# Mechanical Properties and Viscoelastic Behavior of Basalt Fiber-Reinforced Polypropylene

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**ABSTRACT:** In the present article, a series of commercial-grade polypropylenes (PP) filled with different contents of short basalt fibers were studied. This composite material presented deterioration of both mechanical characteristics, for example, stress and strain at yield with increasing of the fiber content. On the other hand, the impact strength was fourfold higher than that of unfilled PP. A poor adhesion between the PP matrix and the basalt fibers was detected. This is why interfacial interactions were promoted by the adding of poly(propylene-g-maleic anhydride) (PP-g-MA). It was observed that the tensile properties of the obtained materials and their impact strengths increased significantly with increasing of the amount of PP-g-MA in the blend. The adhesion improvement was confirmed by scanning electron microscopy as well. Fourier transform infrared spectroscopy was applied to assess if any chemical interactions in the system PP/PP-g-MA/basalt fibers exist. Dynamic mechanical thermal analysis data showed an increase of the storage modulus with increasing fiber content. The conclusion was made that the modification of the PP matrix led to a higher stiffness but its value remained constant, irrespective of the PP-g-MA content. With increasing fiber content, damping in the  $\beta$ -region decreased, but increase of the coupling agent content restored its value back to that of PP. The loss modulus spectra presented a strong influence of fiber content on the  $\alpha$ -relaxation process of PP. The position of the peaks of the above-mentioned relaxation processes are discussed as well. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 523-531, 1999

**Key words:** polypropylene composites; mechanical properties; dynamic mechanical analysis

# **INTRODUCTION**

The expanding use of polypropylene (PP) resins in different production areas is an indisputable fact nowadays. The favorable price-performance ratio encourages new developments, making PP the second most produced thermoplastic in the world. The need to meet growing sophisticated demands has lead to extensive studies in order to find new ways to improve the resin properties. Thus, a great number of studies have appeared in the literature. For some interesting examples, one could refer to articles discussing PP resins filled with smectite,<sup>1</sup> Mg(OH)<sub>2</sub>,<sup>2</sup> wheat and flax straw fibers,<sup>3,4</sup> and bamboo fibers,<sup>5</sup> etc.

It is evident that there are no obstacles in the way of searching for new fillers and for the improvement of the PP properties. Most of the at-

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tempts in recent years focused on increasing the impact strength of PP insofor as PP has a very low impact strength compared to other thermoplastics.

The main goal of this study was to determine the suitability of untreated short basalt fibers as a reinforcing agent for PP and to observe the variation of viscoelastic properties of the composites prepared. These basalt fibers are reported to be comparable to E-glass fibers for the reinforcement of thermosetting polymers.<sup>6</sup> They are produced by melt-spinning technology from naturally existing basalt rock. This type of rock contains, usually, magnetite, augite, and basic plagioclase.<sup>7</sup> Since articles on basalt-fiber reinforcement of thermosetting polymers<sup>8-10</sup> already exist, attention is focused on the possibility to use these inorganic fillers as reinforcing elements for a thermoplastic matrix. A literature search has shown that a similar study has not been published in the last 10 years.

# **EXPERIMENTAL**

## **Materials**

Commercial PP (MONTELL), with a melt-flow index of 11.06 g/10 min at 230°C (ISO 1133), was used as a matrix. The fillers were prepared from a multifilament basalt yarn that contained 150 filaments with an average diameter of 8  $\mu$ m. The tensile strength of the single filament was 430 MPa. The yarn was produced by a small-scale laboratory spinning device. Production technology of these basalt fibers can be found in the Bulgarian patent no. 35 078.<sup>11</sup> They have a composition, according to the producer, as follows: SiO<sub>2</sub> (<56%); Al<sub>2</sub>O<sub>3</sub> (10.5–22%); TiO<sub>2</sub> (<5.5%); Fe<sub>2</sub>O<sub>3</sub> (<6%); FeO (2.5–15%); MnO (<1%); P<sub>2</sub>O<sub>3</sub> (<1.5%); CaO (5–15%); MgO [(FeO > 10%) <2%]; MgO [(FeO < 10%) >3.00%]; Na<sub>2</sub>O (<5.5%).

The coupling agent used was a PP-g-MA copolymer, kindly supplied by Du Pont-Canada under the trade name Fusabond MD-356. Its MA content was 0.8 mol %, as determined by titration.

# Melt-blending and Samples Preparation

The composite preparation was performed by melt-mixing in a Haake Buchler Rheomixer 600, using roller blades and a mixing chamber with a volumetric capacity of  $69 \text{ cm}^3$ . The components

(which were physically premixed) were directly fed into the chamber heated at 200°C in its three zones. Before being added to the PP granules, the continuous yarn was cut to staples. So, the single fibers used as fillers had an average length of 8  $\pm$  2 mm. The melt temperature, reached during the mixing, was 212°C. Two series of samples were prepared by varying the fibers and coupling agent content. In the first series, PP was filled by 10, 20, and 30 wt % basalt fibers. In the second series, 5, 10, and 20 wt % of the PP-g-MA coupling agent were added to PP filled with 10 wt % basalt fibers. The amount of the coupling agent was calculated on the basis of fiber content (i.e., 10 wt % of PP-g-MA means that the content of PP-g-MA in the final composite was 1 wt %). The mixing time was 20 min at a blade speed of 80 rpm. Proof for sufficient mixing time was the constant torque value in the last 10 min of all the torque-time curves, recorded by a Haake Rheocord, Model 5000.

After being removed from the chamber, the mixtures were immediately cooled down to room temperature between steel plates under a load. This procedure was followed to avoid the milling of the material, which had the form of a molted ball, after its removal from the chamber.

# **Mechanical Testing**

The testing of the tensile properties of the samples studied was carried out with an Instron mechanical tester, Model 1122, at a crosshead speed of 5 mm/min (according to ASTM-D-638). The specimens were cut by a dumbbell-shaped die (type II) using plates of the composites prepared by hot pressing in a hydraulic press. Izod impact tests on a Tinius Olsen instrument (according to ASTM-D-256) was carried out as well. Rectangular bar specimens with a 2.5-mm-deep notch at a 45° angle were used.

Before all mechanical testings, the specimens were conditioned according to ASTM-D-618. At least five specimens of each composite were tested and the mean values and standard errors are reported.

# Dynamic Mechanical Thermal Analysis (DMTA)

The dynamic thermomechanical behavior of the samples was studied using a Rheometric Scientific Analyzer, Model MK III. The experiments were carried out using the tensile mode of the

Material	Tensile Yield Strength (MPa)	Yield Strain (%)	Izod Impact Strength <sup>a</sup> (J/m)
Unfilled PP PP + 10 wt % basalt fibers PP + 20 wt % basalt fibers PP + 20 wt % basalt fibers	$\begin{array}{c} 29.5 \pm 0.20 \\ 27.1 \pm 0.46 \\ 25.8 \pm 0.33 \\ 25.2 \pm 0.48 \end{array}$	$17.5 \pm 0.57$ $13.8 \pm 0.65$ $12.1 \pm 0.72$ $10.7 \pm 0.60$	$egin{array}{cccc} 6 & \pm \ 0.3 \ 25.2 \pm \ 0.6 \ 26.2 \pm \ 2.4 \ 25.2 \pm \ 0.1 \ 0.5 $

 Table I
 Mechanical Properties of PP Filled with Basalt Fibers

<sup>a</sup> Notched specimens.

DMTA instrument. The runs were conducted in the temperature range from -50 to  $155^{\circ}$ C with a heating rate of 3°C/min. The sinusoidal excitation had a frequency of 1 Hz and a strain level of 0.071% was applied. A static force was applied to prevent buckling of the samples. Its value was determined so that the experiments could be held in the linear viscoelastic behavior of the samples studied. The specimens were rectangular thin bars with approximate dimensions of  $8 \times 5 \times 0.5$ mm (length  $\times$  width  $\times$  thickness). The exact dimensions of each specimen studied were measured before each scan.

#### Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra were recorded using a Bio-Rad FTS-45A FTIR spectrometer. Each spectrum was obtained by coadding 64 consecutive scans with a 4 cm<sup>-1</sup> resolution. The specimens studied were in thin films (about 70  $\mu$ m thick), prepared by hot pressing in a hydraulic press.

#### **Morphology of Fracture Surfaces**

The fracture surfaces of impact specimens were observed by a scanning JEOL scanning electron microscope (SEM), Model JSM-840A. The scanned surfaces were coated with a gold layer to avoid charging under the electron beam.

## **RESULTS AND DISCUSSION**

#### **Mechanical Properties**

For the fiber-reinforced PP studied in this work, it was important to verify whether the mechanical properties of the system basalt fibers-PP were improved or not. It is well known that a strong effect cannot be obtained if the interfacial interaction between the PP matrix and the basalt fibers is not strong enough. On the other side, usually, rigid fillers such as fibers are added to the composites to reinforce the matrix by bearing some of the load. For this reason, most of the interest in PP filled with basalt fibers is focused on the study of its mechanical properties. The tensile and impact properties of the PP samples filled with different contents of basalt fibers are summarized in Table I.

It is evident that incorporation of fibers in the matrix causes a decrease of both stress and strain at yield. This behavior of the strain value is a widely observed phenomenon in all filled plastics and will not be discussed here. The lower yield stress can be explained on the basis of poor adhesion between the polar basalt fibers and the nonpolar PP. The lack of interfacial bonds makes impossible efficient load transfer from the matrix to the fibers and, in fact, the fibers disturb the continuity of the matrix, instead of reinforcing it. This results in a lowering of the stress value. Saturation is, however, seen for samples with 20 and 30 wt % basalt fibers, which have almost the same yield stress.

The data from Izod impact tests (see Table I) show an increase of the toughness of all types of samples. It is important to stress that the impact strength of the samples with different basalt content have the same value (25–26 J/m), which is about four times higher than that of unfilled PP (6 J/m). This result may be explained by assuming that the fibers dissipate energy when they are pulled out of the matrix. A comparative study of the same type of PP reinforced with E- and M-type glass fibers (6 mm in length) showed an increase of impact strength from 6 J/m to 14 and 16 J/m, respectively.<sup>12</sup> This comparison reveals



**Figure 1** SEM photomicrographs of impact-fractured surfaces of PP composites, containing different amounts of basalt fibers (without using a coupling agent): (a) 10 wt %; (b) 20 wt %; (c) 30 wt %.

the real capabilities of basalt fibers for reinforcing of the isotactic polypropylene (iPP) matrix.

The poor adhesion between the iPP matrix of the above-discussed samples and untreated basalt fibers was found on the fracture surfaces by SEM observation (Fig. 1). The fiber surfaces are not covered with the polymer and well-defined holes of pulled-out fibers could be observed. The distribution of the basalt fibers is uniform throughout the polymer matrix.

It is known that the overall properties of any composite can be improved by introducing interfacial interactions between the filler and the matrix. The chemical composition of basalt fibers is similar to the composition of E-glass fibers.<sup>13</sup> Both of them contain more than 50% SiO<sub>2</sub>. As was reported by Xanthos,14 maleated PP is an effective coupling agent for various silicates embedded in a matrix of PP. This is due to reactions of MA groups with hydroxyl groups of the silicate. In addition, hydrogen bonds could be formed between the created carboxylic groups and hydroxyl groups of the silicate. The sample with 10 wt % basalt fibers, having the highest values of yield stress and yield strain, was chosen for in situ modification with the PP-g-MA copolymer as a coupling agent. The added amount of copolymer was based on basalt fiber content. Thus, the maximum amount of the copolymer was 2 wt % (for a level of 20 wt % based on basalt). For this reason, its effect on the mechanical properties, as a third different component, is rather insignificant. Thus, any observed differences will be due to the different extent of adhesion between PP and the basalt fibers. A further increase of PP-g-MA content would also deteriorate the matrix properties because it has lower yield stress (18.8 MPa) compared to PP.

As can be concluded from the results in Table II, the yield stress increases monotonically with increasing PP-g-MA content. On the other hand, the yield strain slowly decreases. The probable explanation is that, as far as the material becomes harder and stiffer, the elongation at yield decreases. The sample with 20 wt % PP-g-MA (+10 wt % basalt fibers) reaches a stress value of 35.5 MPa. This is concurrent with the yield strength value of 34 MPa of PP reinforced with short glass fibers possessing good adhesion, as reported by Gupta et al.<sup>15</sup> For comparison, one can quote the relevant properties of PP filled with other fibers. Horsby et al.<sup>4</sup> published values of the tensile yield strength of PP reinforced with 25 wt % flax straw (36.4 MPa without a coupling agent and 39.1 MPa with 5 wt % PP-g-MA on fiber content), wheat straw (29.7 MPa without a coupling agent and 32.3 MPa with PP-g-MA), and glass fibers (35.2 MPa without a coupling agent). In their study, the strength of unfilled PP was 32.9 MPa. Comparison of the reported data with

Material	Tensile Yield Strength (MPa)	Yield Strain (%)	Izod Impact Strength <sup>a</sup> (J/m)
PP + 10 wt % basalt fibers + 5 wt % PP-g-MA	$29.8\pm0.70$	$11.9\pm0.51$	$28.5\pm0.6$
PP + 10  wt  %  PP-g-MA $+ 10  wt  %  PP-g-MA$	$31.2\pm0.84$	$11.6\pm0.37$	$32.6\pm2.5$
PP + 10  wt  %  basalt fibers + 20 wt % $PP$ -g-MA	$35.5\pm0.48$	$10.8\pm0.62$	$32.8\pm0.9$

 Table II
 Mechanical Properties of Basalt Fiber-reinforced PP Modified

 with PP-g-MA
 PP-g-MA

<sup>a</sup> Notched specimens.

the results mentioned above is not possible because of a difference in fiber length and PP grade. It is, however, obvious that the same order of magnitude in the figures is a demonstration for the potential of short basalt fibers to reinforce the PP matrix when they are used together with the PP-g-MA copolymer.

The use of a coupling agent further increases the impact strength (see Table II), which reaches a constant level for samples with 10 and 20 wt %PP-g-MA (33 J/m). These results are comparable to the impact strength values of short glass fiberreinforced PP. Gupta et al.<sup>15</sup> reported a threefold increase in toughness from 22 J/m (for unfilled PP) to 66 J/m (for PP filled with 10 wt % glass fibers, having good adhesion with the matrix). In our case, 10 wt % basalt fibers enhances the impact strength over fives times (from 6 to 32.8 J/m) when PP-g-MA is added. This difference is possibly due to the larger specific area of the basalt fibers, which increases the frictional work (more energy dissipation) during pulling the fibers out of the matrix. The efficiency of the coupling agent is displayed by the SEM micrographs of the impact fractured surfaces (Fig. 2). In the composite that contains 5 wt % of the PP-g-MA copolymer, the adhesion remains very poor. The amount of the copolymer in this case was rather small (only 0.5 wt %) to improve adhesion. On the contrary, when the copolymer is added in higher amounts, such as 10 and 20 wt % of the fiber content, the SEM photographs manifest improved adhesion. In this case, the fiber surface is impregnated by a thin polymer layer while the fibers appear well separated and without clustering. In the same case, gaps between the matrix and some fibers are visible, probably due to displacement of the fibers

by impact forces. The rest of the fibers seem to be tightly held by the matrix.

To examine the existence and the type of interfacial bonds in the system, FTIR experiments were performed on the studied composites and compared with the pure materials (Fig. 3). In the spectrum of the copolymer, excepting the PP peaks,<sup>16</sup> the characteristic peaks of the MA group at 1865, 1788, and 1717 cm<sup>-1</sup> are also observed. Since these three peaks are not detected in the composites containing basalt fibers [Fig. 3(a)], it can be concluded that all the MA groups have reacted with the hydroxyls of the basalt fibers.

#### **Dynamic Mechanical Analysis**

The viscoelastic behavior of the obtained composite materials was studied using a DMT analyzer. The temperature dependencies of the dynamic mechanical properties are presented in Figures 4–7 and related data in Table III.

It is evident that the stiffness (tensile E' modulus) increases with increasing basalt fiber content (Fig. 4). The use of a coupling agent (PP-g-MA) enhances further the storage modulus (E') but the effect is not so pronounced (Fig. 5). The viscoelastic modulus (E') reaches a constant level for samples with 10 and 20 wt % PP-g-MA. Therefore, further addition of coupling agent is not expected to improve the properties of the final materials to a large extent.

It is worth pointing out that the E' values of the sample with 5 wt % PP-g-MA are equal to those of the sample without PP-g-MA (0 wt %) below 0°C. Nevertheless, the E' values of the samples with 10 and 20 wt % PP-g-MA become equal at temperatures above 50°C. It should be



**Figure 2** SEM photomicrographs of impact-fractured surfaces of PP composites reinforced with 10 wt % basalt fibers, containing different amounts of PP-g-MA: (a) 5 wt %; (b) 10 wt %; (c) 20 wt %.

mentioned that the tensile E' modulus at 23°C of PP filled with 10 wt % short glass fibers is 2100 MPa, as reported by Amash and Zugenmaier.<sup>17</sup> In their study, the unfilled PP had an E' modulus of 1578 MPa at 23°C and the measurements were performed at a frequency of 10 Hz. In principle,



Figure 3 FTIR spectra of (a) PP + 10 wt % basalt + 20 wt % PP-g-MA, (b) PP + 10 wt % basalt, (c) unfilled PP, and (d) PP-g-MA.

the higher the frequency, the higher is the modulus. Thus, the basalt fibers are quite competitive reinforcing elements for PP resins, from a mechanical properties' point of view.

To analyze correctly the spectra of the studied samples, it is useful to mentioned some features of the PP spectra. As reviewed by McCrum et al.,<sup>18</sup> the tan  $\delta$  curves of iPP show three relaxation peaks at  $-80^{\circ}$ C ( $\gamma$ ),  $8^{\circ}$ C ( $\beta$ ), and  $100^{\circ}$ C ( $\alpha$ ). The temperature of the  $\beta$ -relaxation maximum is believed to correspond to the glass transition temperature ( $T_g$ ), and the  $\alpha$ -relaxation, which looks like a shoulder, is related to a slip mechanism of polymer chains in the crystallites. The  $\gamma$ -peak is



**Figure 4** Storage modulus (E') versus temperature (°C) as a function of basalt fiber content at a frequency 1 Hz.



**Figure 5** Storage modulus (E') versus temperature (°C) as a function of PP-*g*-MA content at a frequency 1 Hz.

due to motions of small-chain groups like methyl and methylene. In this article, we prefer to present the loss modulus (E'') spectra instead of the tan  $\delta$  spectra because the exact evolution of  $\alpha$ and  $\beta$ -relaxation is clearer to observe in loss modulus (E'') curves. At this point, it can be mentioned that the magnitude of the  $\alpha$ -peak depends on the molecular weight of the studied PP (according to our own unpublished data). The higher the molecular weight, the smaller is the peak. This explains why, in some cases, the  $\alpha$ -peaks cannot be distinguished on E'' curves.

Some important data from the damping  $(\tan \delta)$  spectra are, however, presented in Table III. They



**Figure 6** Loss modulus (*E*") versus temperature (°C) as a function of basalt fiber content at a frequency 1 Hz.

show that the incorporation of basalt fibers in the matrix shifts the maximum of  $\beta$ -relaxation (i.e., the  $T_{\sigma}$  of PP) to a lower temperature and decreases the peak magnitude. The smaller magnitude indicates that the matrix toughness diminishes. At the same time, the impact strength of the composites (see Table I) is higher compared to that of unfilled PP. This result can be interpreted by the assumption that the energy dissipation, when fibers are pulled out of the matrix, plays a major role for the elevated impact strength. The lower  $T_g$  values signify that the filler affects the mobility of the PP chains. The maximum of  $\beta$ -relaxation is lowered additionally when PP-g-MA is added. In this case, however, the peak intensity does not show a clear trend.



Figure 7 Loss modulus (E'') versus temperature (°C) as a function of PP-g-MA content at a frequency 1 Hz.

	Storage Modulus $E'$ (Mpa) at		Damping at β Maximum		Loss Modulus $E''$ (MPa)				
Material	-20°C	23°C	50°C	$\begin{array}{c} T_g \\ (^{\circ}\mathrm{C}) \end{array}$	tan δ	T (°C)	β-Peak E″	T (°C)	α-Peak E″
Unfilled PP	2202.9	1528.9	1150.0	16.8	0.0461	12.7	82.1	70	56.6
PP + 10 wt % basalt fibers	3003.3	2102.3	1613.2	13.8	0.0425	10.0	101.9	76.6	102.6
PP + 20 wt % basalt fibers	3213.7	2520.5	2092.7	12.8	0.0335	10.0	91.7	90.6	208.8
PP + 30 wt % basalt fibers	3218.1	2665.9	2281.4	11.0	0.0290	9.7	83.4	100.7	226.7
PP + 10 wt % basalt fibers + 5 wt % PP-g-MA	3005.4	2240.9	1808.4	12.7	0.0378	10.0	93.7	80.4	83.1
PP + 10 wt % basalt fibers + 10 wt % PP-g-MA	3144.9	2281.8	1802.2	11.6	0.0376	7.9	98.3	75.7	77.8
PP + 10 wt % basalt fibers + 20 wt % PP-g-MA	3248.6	2281.8	1820.5	11.3	0.0401	8.8	104.5	75.2	76.5
PP-g-MA	2409.3	1130.9	693.3	10.1	0.0746	-1.5	117.2	62.1	48.6

Table III Dynamic Mechanical Properties of the Materials Measured at 1 Hz

The temperature dependencies of the loss modulus as a function of the basalt fiber and PP-g-MA content are presented in Figures 6 and 7, respectively. A decrease of the intensity of the  $\beta$ -peak is observed for samples with a greater amount of basalt fibers. However, in all the composites, the intensity is higher compared to that of unfilled PP (Fig. 6).

The temperature position of the  $\beta$ -peak shifts to a lower temperature, which is not influenced by the fiber presence (see Table III). The magnitude of the  $\alpha$ -peak grows significantly with the fiber content and its maximum moves gradually to a higher temperature, if there is no PP-g-MA.

The improved adhesion between the components (Fig. 7) modifies the  $\beta$ -relaxation process but without showing a clear tendency. Regarding the process of  $\alpha$ -relaxation, the increase of the PP-g-MA content leads to a decrease of the intensity of the  $\alpha$ -peak. An overlapping of  $\alpha$ -peaks of the samples containing 10 and 20 wt % PP-g-MA is observed. Finally, it must be mentioned that the variations in the DMTA curves of the PP composites studied manifest the same tendency as do the changes in the curves of PP composites filled with glass fibers.<sup>17</sup>

# **CONCLUSIONS**

This work has shown that the incorporation of untreated short basalt fibers in a matrix of PP deteriorates its tensile properties because of the poor fiber/matrix adhesion. To enhance the interfacial interactions, PP-g-MA was used as a coupling agent. The so-modified composites present a considerable increase of the stress value at yield. A significant increase of impact strength is also observed in all types of samples containing basalt fibers. The effect is attributed mainly to the frictional work during the pulling of the fibers out of the matrix.

The increase of basalt fiber content of the composites enhances their stiffness (E'). However, the storage modulus remains unchanged with the content of PP-g-MA in the composites over a wide temperature range. The fiber reinforcement and the additional modification with a coupling agent produce a pronounced effect on the damping properties of the matrix. The loss modulus curves reveal clear tendencies in the alteration of  $\alpha$ - and  $\beta$ -relaxation processes depending on filler content and adhesion improvement. Therefore, the conclusion can be made that the use of basalt fibers as a nontraditional material is possible for PP reinforcement.

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