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Use of Reactive Surfactants in Basalt Fiber Reinforced Polypropylene Composites

Sz. Matkó, P. Anna, Gy. Marosi, A. Szép, S. Keszei, T. Czigány, K. Pölöskei*

Budapest University of Technology and Economics, Műegyetem rkp. 3., 1111 Budapest, Hungary
E-mail: gmarosi@mail.bme.hu

Summary: Basalt fibers, similarly to other silicate fibers, can be introduced into both thermoplastic and thermosetting polymer matrices. In this work some basalt fiber reinforced polypropylene composites were investigated. The fiber-matrix adhesion was improved by commercial and non-commercial maleic anhydride derivatives. The latter types, called reactive surfactants, were prepared in laboratory scale and the progress of the syntheses was determined by Raman microscopy. The additives allowed performing reactive interface modification during the compounding process. Due to the interface modification with the additives in low concentration the mechanical properties improved. The boundary layers on the surface of the reinforcing fibers were observed using scanning electron microscopy (SEM).

Keywords: basalt fiber; interface modification; reactive surfactant; reinforced polypropylene; scanning electron microscopy (SEM)

Introduction

The effectiveness of maleic anhydride derivatives as interfacial additives (coupling agents) in e-glass fiber reinforced polyolefin composites is well known. Using these compounds as modifiers, the mechanical properties improve.[1-5] The similarities between glass and basalt fibers suggest that widely used interface modifiers, like maleic anhydride derivatives, can be advantageously applied in the lower cost basalt fiber reinforced polymer composites as well. Reactive surfactants, however, being able to reach the interfaces and reacting there with both phases within the short residence time spent in a compounding machine, have not been studied in such systems.

Basalt based silicate fibers can be produced from the naturally occurring igneous basalt rock, which consists of a high proportion of basic magnesium silicates such as horn-blende, pyroxene, olivine and some feldspar.[6] The fiber is formed at high temperatures by different

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technologies, such as drawing and melt-spinning. The mechanical properties of basalt fibers span over a wide range depending on their diameter, chemical composition, structural homogeneity, surface porosity and temperature.[7-10]

These fibers can be introduced into both thermosetting[11-16] and thermoplastic[17-20] polymer matrices as well as into rubbers.[21] Interfacial contacts formed spontaneously between basalt and most of polymers are released easily if thermal or mechanical effects initiate local stresses. The poor fiber-matrix adhesion can be improved with different types of coupling agents such as silane compounds[11-14] or maleic anhydride (MAH) derivatives. In polypropylene composites the most widely used compound is polypropylene-g-maleic anhydride (PP-g-MAH).[17,22] The key question is how to find a method for the modification of the interfacial structure that is both efficient and economic. In case of short fibers this method is undoubtedly reactive compounding/processing wherein the surface modifier molecules have to reach the interfacial region within a short residence time. The most active molecules, designed to find interfaces rapidly, are surfactants, which, however, cannot bind phases together. Recently developed reactive surfactants are designed to combine the advantages of surfactants and coupling agents, facilitating the efficient in-line reactive interface modification.[23] One of the proposed ways to synthesize reactive surfactants, being able to react with both of the neighboring phases, is the introduction of MAH into hydrocarbon molecules containing one or more C=C bond. MAH derivative type reactive surfactants could be effectively used in polypropylene (PP) composites.[24] The molecules containing maleic anhydride or maleic acid (MA) group and double bond may couple to the surface of polar silicate via their MAH or carboxyl group by ionic or secondary chemical bonds. Furthermore the long carbon chain may be grafted onto the PP-chains by means of its double C=C bond in the presence of peroxide initiators.

In this work various reactive interface modifier additives were compared to each other in short basalt fiber reinforced PP composites.

Experimental

Materials

Basalt fibers: chemical composition: SiO_2: 46.2, Al_2O_3: 13.0, Fe_2O_3: 12.0, MgO: 10.0, CaO: 10.0, TiO_2: 2.0, K_2O: 1.8, Na_2O: 3.5, others: <1%. Manufacturer: Toplan Bazaltgyapot Kft.,

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Tapolca, Hungary. The length of fibers, which were produced by the Junkers melt spinning technology from natural basalt rock between 1300 and 1500°C ranges from 5 to 10 cm. As a result of the aerodynamic conditions occurring during the process large ball-like heads are formed at the end of the fibers. Figures 1 and 2 show the model of the melt spinning and the SEM photograph of a fiber-end respectively.

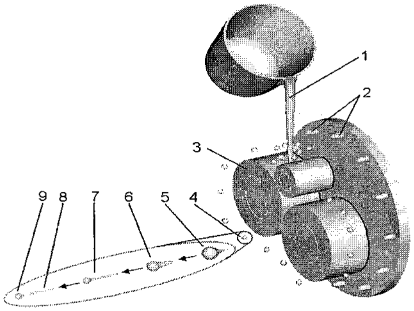

Fig. 1. The model of melt spinning.

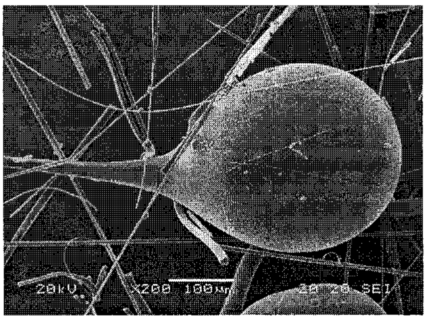

Fig. 2. SEM photograph of a large ball.

The short fibers with diameters ranging from 2 to 30 µm were made from these long fibers by milling in a hammer mill. As a result of stresses arising during grinding the fiber length decreased drastically and the balls of fiber-ends broke down. The average fiber length after the milling was in the range of 2-10 mm. In order to investigate reinforcing effect the short fibers' alone the balls were removed from the milled product in water. The balls, because of their lower hydrodynamic resistance, settled faster than the fibers. After the sedimenation of the balls the floating fibers were filtered from the water. Repeating this process four times the whole fraction of balls could be separated from the milled product. Then the clean milled product was dried in an oven between 80 and 100°C.

Polypropylene (PP): Tipplen H384F (Tiszai Chemical Works (TVK) Co., Tiszaújváros, Hungary), melt flow index (230°C, 21.6 N): 12.0 g/10 min. Maleic anhydride grafted polypropylene wax (PP-g-MAH): Licomont AR 504 (Clariant GmbH., Germany). Peroxide initiator: Luperox F90P (Elf Atochem Italia S. r. I.), $C_{20}H_{34}O_4$ (1,3-1,4 bis-ter-buthylperoxyisopropyl benzene), molecular weight: 338.49 g/mole.

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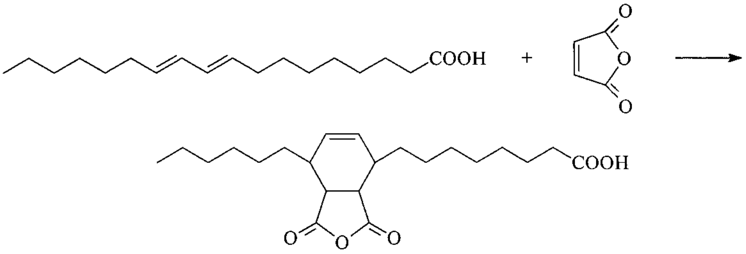
Methods

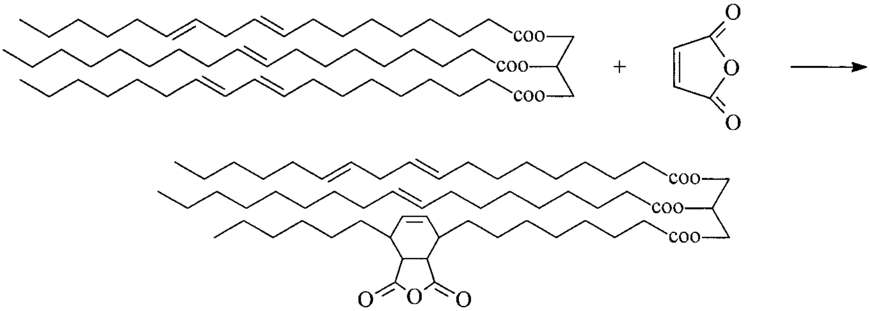
Preparation of reactive surfactants was carried out in laboratory scale by means of Diels-Alder and esterification reactions.

The LIN-MAH compound was formed by the reaction of maleic anhydride and 9,11-linolic acid (LIN) in the presence of $5 \cdot 10^{-3}$% hydroquinone inhibitor for avoiding the polymerization of the LIN; initial mole ratio was 1:1, temperature was 120°C, duration of the reaction was 90 min.



Scheme 1

SFO-MAH additive was prepared from maleic anhydride and sunflower oil (SFO) containing $5 \cdot 10^{-3}$ % hydroquinone, initial mole ratiowas 1:1, temperature was 120°C, duration of the reaction was 90 min. (SFO is a triglyceride of unsaturated (9,11-linolic acid: 26-34%, 9,12-linoleic acid: 26-34%, oleic acid: 22-39%) and saturated (5-7%.) fatty acids.)



Scheme 2

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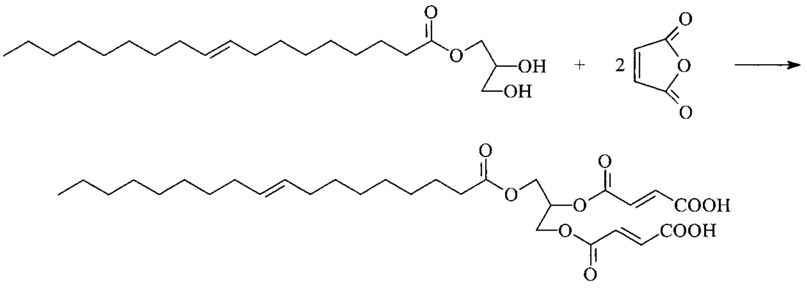
GMO-MAH additive is the diester of the glycerine monooleate (GMO) and maleic anhydride. The initial mole ratio in esterification reaction was 1:2, the temperature was 80°C, the duration of the reaction was 90 min.



Scheme 3

In order to remove the excess of solid maleic anhydride grains at the end of the reactions from the products the liquid was dissolved in toluene and filtered on a glass filter funnel. The solvent was distilled from the filtrate at atmospheric pressure (bp.: 110.6°C).

Raman microscopy was applied for monitoring the reactions, using a Jobin Yvon "LabRam" dispersion Raman microscope equipped with a CCD detector and three changeable excitation light sources: a He-Ne laser (632 nm), a frequency-doubled Nd:YAG laser (532 nm) and a diode laser (785 nm). The optical resolution of the instrument (the size of the examined area) was adjustable by means of objectives according to the features of the sample. The best available optical resolution for microscopic analysis is 0.709 μm (exciting line at 532 nm, 100x magnification, NA = 0,9 objective), while the resolution of the objective attached to an optical fiber, called "Super Head" is 0.5 mm. In the applied system the Super Head operates at the frequency of Nd:YAG laser. The laser power at the output was 50 mW.

Compounding was carried out in a Brabender Plasti Corder PL 2000 internal mixer. Polypropylene was fed into the equipment first, and immediately after the melting of the whole mass of basalt fibers and interface modifier were added. The temperature of compounding was relatively high (230°C) the processing time (15 min) and the rotation speed (15rpm) were relatively small, in order to reduce the fragmentation of the fibers. The LIN-MAH, NFO-MAH and GMO-MA additives were grafted onto the polypropylene chains by adding a calculated

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amount of Luperox F 90 P peroxide initiator ($5 \cdot 10^{-3}$ weight% of the composite). The peroxide, the surface treating compounds and the basalt fibers were mixed before adding them to the molten polypropylene. In the case of interface modification by PP-g-MAH no peroxide initiator was used. Each composite contained 20.0 weight% basalt fibers. The amount of interfacial additives was 2.0 weight% relative to the mass of fiber which means 0.4 weight% of the whole composite. Compression moulding of 160×160×4 and 160×160×2 mm size plates was performed in a Collin P200E press at 230°C applying 20 bar pressure and 15 min pressing time. Differential Scanning Calorimetry measurements were performed in Setaram DSC 92 equipment. The non-isothermal crystallization behavior of the virgin PP H384F and the composites was determined by heating the samples at first were up to 230°C at a rate of 20K/min, and then the crystallization curve was recorded at a cooling rate of 10K/min. The curves were evaluated with the Setsoft 2000 1.6.3 software.

Mechanical testing was carried out at room temperature: Charpy fracture tests were performed using a Ceast-DAS 8000 equipment according to the ISO 179 1:2000(E) standard. The notched specimens of 80×10×4 mm size had an „A" type slot and were broken with a 2J energy hammer on a 62 mm thick span holder. Three point bending tests were carried out using a Zwick Z020 equipment according to ISO 178:2001(E) standard: the 80x10x4 mm size specimens were bent on a 62 mm thick span holder with 5 mm/min cross-head speed, the Young modulus values were calculated from the initial segments of the curves. Tensile characteristics were determined by the same equipment according to the ISO 527-1 standard, the results were evaluated by the Testxpert 6.01 software.

Scanning electron microscopic (SEM) observation of the fiber-matrix boundary layers of the composites was made using a JEOL 5500 LV instrument.

Results and Discussion

The synthesis of reactive surfactants was carried out at first and the reactions were controlled using the fiber optic head of Raman microscope. The results of the synthesis of a Diels –Alder adduct is shown here as an example. Before Raman microscopic monitoring of the synthesis the spectra of the row materials (LIN and MAH) and the product (LIN-MAH) were determined, as shown in Figure 3.

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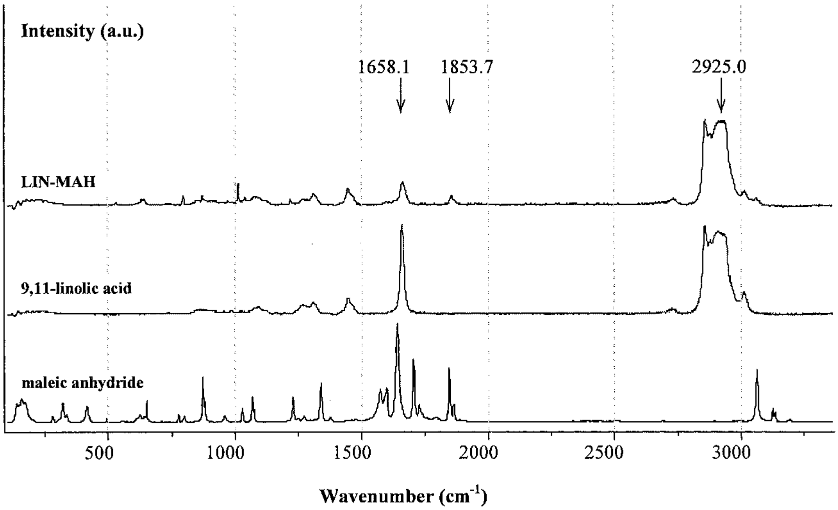

Fig. 3. The Raman spectra of linolic acid (LIN), maleic acid (MAH) and LIN-MAH compound.

The series of spectra recorded during the preparation of the LIN-MAH additive is shown in Figure 4.

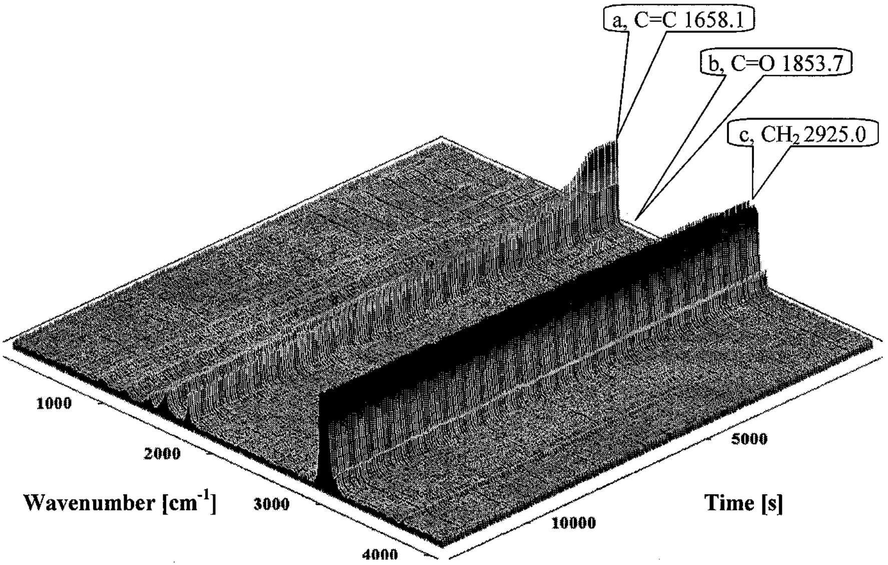

Fig. 4. Series of spectra registered by Raman microscope during monitoring the Diels-Alder synthesis showing the changing intensity of the characteristic stretching vibrations of the C=C (a), C=O (b) and CH_2 (c) groups.

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As shown in Scheme 2, 9,11 linoleic acid contains two conjugated C=C bonds. The characteristic symmetric stretching vibration of these bonds appears at 1658.1cm^{-1} and its intensity decreases in time. The symmetric stretching vibration of the C=O bond in the maleic anhydride appears at 1853.7cm^{-1}. Its intensity increased after feeding then decreased due to the reaction. The intensity of the stretching vibration of the CH_2 group appears at 2925.0cm^{-1}. The intensity of this group slightly increased in time.

The prepared additives were used at compounding of PP and basalt fibers as reactive interface modifiers. After compounding the crystallization characteristics were analysed.

Differential Scanning Calorimetric measurements were made to detect the possible nucleation effect of basalt fibers on PP. DSC curves in Figure 5 show that the non-treated basalt fibers (Curve 2), similarly to the virgin glass fibers[25] have no influence on the crystallization of the polypropylene matrix (Curve 1). Crystallinity, calculated from the heat of the crystallization, decreased by 5%. The fibers at their surface probably hinder the ordering process of the polymer chains during the crystallization of the matrix.

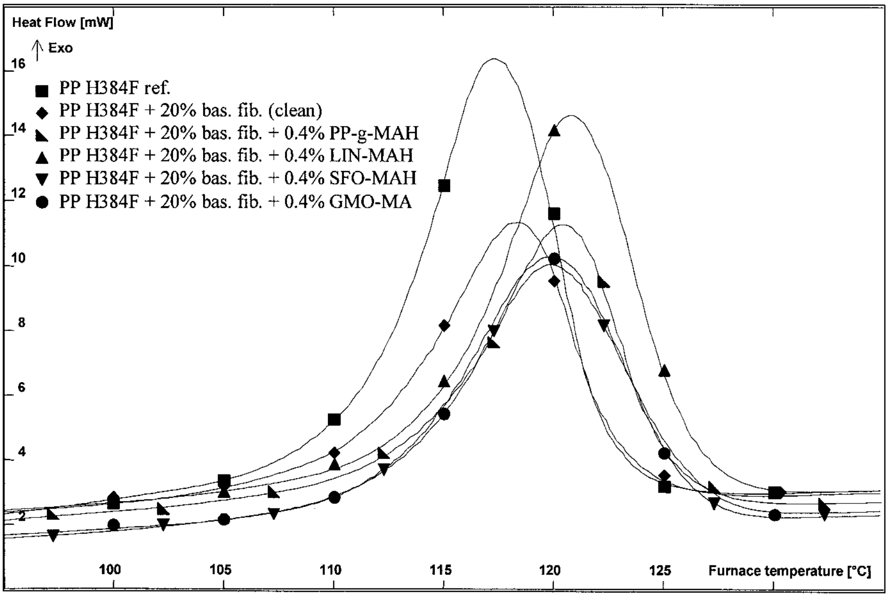

Fig. 5. The DSC curves of the virgin polypropylene and the composites.

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It can be seen from the Curves 3, 4, 5 and 6 that the surface treated basalt fibers exert an influence on the crystallization process of the PP H384F matrix. The T_{cp} (crystallization peak) values shift toward higher values by 2.6-3.5°C. Crystallinities increased as compared to the non-treated case by 4-9%. The reactive surfactant molecules adsorbed on the surface of the fibers may promote the ordering of the polyolefin chains during the crystallization, thus overcompensating the blocking effect of the fibers.

Table 1. The results of the DSC measurement.

Sample	Peak of the curve of crystallization	Crystallization heat	Crystallinity*
	°C	J/g	%
1. PP H384F ref.	117.3	- 72.43	52
2. non treat. clean fibers	118.3	- 52.53	47
3. PP-g-MAH	120.5	- 59.37	53
4. LIN-MAH	120.8	- 62.80	56
5. SFO-MAH	119.9	- 61.30	55
6. GMO-MA	119.9	- 56.73	51

* Calculated with the using of the crystallization heat of the 100% crystalline PP (- 138 J/g).[26]

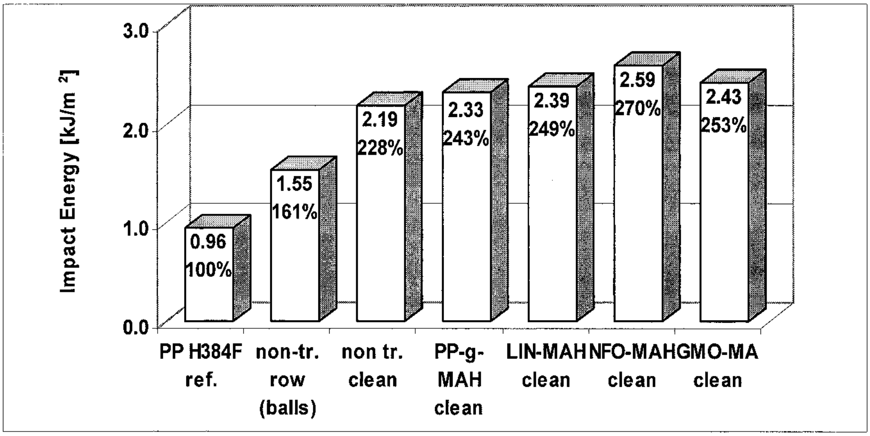

Fig. 6. The results of the Charpy fracture tests.

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Mechanical testing results show the effect of removing the fiber ends (cleaning) and modification of the interfaces The results of the mechanical tests are shown in Figures 6, 7 and 8.

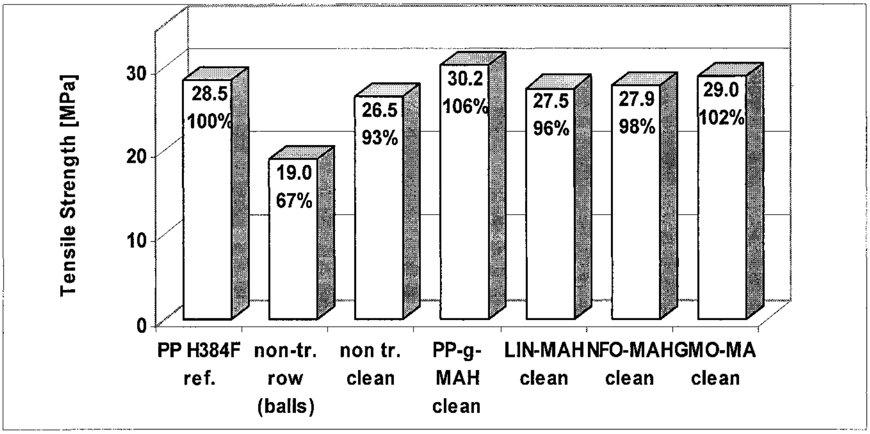

Fig. 7. The results of the tensile tests.

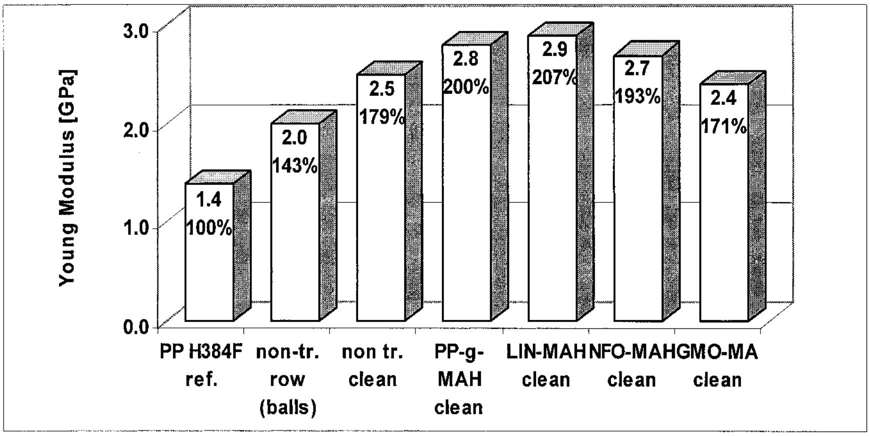

Fig. 8. The Young modulus values calculated from the bending curves.

Introducing the row basalt fibers (milled without removing the ball fraction) into the PP H384 matrix increases both impact resistance and Young modulus significantly. The improvements of these values are 61 and 43% respectively. At the same time the tensile strength is reduced by 33% as compared to the virgin PP H384F sample.

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Cleaning the milled product from the broken fiber-ends and mixing it into the polypropylene matrix improves each mechanical property. The impact resistance improves further by 67% and becomes more than twice higher than the value of the PP H384F. The increase of the tensile strength is 26% which means that it is just slightly lower than that of the matrix. The toughness of the composite increased further by more than 30%.

The surface treatment of the fibers yields further improvement in the mechanical properties. The impact resistance improves by 15-42%. The increase of the tensile strength in the case of LIN-MAH and SFO-MAH are modest (3 and 5%). The tensile strength values of these composites are comparable to that of the matrix. In the case of the GMO-MA and PP-g-MAH additives the improvement is about 10%. The Young modulus values generally increase. The only exception is the GMO-MA treatment where moderate decreasing was found.

The improved mechanical properties can be explained by increased fiber-matrix adhesion. The SEM photograph in Figure 9 shows that the absence of interlayer modification yields weak fiber-matrix adhesion. In this case the polymer matrix and the fiber are separated, due to the local stresses initiated by mechanical or thermal effects. In contrast, Figure 10 shows that in the system containing surface treating additive the adhesion of the fibers to the PP increases, therefore the polymer matrix adheres to the surface of the reinforcing fibers and does not separate from it easily.

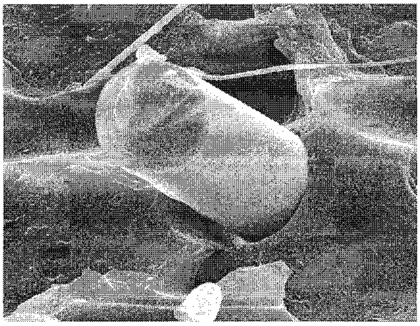

Fig. 9. The SEM photograph of the fracture surface without interface modification.

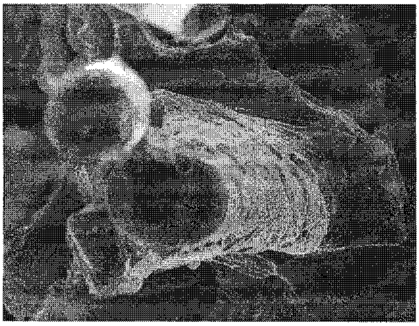

Fig. 10. The SEM photograph of the fracture surface in presence of the PP-g-MAH.

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Conclusion

New type of reactive interface modifiers could be prepared by means of Diels-Alder reaction and esterification. These additives combining the advantages of surfactants and coupling agents facilitate the reactive compounding/processing. They reach the interfacial region within the short residence time and bond phases together by reacting with both of them. Raman microscopy was found to be a suitable method to follow the progress of Diels-Alder reaction. The results of the DSC measurements show that the basalt fiber is inactive, but the interfacial additives have a nucleating effect on the polypropylene matrix.

The fiber-ends exert a weakening effect on the mechanical properties of the composites. Applying a cleaning process on the fibers, and reactive interface modification improved the mechanical properties significantly. The results show that both the commercial and the prepared non-commercial interfacial additives are effective at low concentration. The bonding to the PP matrix is promoted in case maleated PP wax by penetration PP chains into the matrix and in case of reactive surfactants by means of radical reactions. These compounds increased the fiber-matrix adhesion as confirmed by scanning electron microscopy (SEM) images.

Acknowledgment

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