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Z. Nogellova[a]; B. V. Kokta[b]; I. Chodak[a]
[a] Polymer Institute Slovak Academy of Sciences, Bratislava, Slovak Republic [b] University of Quebec, Trois Rivieres, Canada

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A COMPOSITE LDPE/WOOD FLOUR CROSSLINKED BY PEROXIDE

Z. Nogellova,[1] B. V. Kokta,[2] and I. Chodák[1]

[1]Polymer Institute
Slovak Academy of Sciences
842 36 Bratislava, Slovak Republic

[2]University of Quebec
Trois Rivieres, Canada

Dedicated to the founder of the Polymer Institute, Professor Milan Lazar in honor of his 70th birthday.

ABSTRACT

The properties of a composite consisting of low density polyethylene (LDPE) filled with wood flour were investigated in a broad concentration range of the filler. The adhesion between the matrix and the filler was increased via peroxide-initiated crosslinking. A decrease in both tensile strength and elongation at break and modest increase in Young's modulus with rising filler content was found for uncrosslinked samples. Crosslinking results in a substantial increase of tensile strength and extreme rise of the Young's modulus values with an increase of both filler content and peroxide concentration, compared to uncrosslinked composites. A formation of covalent bonds between the filler surface and polymer chains are proposed as the reason for the observed effect of crosslinking. The extraction and swelling data are presented to support this explanation.

INTRODUCTION

Crosslinking of polyethylene is a rather common way of modification of this polymer. It was found that a beneficial effect on properties can be achieved by crosslinking not only of polyethylene itself but also by crosslinking the blends [1] or particle filled materials [2] with polyethylene matrix. In our earlier papers, extensive work has been done on investigation of properties of crosslinked LDPE matrix filled with various grades of silica. The crosslinked materials proved to be superior to uncrosslinked analogs regarding their mechanical properties, especially considering drawability, impact strength, and resistance to crack growth [3].

Using the fillers of an organic nature brings about new opportunities for tailoring the materials. Wood particles as filler can be advantageous, not only due to the low price, but also because of its possible biodegradability and low density of the composites. On the other hand, serious problems may arise when using this filler, because of low adhesion between the filler and polyolefin matrix, certain instability of properties resulting from a water sorption, and lower thermal stability leading to a need of using a lower processing temperature and/or lower processing time. The disadvantage of a low polymer-filler interaction is solved by using various ways of modification. Kokta has done extensive research on the effect of the grafting of various monomers on the filler surface [4]. An addition of maleic anhydride itself or a maleic anhydride graded polymer is another way for an increase of adhesion between the matrix and the filler [5, 6]. Sapieha [7, 8] observed an improvement of mechanical properties of polypropylene/cellulose composite after modification with peroxide, however, no crosslinking occurred in this case.

In this paper, we have investigated the possibilities of modification of properties of LDPE/wood flour composites by peroxide-initiated crosslinking of the matrix.

EXPERIMENTAL

Low density polyethylene Bralen RA 2-19 (Slovnaft, Slovakia, MFI 2.0 g/10 minutes) was used as a matrix, filled with wood particles (beech, particle size 0.2-1.0 mm). An initiator 2,5-dimethyl-2,5-ditertbutyl peroxy hexyne-3 (Luperox 130, Luperox GmbH, FOG) with 95% of active component was used as received. composites have been prepared in a 50 ml mixing chamber of a Brabender Plasticorder PLE 331 at 140°C and mixing rate 35 rpm for 10 minutes. Plaques 1 mm thick were made by compression molding at 180°C for 2 and 20 minutes for

TABLE 1. The Mechanical Properties (Stress σ and Deformation e at Break and Young's Modulus E) of LDPE/Wood Flour Composites in Dependence on the Filler Concentration for Uncrosslinked (O) and Crosslinked (1% of Peroxide, XL) Material

filler	σ, MPa		e,%		E, MPa	
wt. %	0	XL	0	XL	0	XL
0	14.0	21.1	647	603	105	162
10	6.9	8.1	30	62	227	157
30	4.0	9.9	8	12	218	328
50	3.2	13.0	4	7	327	618
60	3.0	14.4	2	4	392	925
70	3.0	17.3	2	2	504	1351
80	*	9.8	*	1	*	1259

* The uncrosslinked samples with 80% of the filler have not been compact after compression molding.

uncrosslinked (without peroxide) and crosslinked samples, respectively. Specimens for evaluation of mechanical properties were prepared by cutting a dog-bone shape specimens from the plaques. Tensile tests were made at a room temperature using a Instron 4301 Universal Testing Instrument at deformation rate 10 mm/minute. The insoluble portion was determined by weight of the specimens after 14 hours extraction in boiling xylene. The remains of the specimens after extraction were used for determination of equilibrium swelling reached after 4 hours in xylene at 110°C.

RESULTS AND DISCUSSION

The comparison of mechanical properties for crosslinked and uncrosslinked samples in dependence on the content of the filler present in the composite is shown in the Table 1. It is seen that for uncrosslinked materials an increase of filler content leads to a decrease of both tensile strength and elongation at break and to an increase of modulus. A drop in tensile strength and especially of deformation at break is rather extensive. This behavior is in accordance with a low adhesion between the filler and the matrix if no surface modification of the filler occurred.

The nature and extent of the changes of the mechanical properties due to crosslinking is rather surprising. It is seen that a decrease in the deformation at break is substantial, similar to uncrosslinked samples, and the values are about double of those for unmodified material On the other hand, the tensile strength dependence shows opposite tendencies for uncrosslinked and crosslinked samples. A steady drop with rising filler content is characteristic for uncrosslinked LDPE matrix while the strength for crosslinked composites, after initial decrease at 10% of the filler, increases.

Unexpectedly high values of Young's modulus have been found as a result of crosslinking. An introduction of a filler leads to an increase of modulus as anticipated. However, this effect is extremely magnified if crosslinking is applied; the effect of crosslinking is higher at higher filler content so that the modulus of composites containing 50 or more % of wood particles is higher by a factor of 2.5 compared to uncrosslinked analogues. Similar conclusions can be drawn from dependence of mechanical properties on an initiator concentration at constant content of the filler as is seen in the Table 2.

Distinct differences are observed when comparing the effect of increasing the initiator content on mechanical properties. The tensile strength of the composite with 10% of the filler is almost uninfluenced by the crosslinking; a substantial increase is observed for the material with 50% of wood particles. Similar behavior was observed if considering the elongation values; the composite with lower filler content appeared to be much more sensitive to crosslinking. Different tendencies were found for the Young's modulus values. A less pronounced drop was observed with a rising peroxide content for material containing 10% of wood, while more than a doublefold increase was found if the composite with 50% of filler was investigated. It is worth mentioning that the nature of the stress/strain curves is not changed due to crosslinking as demonstrated in the Figure 1. The only difference is the increase of the elongation at break and especially of the stress at break values with the rising peroxide content. However, the amount of peroxide added must not be too high; as seen from Table 2 and Figure 1, since crosslinking above certain level results in lower values of all parameters in question.

Compared to LDPE composites with inorganic fillers, the most striking phenomenon is the substantial modulus increase due to crosslinking. This behavior

TABLE 2. The Mechanical Properties (Stress σ, and Deformation e at Break and Young's Modulus E) of LDPE/Wood Flour Composites in Dependence on the Peroxide Concentration for the Composites Containig 10 or 50% of the Filler

peroxide wt. %	σ MPa		e %		E MPa	
0	6.9	3.2	30	4	228	327
0.2	8.7	4.3	47	6	195	203
0.5	8.3	10.7	54	5	196	587
1.0	8.3	13.0	62	7	156	618
1.5	8.5	14.4	68	7	167	717
2.0	7.8	13.1	53	7	162	580
filler wt. %	10	50	10	50	10	50

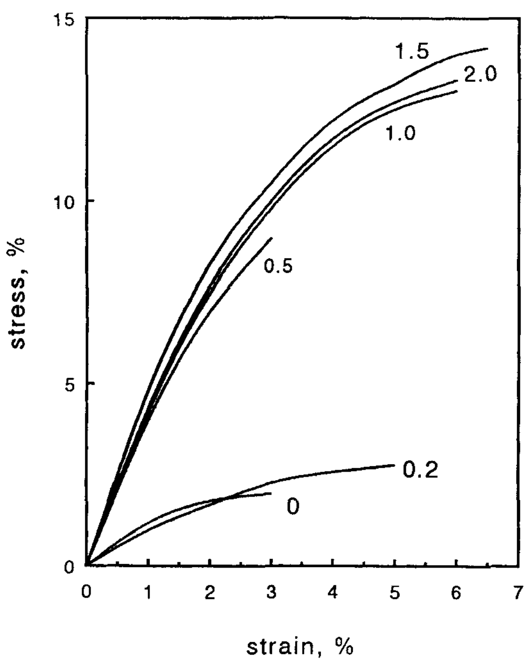

Figure 1. The stress-strain curves of LDPE filled with 50 wt% of wood flour crosslinked with different amounts of peroxide. The concentration of peroxide (in wt%) is given by a number on the curve.

is rather unique since the crosslinking of LDPE leads usually to a certain reduction of crystallinity resulting in a drop of yield strength and modulus [2]. The explanation of a significant increase of the strength and modulus values must result from an increase of interaction between the filler and a matrix. The only possible way to obtain the interaction of such extent is a formation of direct covalent bonds between the filler surface and the polyethylene matrix. Of course, this is easily acceptable, considering the chemical composition of wood with hydrocarbon structures and plenty of various functional groups in the molecule. Many of these can react either with oxyl radicals formed by decomposition of peroxide or with polyethylene macroradicals generated by the reaction of PE chains with radicals being present in the system.

This conclusion is supported also by the extraction and swelling data of crosslinked samples. The insoluble portion in uncrosslinked samples roughly corresponds to the filler content, while in crosslinked samples the values are between 85 to 97 wt% and have been found to be slightly higher at a higher filler content. The swelling data are presented for different wood content in a matrix crosslinked by 1% of peroxide. As seen from Figure 2, the degree of swelling decreases significantly with the increase of filler content in the composite. Such a shape of a dependence is related to rather strong interactions between the filler and the matrix. Filler particles act in this case as additional crosslinks, increasing the network density resulting in a lower swelling [9].

The properties of PE/wood flour composites may be affected by a moisture sorption by the filler during storage. To estimate an extent of this effect, we made some measurements of tensile properties after storing the material at room temperature for a few hours/days. Two sets of experiments have been done, namely the samples had been compression molded immediately after mixing and then stored for different times before tensile measurements, or the mixed samples were stored for a certain time before compression molding and the properties of samples were measured after constant time. The results are given in Table 3.

The results clearly show that a rather strong influence of the storing time exists. Nothing definitive can be said about the reason for this behavior; nevertheless, it is expected that the moisture sorption would be the most probable explanation. From this point of view, it is of interest that storing after compression molding has very little effect on the properties, unlike storing after mixing before compression molding (Table 3a). Apparently, a few days storage in ambient conditions results in certain moisture uptake leading to a weakening of the interactions between the filler and the polymer. Subsequent compression molding is

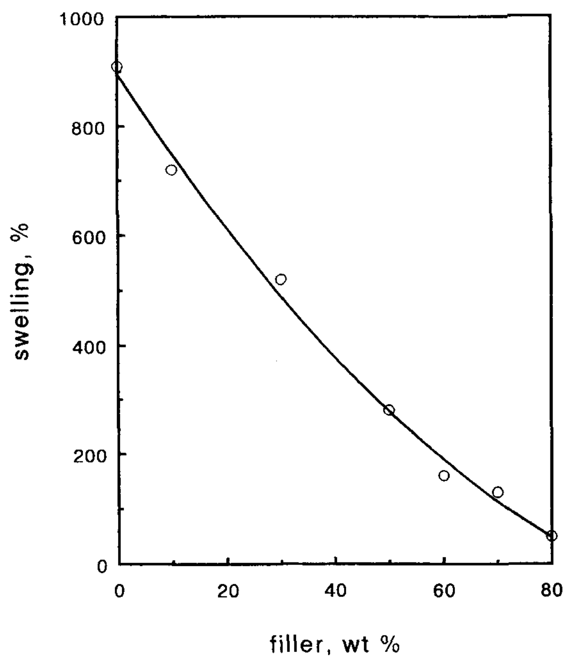

Figure 2. The dependence of swelling degree on the concentration of the filler of LDPE/wood flour composites crosslinked with 1 wt% of peroxide.

too short to remove the moisture from the sample in spite of a rather high temperature (180°C). On the other hand, a storage of the specimens after compression molding does not change the interactions in the composite too severely.

As seen from Table 3b, crosslinking has certain beneficial effects on the properties after storing. The mechanical properties after storing drop by 25% of original value in uncrosslinked samples, while less than a 10% difference was observed in crosslinked material.

CONCLUSION

An addition of unmodified wood flour in LDPE results in a decrease of tensile strength and deformation at break.

Peroxide-initiated crosslinking leads to a substantial increase in tensile strength and Young's modulus compared to uncrosslinked composites.

TABLE 3. The Changes of Mechanical Properties (Tensile Strength σ, Elongation at Break e, Young's Modulus E) of LDPE/Wood Flour Composites after Storage at RoomTemperature after Mixing (Mix) or Compression Molding (Cmld)

a) uncrosslinked mixture, 30 wt% of filler

storing days after Mix	Cmld	σ Mpa	e %	E MPa
0	0	5.0 (0.2)	10.4 (1.8)	250 (33)
0	2	5.0 (0.3)	10.3 (1.7)	291 (39)
0	7	5.6 (0.2)	9.2 (1.1)	351 (20)
0	2	5.0 (0.3)	10.3 (1,7)	291 (39)
1	2	4.0 (0.3)	6.6 (1.5)	225 (41)
3	2	3.5 (0.3)	6.1 (1.7)	206 (26)
12	2	3.8 (0.2)	6.7 (0.9)	278 (42)

standard deviation of the measurement given in parentheses

b) comparison of uncrosslinked (0) and crosslinked (XL) samples with 50 wt. % of the filler

storing		σ Mpa		e %		E MPa	
Mix hrs	Cmld days	0	XL	0	XL	0	XL
0	2	4.1	14.1	2.9	6.1	464	706
1	2	3.5	13.7	2.5	6.7	398	701
4	2	3.2	13.7	3.1	6.9	366	656

The experimental data are explained in terms of increased adhesion between polymeric matrix and the filled surface. A formation of covalent bonds are proposed as a reason for the adhesion increase.

It was found that crosslinking has certain beneficial effect on the properties after storing.

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