibilizers by co-crosslinking on the boundary of the phases.

In LDPE filled with silica, the main effect consists in a higher elongation at break and increased toughness, although the effect is lower than that in LDPE/PP blends. An increased resistance to crack growth was demonstrated to be the reason for the observed behaviour.

In LDPE filled with organic fillers, formation of direct covalent bonds on the interface and a significant increase in adhesion is suggested to be the reason for the enormous increase in Young's modulus and tensile strength observed.

Acknowledgement

The first two authors appreciate financial support of the Slovak grant agency VEGA (grant No. 2/5032/98)

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