Macromol. Symp. ***170**, 157–164 (2001)*

Poly(Ethylene-*co*-Methacrylic Acid) Copolymer as an Effective Compatibilizer of LDPE / Wood Flour Composite

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Summary: The mechanical properties of a ternary system consisting of low density polyethylene (LDPE), poly(ethylene-*co*-methacrylic acid) copolymer (EMAA) and wood flour (WF) were investigated. For a better understanding of the mutual interactions between the components, binary blends LDPE / EMAA and EMAA / WF were studied as well, and the results were compared with published data for LDPE / WF composite. Mechanical properties for LDPE / EMAA blend exhibit almost additive behavior, while the properties for EMAA / WF mixtures are similar to those of composites LDPE / WF compatibilized in situ by peroxide crosslinking. In ternary blends, an addition of 5 to 10 wt.% of EMAA is sufficient to achieve high tensile strength and Young modulus. The beneficial effect of the copolymer is explained by introducing a close contact between the organic filler and polyolefinic matrix on the phase boundaries.

Introduction

Multi-component polymer systems made of components with different polarities often lead to materials with interesting properties. This way is particularly attractive when (i) a given material is produced at a lower cost and/or simpler process, and (ii) the major component belongs to the category of the materials from the renewable resources. The above features are likely to be met in the composite materials consisting of the non-polar thermoplastic polymer matrix (polyolefins) and polar filler (naturally occurring polymers). As the nature of interface determines the ultimate mechanical properties, due to a different polarity of both components their interface needs to be modified to induce the interfacial adhesion.[1,2] One of the simplest methods to introduce the interactions between a non-polar matrix and a polar filler is using a compatibilizing agent possessing both polar and non-polar moieties.

The principle of compatibilization of polyethylene / polypropylene blends by their mutual co-crosslinking using a peroxide initiator[3] was used to improve the mechanical

CCC 1022-1360/00/$ 17.50+.50/0

properties of the composite material made of low density polyethylene (LDPE) and wood flour (WF).[4] The idea of formation of the covalent bonds on the phase boundaries is suggested and supported by extraction and swelling data. Improved contact on the interface results in a pronounced increase of tensile strength and Young modulus. This approach has been proved to be beneficial when investigating the composites of LDPE filled with other organic fillers.[5]

The mechanical properties, namely elongation at break and tensile strength, of recycled LDPE filled with WF were improved by using a maleated triblock copolymer styrene-ethylene/butylene-styrene as a compatibilizing agent.[6] The copolymers of ethylene with (meth)acrylic acid, E(M)AA, represent a relatively common type of compatibilizer used both in acidic and partially ionized form[7] and they have been used in the systems similar to those studied in Refs.[4,5] These copolymers contain a low amount of the polar acid monomer units, usually below 7 mol.%, statistically distributed among the non-polar ethylene units. Addition of this type of compatibilizer up to 2 wt.% of solids in the system LDPE / starch did not significantly affect the elongation and tensile strength but yielded an increase of the tensile modulus by inducing adhesion acting during the initial (elastic) stage of loading.[8] A range of 25 to 50 wt.% of EAA copolymer was used in the composite films of LDPE with wheat starch[9] to reach an elongation well above 100 % even at the starch content up to 50 wt.%. This type of copolymer was also used as a compatibilizing agent for blending lignin with polyolefins (LDPE, polypropylene and high density polyethylene).[10] The maximum content of lignin was 30 wt.% in this case. The overall mechanical properties of polyolefins significantly reduced by incorporation of lignin were improved when EAA was used as a compatibilizer.

The aim of this work is to investigate the compatibilization effect of the copolymer poly (ethylene-*co*-methacrylic acid) in the thermoplastic composite LDPE / WF. Based on the data presented above for the systems LDPE / starch and LDPE / lignin, a significant compatibilizing effect of this copolymer may be also expected for the composite LDPE / WF.

Experimental

The following commercially available polymers were used in this work: LDPE (Bralen

RA-2-19, Slovnaft, Slovakia), MFI of 2.0 g/10 min (ASTM 12138) and EMAA copolymer (HC1202, DuPont, USA), MFI 1.5 g/10min containing 11.5 wt.% of methacrylic acid monomer units. A WF from birch is characterized by the average length 460 µm and thickness 100 µm and it was dried prior to blending at 120 °C for 2 hours.

The samples were prepared in a Brabender plasticorder PLE 331 mixing chamber at 140°C, time of mixing 10 min and mixing rate 35 rpm. The blended samples were compression molded at 170 °C for 2 min. The tensile properties were measured at room temperature on the dog-bone specimens (30 x 6 x 1 mm testing part) using an Instron 4301 (Instron Ltd., USA) testing machine at crosshead speed 10 mm/min. Dynamic mechanical data were obtained by using DMTA MkIII apparatus (Rheometric Scientific, UK) in a bending mode, specimen size 8 x 12 x 2 mm, frequency 10 Hz, temperature interval from –50 up to 140 °C, heating rate 3 °C/min with the temperature equilibration for 15 min at –50 °C before starting the experiment.[11]

Results and Discussion

Prior to discussing the data for a ternary system LDPE / EMAA / WF, the main features of the binary systems will be specified.

LDPE / WF. As given in,[4] a sharp drop in the elongation at break (from 600 to 30 %) as well as a drop in the tensile strength (from 14 to 7 MPa) is observed already after addition of 10 wt.% of WF to LDPE. Both these parameters keep decreasing rather extensively as the WF content is augmented to 70 wt.%. Within this composition range, the modulus increases from 100 to 500 MPa. This behavior points at the introduction of substantial number of defects into the matrix as a result of the WF presence. The main reason is seen in a low adhesion between the filler and the polymer matrix.

LDPE / EMAA. A few data have been published on the binary blends of LDPE with E(M)AA copolymers.[9,12] They suggest that these two polymers may form mechanically compatible blends within their entire concentration ratio. Figure 1 shows the tensile properties for a blend of LDPE with the EMAA copolymer used in this study (a detailed study on the blends of LDPE with EMAA copolymers of different type and degree of neutralization will be given elsewhere[13]). Tensile strength in a full composition range and elongation at break at a higher EMAA content follow the additive rule between the pure blend components, while the Young modulus seems even to reveal the synergistic behavior. Both Young modulus and elongation of break of virgin polymers are identical, while tensile strength is about twice higher for the EMAA copolymer. Due to a different polarity the polymers are assumed to be immiscible with the poor mechanical properties. Figure 1 demonstrates that this is not a case.

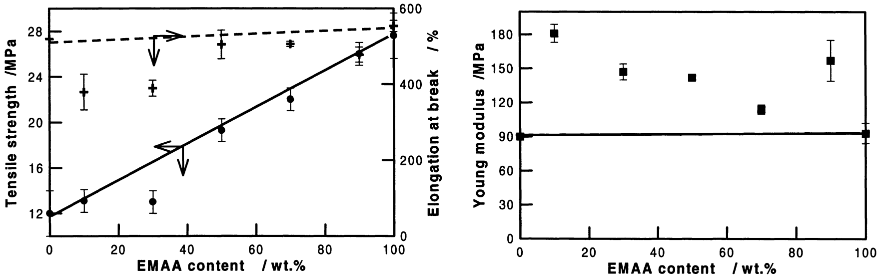

Figure 1. Tensile strength (●), elongation at break (✚) and Young modulus (■) determined for binary blend LDPE / EMAA as a function of blend composition. Lines follow the additivity rule.

EMAA / WF. Figure 2 depicts the tensile and dynamic mechanical data for the binary system EMAA / WF as well as the data from Ref.[4] Above 10 wt.% of WF the elongation at break drops. Interestingly, identical trend and very similar data as for LDPE / WF with covalently crosslinked interface by peroxide[4] are observed for tensile strength and Young modulus for the EMAA / WF composite. The tensile strength decreases by about half of that for virgin EMAA after addition of WF and increases towards 70 wt. % of WF. The modulus increases gradually with the increased content of WF reaching the value above 1000 MPa for 70 wt. % of WF. These data indicate an improved contact between EMAA copolymer and WF, presumably via hydrogen bonding of the hydroxyl groups present in both components, resulting in the transfer of applied stress from EMAA matrix to the WF particles.

Dynamic mechanical data, expressed as a loss tangent, support this statement. A shift of the β'-relaxation peak of the EMAA carboxylic dimers[14] to the higher temperature with increasing the content of WF indicates a stiffening of the polymer matrix by its interaction with the WF. Importantly, an intense interactions at high WF content maintain the viscoelastic behavior of EMAA matrix even at the temperature much above the melting temperature (at 140 °C: tan δ = 0.6 at 70 wt. % and 1.0 at 50 wt.% of WF, respectively). This resembles the situation with the crosslinked interface between LDPE and grass or paper fibres.[5] Figure 2 reveals that this composite material reaches the same mechanical properties as that when a more complex chemistry (crosslinking) is involved.

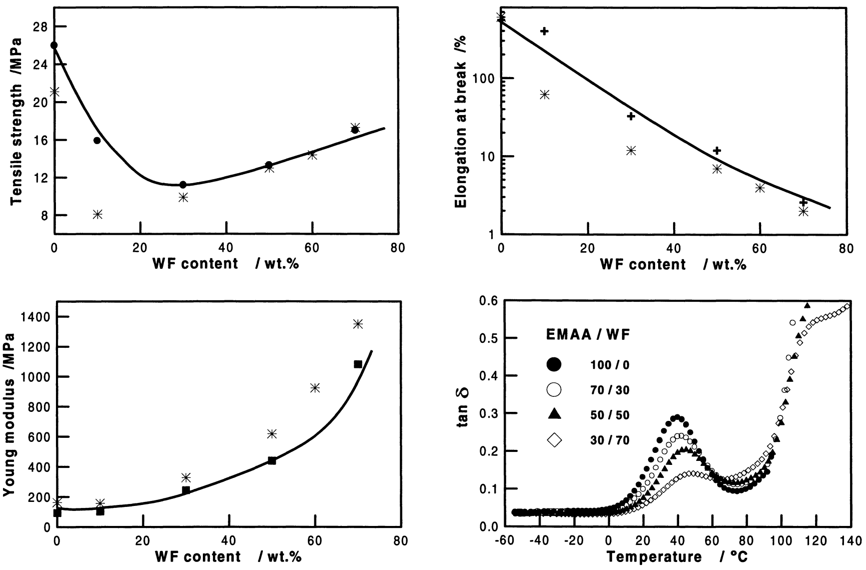

Figure 2. Tensile strength (●), elongation at break (✚), Young modulus (■) and loss tangent determined for the composite EMAA / WF at increased content of WF. Lines in tensile experiments connect the experimental points obtained in this work. For comparison, data for the LDPE / WF with a covalently crosslinked interface[4] are also included (✳).

LDPE / EMAA / WF. The effect of EMAA on compatibilization of WF in the LDPE matrix is expressed in two ways.

Firstly, the effect of EMAA addition to the LDPE / WF has been examined by the tensile experiment (Figure 3). The LDPE / WF weight ratio being 30/70 was kept constant upon rising the EMAA content. The data well support a picture about the interactions developed between LDPE and WF introduced by EMAA. Both tensile strength and Young modulus reach maximum after addition of 5 to 10 wt.% of EMAA. Although the amount of EMAA is really low at this composition range, the tensile strength is in the region of that for virgin EMAA and Young modulus is significantly above that determined for both virgin components and binary systems.

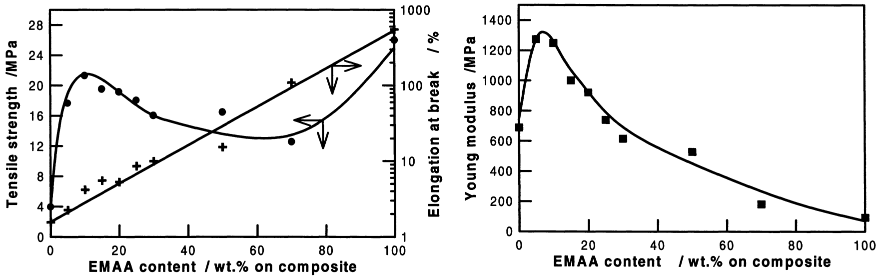

Figure 3. Tensile strength (●), elongation at break (✚) and Young modulus (■) determined for LDPE / EMAA / WF composite by addition of EMAA to LDPE / WF equal to 30 / 70 by weight. Lines connect the experimental points.

It is important to note that the effect of EMAA is not only on increased Young modulus, due to interactions causing lesser slippage at the interface at low elongation, but also on the increased tensile strength, which has not been observed for LDPE / EMAA / starch at low loading (up to 2 %) of EMAA copolymer.[8] This phenomenon in our case is likely related to the stiffened polymer material forming a distinct polymer interphase at the vicinity of the WF surface. Also a low elongation within this EMAA concentration range reflects a high stiffness. Beyond 10 wt.% of EMAA, both tensile strength and modulus decrease while elongation at break increases, which reflect lower overall WF concentration and the fact that the tensile properties are controlled by the polymer matrix (blend of LDPE and EMAA).

Secondly, the ratio between LDPE and EMAA (up to 50 wt.% of EMAA based on polymer matrix) is varying while the WF content is kept constant, either 50 or 70 wt.% calculated to the entire system. The results are shown in Figure 4. Similarly as in Figure 3, a small addition (3 wt. % on entire system) of EMAA to LDPE at 70 wt.% of WF markedly improves tensile strength and Young modulus, which exhibit maximum at 30 wt.% of EMAA on polymer matrix (9 wt. % on the entire system). The elongation at break increases moderately in this composition range.

The situation for 50 wt.% of WF is different. At glance, the Young modulus remains constant at the value 700 MPa, however, by addition of the minimum amount of EMAA the material looses brittleness and shows the tensile strength that of virgin LDPE. The elongation at break is 2-fold higher than for 70 wt.% WF due to a higher polymer content. It should be noted that the addition of a minor amount of EMAA yields superior tensile properties which are comparable (even slightly better) to the interfacial covalent crosslinking between LDPE and WF.[4]

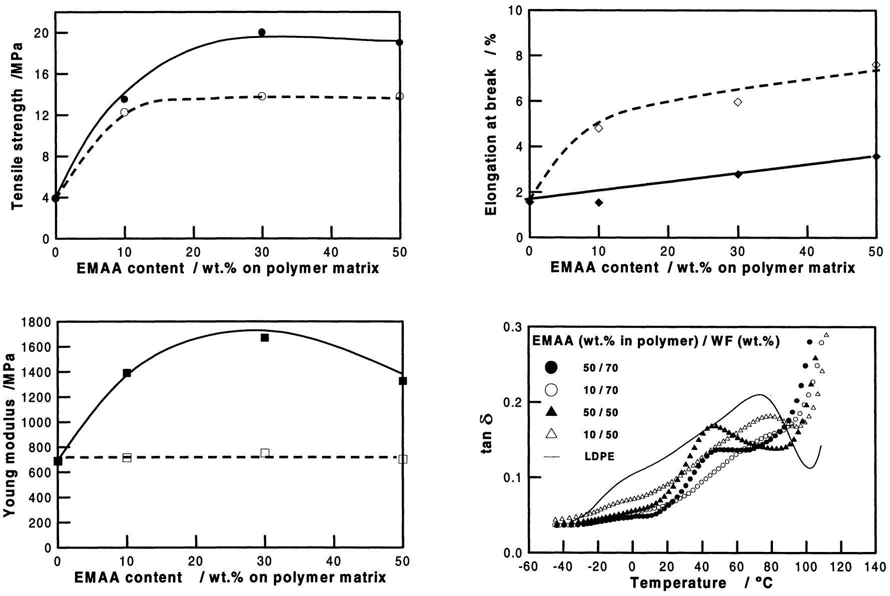

Figure 4. Tensile strength, elongation at break, Young modulus and loss tangent determined for the composite LDPE / EMAA / WF. Overall WF content: 50 wt.% (dashed lines), 70 wt.% (solid lines).

A difference between the composites containing 70 and 50 wt.% of WF is also demonstrated by the dynamic mechanical analysis. The loss tangent temperature dependencies are shown for both WF contents at 10 and 50 wt.% of EMAA in the polymer matrix. The β'-relaxation is only identified for composites with higher EMAA concentration (50 wt % in polymer matrix; filled triangles and circles for the respective WF contents). When the EMAA content in polymer matrix is lowered to 10 wt.%, peak associated to the β'-relaxation disappears (empty triangles and circles for the respective WF contents). Likely most of EMAA takes part in bonding to the WF surface, which hinders the mobility of the polymer chains at the temperature of β'-relaxation since at this EMAA content, the tan δ dependencies resemble the behavior of polyethylene.

Conclusion

This work reveals a suitability of using poly(ethylene-*co*-methacrylic acid) copolymer to compatibilize the LDPE / WF composite. Both mechanical and dynamic mechanical results indicate a formation of interactions between LDPE and WF introduced via the EMAA copolymer. Tensile and thermal properties can be adjusted in a wide range by selecting the proper WF content as well as the composition of the polymer matrix. A high content of WF and low amount of EMAA copolymer in the polymer matrix yield materials with high modulus and high tensile strength, which makes them interesting from many points of view taking into consideration such factors as process simplicity, cost and high content of material from renewable resources. The further investigation of these materials is underway in our laboratory.

Acknowledgement

This work was supported by the Slovak grant agency, grants 2/7044/20 and 2/1060/21. M. Stach and Z. Nogellová are thanked for consulting the dynamic mechanical analysis and composite preparation, respectively.

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