The effect of crosslinking on properties of low-density polyethylene filled with organic filler

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SUMMARY: Scanning electron microscopy was employed to investigate the effect of peroxide-initiated crosslinking on behaviour of composites of low-density polyethylene filled with wood flour. The improved wetting of the filler by the matrix and/or the increase in the matrix/filler adhesion was shown to be the main consequence of crosslinking, with the obvious influence on the physical, especially mechanical properties.

Introduction

Organic fillers are attracting attention as fillers for various plastics mainly due to their low price, low density and renewable nature. However, their direct application as a filler for thermoplastics generally and particularly for polyolefins is hindered by a serious drawback, namely insufficient wetting of the hydrophilic filler by hydrophobic polymeric matrix resulting usually in inferior mechanical properties. Numerous procedures were suggested for improving the polymer - filler interactions in the polypropylene or polyethylene filled with carbohydrate polymers such as cellulose, starch, sawdust, or aspen fibers. Usual approach consists in a modification of the filler surface to make it less hydrophilic. Application of various coupling agents such as silanes[1-3)], isocyanates[4)], or derivatives of triazine or melamine[5-7)] was reported leading to an improvement of properties of polyethylene or polypropylene filled with particles or fibers of various organic nature. Better mechanical properties of polypropylene filled with wood fiber were reported if

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silanes and maleated polypropylene was added to the mixture[8]. Maleated polypropylene was also examined as a compatibilizing agent for polypropylene filled with reclaimed paper; dicumyl peroxide was added as a radical initiator[9]. The same reactants were also used for improvement of properties of linear low-density polyethylene filled with chemithermomechanical aspen pulp[10]. An alternative procedure consists in a modification of the filler by grafting with styrene, acrylamide or their mixtures while the process was initiated by ozonation of the filler surface[11].

A substantial improvement of mechanical properties was also observed for polyethylene filled with cellulose fibers if the composite was modified via radical reaction initiated with organic peroxide[12,13]. No other agent was added in this case and crosslinking to a low degree occurred.

Peroxide-initiated crosslinking to a rather high level was shown to be a powerful tool to compatibilization of blends of polypropylene/polyethylene[14,15], and proved also to be beneficial to improvement of mechanical properties of polyethylene filled with inorganic fillers, such as silica[16]. .In our previous paper the effect of crosslinking on the low-density polyethylene (LDPE) filled with wood flour was investigated[17]. A substantial increase in Young's modulus was observed accompanied with an increase in tensile strength and elongation at break as a result of crosslinking of the matrix. An increase in polymer - filler interactions due to grafting of polyethylene onto the filler surface via formation of covalent bonds between the matrix molecules and filler surface was suggested as an explanation of these effects; however, no direct evidence was provided. In this paper, the same effect was investigated for wood beech flour and the idea of a formation of grafting of the matrix onto the filler surface is supported by direct SEM observations.

Experimental

Materials : Low density polyethylene Bralen RA 2-19 (Slovnaft, Slovakia, MFI 0g/10minutes) was used as a matrix. 2,5-dimethyl-2,5-ditert butylperoxy hexyne was used as the peroxidic initiator of crosslinking. Wood beech flour has been used as the filler. The size and shape of the filler can be seen in Fig. 1.

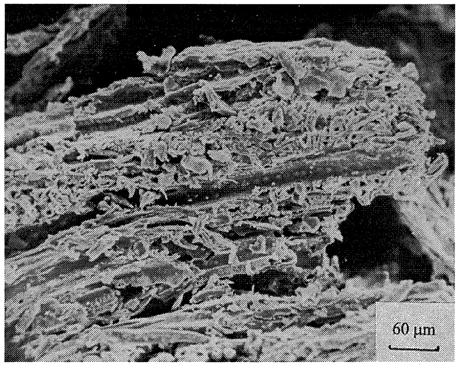


Fig.1: SEM image of the filler use (wood flour).

Sample preparation : A mixture of the LDPE with the filler and peroxide was prepared in the 50 ml mixing chamber of a Plastograph Brabender PLE 330 at 140 °C by mixing for 10 minutes at a speed 35 rpm. The slabs were prepared by compression moulding at 140°C for 2 min without peroxide and at 180°C for 20 min with the peroxide. More than 97 % of the peroxide present was decomposed under these conditions. The dog-bone specimens for testing were cut from the slabs at room temperature.

Testing methods : Mechanical properties of the materials were investigated using an Instron 4301 testing machine at the deformation rate 10 mm/min.

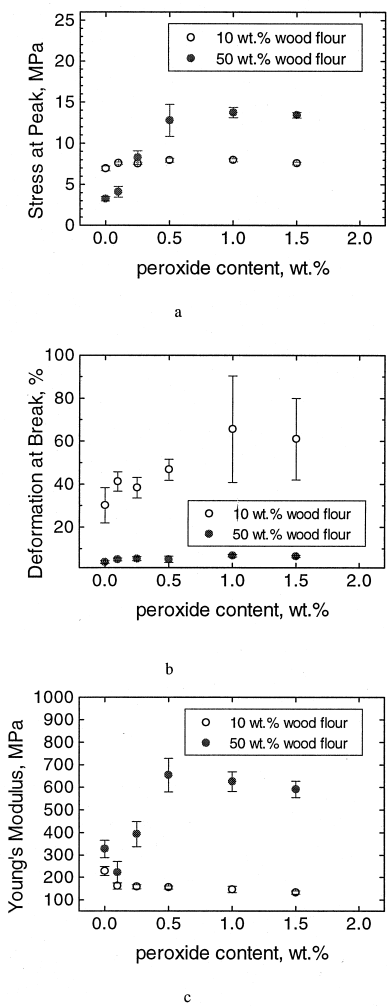
SEM: Fracture surfaces of the notched samples prepared at room and at the liquid nitrogen temperature were observed. A notch of depth 2 mm was made by razor blade at the shorter side of the sample cross-section and bending was applied to the sample so that the tensile deformation at the edge of the notch caused the fracture initiation. Ductile fracture was achieved at the room temperature and brittle fracture occurred at the temperature of liquid nitrogen.

The specimens were sputter-coated (SCD 050, BALTEC) with a thin layer of platinum (cca 4 nm). Scanning electron microscope JSM 6400 (JEOL, Japan) was used for observation and micrographing.

Results and discussion

Dependences of mechanical properties on the filler content are shown in Fig. 2 for both crosslinked and uncrosslinked matrices. An increase in the Young's modulus data and a decrease in the elongation at break with the rising filler content are observed. The dependence of the tensile strength is more complex reflecting the increased stiffness as well as the decreased elongation due to the rising filler content and a change of deformation behaviour from ductile (neck formation, yielding) to more brittle at higher filler contents.

The effect of crosslinking of the matrix on mechanical properties is similar to that observed in our previous paper (Ref. 17) on composites filled with wood flour of different source than the one used in this paper. It consists in a substantial increase in Young's modulus and certain increase in tensile strength as a result of crosslinking. Regarding Young's modulus data, the increase is surprising, indeed, since generally a decrease in Young's modulus was observed due to crosslinking of both low-density polyethylene and LDPE filled with inorganic filler, e.g. silica (Ref. 16) as a result of a decrease in crystallinity of the matrix. The positive effect of crosslinking on the strength and stiffness depends on the degree of crosslinking given by the initiator concentration, as seen in Fig. 3. At low peroxide concentrations (low crosslinking degree) a minor effect was observed. Increased peroxide concentration presumably leads to improved interfacial interactions and substantial gain in strength and stiffness was observed (Ref. 17). At high initiator contents, i.e. high crosslinking degrees, the effect of the decrease in crystallinity is significantly pronounced and prevails over the beneficial effect of crosslinking on polymer - filler interaction. Direct SEM observations of the fracture surfaces were used as an attempt to support the explanation based on the increased polymer - filler interactions due to chemical process initiated by a radical initiator between the polymer and organic filler on the filler surface. Three types of fracture have been investigated, namely a brittle impact fracture at temperature of liquid nitrogen, ductile impact fracture of of notched specimens at room temperature and the fracture surfaces of the samples broken in an Instron tensile tester at room temperature and strain rate 10 mm/min (about 30 %/min).



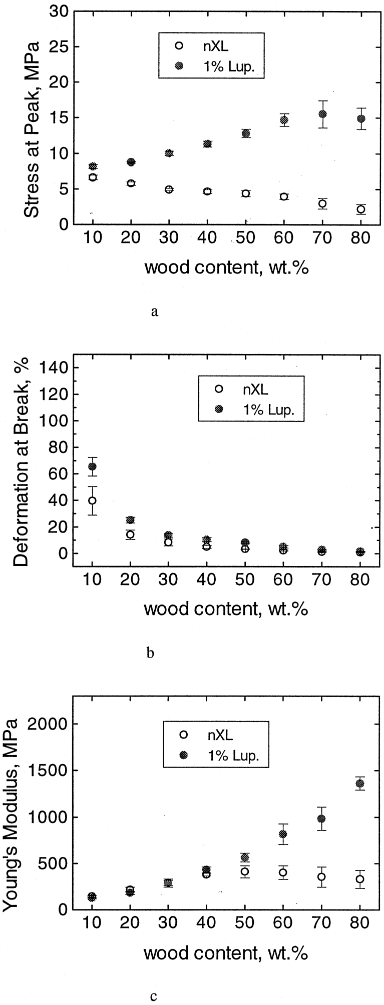
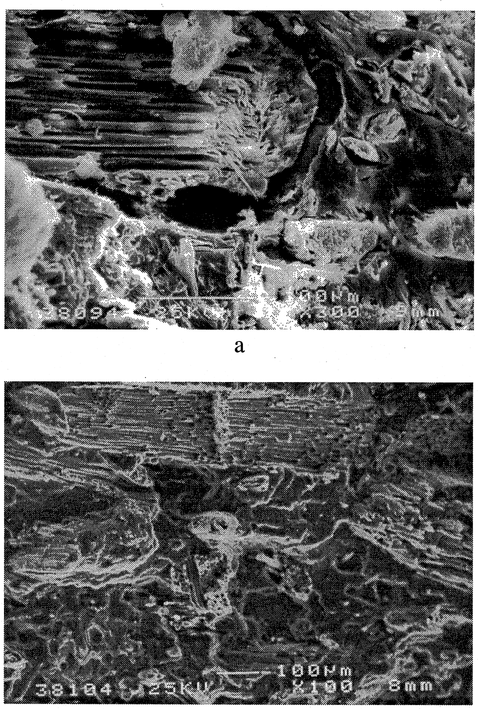


Fig.2: Mechanical properties of LDPE filled with wood flour in dependence on the filler content; a = tensile strength [MPa], b = deformation at break [%], c = Young's Modulus [Mpa].

Fig.3: The effect of crosslinking degree given by the peroxide cocentration on mechanical properties of LDPE filled with wood flour: a = tensile strenght [Mpa], b = deformation at break [%], c = Young's Modulus [Mpa].

The surfaces obtained by brittle fracture of the composites containing 50 wt.% of the filler are shown in Fig. 4. A clear sign of dewetting can be seen on the filler surface for uncrosslinked (Fig.4a) sample while patterns of cohesive fracture through the filler particles are visible for crosslinked material (Fig.4b). This observation is in accordance with the mechanical properties. For uncrosslinked sample the adhesion between the filler and the matrix is low and dewetting occurs at a rather low stress. On the other hand, after crosslinking adhesion between the phases is substantially increased. No dewetting occurs and the fracture proceeds through the filler particles since the stiffness of the matrix is quite high at a rather low temperature under Tg of LDPE while large filler particles are less resistant towards fracture.

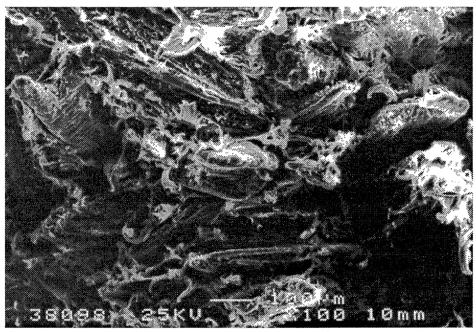


a

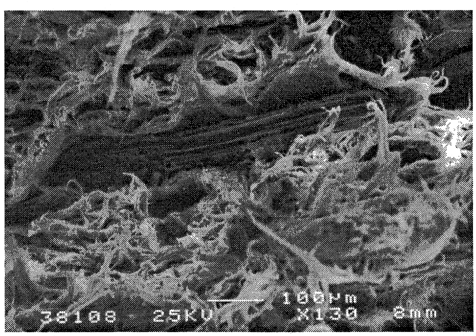
b

Fig. 4: Brittle fracture surface of the composite LDPE with 50 wt.% of wood flour; a = uncrosslinked, b = crosslinked.

Only slightly different features, characterized mainly by patterns of plastic deformation, have been observed for ductile impact fracture of notched specimens (Fig. 5). A cohesive fracture through the matrix is seen in the uncrosslinked sample (Fig.5a). Thus, the fracture starts on the tip of the notch, dewetting being incomplete and the fracture path continues partially on the filler surface but mainly through the matrix. Anyway, it should be admitted that the polymer - filler interface is strengthened to a certain extent by interactions between the polymer and the filler surface during mixing and compression-moulding even in the absence of peroxide. The process might be initiated by the presence of small amounts of hydroperoxides inherently present in the polymer or by macroradicals formed



a



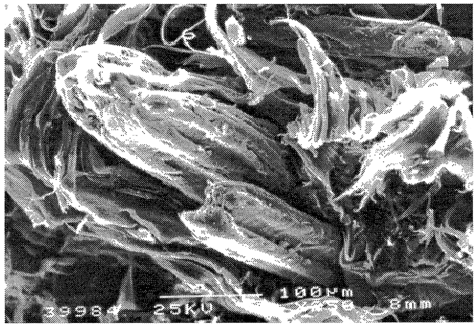
b

Fig.5: Ductile impact fracture surface of the composite LDPE with 50 wt.% of wood flour; a = uncrosslinked, b = crosslinked.

either in the matrix or on the filler surface by thermal and/or mechanical stress during processing. On the other hand, the fracture proceeds through the filler particles for crosslinked samples indicating that adhesion is high enough to prevent dewetting if the material is crosslinked (Fig. 5b). The fracture energy is transferred by the well interacting interface and the stress concentration sites are localized on the filler surface or within the filler particles where some cavities are present can be seen in Fig. 1.

SEM pictures of the surfaces of slow ductile fracture occurring during tensile tests confirms the considerations mentioned above (Fig. 6). For uncrosslinked sample a pronounced dewetting occurs accompanied by clear plastic deformation of the matrix (Fig.6a). In this case no notch is present to initiate the crack and the fracture starts on the weakest point, i.e. on the polymer - filler interface. Almost no dewetting was observed for crosslinked samples (Fig. 6b). In this case, due to slow deformation rate as compared with impact ductile fracture, the energy is transferred to the matrix which has enough time to be strained and broken by cohesive fracture.

The different SEM patterns observed for uncrosslinked and crosslinked composites support the idea of strengthening the interface by formation of chemical interactions between the filler surface and the polymeric matrix. These interactions arise during the peroxide-initiated crosslinking of the matrix. It is acceptable to assume that the oxy radicals formed by thermal decomposition of the peroxide may also attack the filler surface, besides the polyethylene matrix. Thus, radicals are formed on the filler surface which can recombine with the polyethylene macroradicals. Grafting of polyethylene macromolecules onto the filler surface occurs in such a way, wetting of the filler surface is improved and the filler/matrix adhesion on the phase boundaries is increased. The mechanism suggested above is responsible for the observed effect of crosslinking on mechanical properties of the LDPE/ organic filler composites.



a

b

Fig. 6: Slow ductile fracture of the composite LDPE with 50 wt.% of wood flour; a = uncrosslinked, b = crosslinked.

Conclusion

Crosslinking of composites consisting of low-density polyethylene and an organic particulate filler results in a surprising increase in both Young's modulus and tensile strength accompanied by a modest increase in strain at break. SEM observation brings a strong support for the explanation based on a formation of direct covalent bonds between the filler surface and the polyethylene matrix.

Acknowledgement

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