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Dynamic Mechanical Behavior of PP/PET/MAPP Blends Filled with Glass Beads

M. A. Rodríguez-Pérez,[1] J. I. Velasco,*[2] *J. I. González-Peña,*[1] *J. L. Ruiz-Herrero,*[1]
D. Arencon,[2] *J. A. de Saja*[1]

[1] Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid, Spain
E-mail: marrod@fmc.uva.es
[2] Centre Català del Plàstic, Universitat Politècnica de Catalunya, Colom 114, 08222 Terrassa. Spain

Summary: PP/PET/MAPP blends have been filled with 50 wt% of glass beads. The orientation of the PP crystalline phase, the crystallization behavior and the dynamic mechanical response of these materials have been analyzed. The dynamic mechanical response is strongly affected by the presence of the glass beads, being possible to detect the effect of PET and MAPP on the storage modulus and loss factor values. Moreover, the alpha relaxation of the composites is visibly affected by thermal treatments.

Keywords: composites; differential scanning calorimetry; dynamic mechanical analysis; fillers; poly(propylene)

Introduction

Glass bead-filled polypropylene (PP) composites have a good processability, small and well-distributed internal stresses, good dimensional stability, and good service performance [1-3] . Due to these reasons several investigations have been performed for these kind of composites, focused on aspects related with the particle size, filler content, mechanical properties, interfacial adhesion, etc.[1-7]. However, taking into account the intricate micro-structure of these materials there are several aspects, as for example the dynamic mechanical behavior, in which more detailed studies seems to be necessary.

From a scientific point of view, it is very well known that particles with high aspect ratio are one of the main sources for the anisotropy of composites, examples of these materials are PP-talc, PP-aluminum hydroxide or PP-glass fibers [8]. One interesting feature of glass beads particles is their isotropy due to their spherical shape, and therefore they do not contribute to the composite anisotropy, so the induced polymer orientation due to the filler should also be reduced. It is also well known, that filler and polymer matrix orientation play an important role in the structure-

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property relationships of a polymer filled system. In fact the effect of this parameter could cover the effect of other important structural aspect such as filler content, adhesion between filler and polymer, particle size distribution, etc. Therefore, it is expected that due to glass beads isotropy, more simple structure-property relationships could be obtained for the composites under study.

One of the most important aspects which modify a given polymer filled system is the interfacial adhesion between the filler and the polymer. In this investigation three different approaches have been considered to modify this feature. First, maleic-anhydride grafted polypropylene (MAPP) has been blended with the PP matrix, second glass particles have been treated with different coupling agents based on silanes, and finally poly(ethylene terephthalate) PET has also been added. It has been proposed the use of some polar thermoplastic polymers, such as polyamide [9] or polycarbonate [10], as efficient adhesion promoters in filled PP composites. Following this idea, we analyse here the use of poly(ethylene terephthalate-co-isophthalate) (co-PET) in glass bead filled PP.

Bearing the previous ideas in mind, in the present work, an attempt has been made to show how the dynamic-mechanical behavior of a series of PP-glass bead composites is affected by the addition of PET, maleic-anhydride grafted polypropylene (MAPP) and silane treated glass beads.

Materials

The polypropylene (Isplen PP050) used in this study was provided by Repsol-YPF. It is an isotactic homopolymer grade with a MFI (230 °C, 2.16 kg) of 5.0 dg/min. Glass beads with an average particle size of 20 μm were used as filler, being kindly provided by Sovitec Ibérica, S.A. A commercial grade of maleated polypropylene (EPOLENE G-3003), with an acid number of 8, was supplied by Eastman Chemical. Extrupet EW36 was the copolymer grade of PET manufactured by Catalana de Polímers S.A. (intrinsic viscosity of 0.8 dl/g) used in this investigation. Four different matrix compositions were selected as shown in Table 1a. Four different silane coupling agents were employed for surface tretament of the glass beads (Table 1b). The following procedure was used to homogeneously coat the glass bead with the silane: a solution containing 30 ml of silane, 250 ml of methanol, 60 ml of water and 5 ml of acetic acid was added to 1.5 kg of glass beads. This solution was stirred for 20 min to assure the hydrolysis of the alkoxy group in the silanes. The solution was transferred into a flask and glass beads were then added gradually while stirring. The mixture was then heated up to 40 °C to evaporate the solvent. Stirring was continued as long as the viscosity of the mixture was low enough. The non-reacted silane was washed out with methanol.

Composites containing nominally 50 wt% of glass beads and different matrix compositions were prepared using a Collin ZK-35 twin screw extruder. Standard dumb bell specimens (type "I" according to ASTM D638) were injection-molded using a 440/90 injection molding machine and a mould (tempered at 60°C) as described in Figure 4 (ASTM D-647 standard). In order to eliminate any residual stresses produced during injection molding the dumb bell test specimens were annealed at 110 °C for 24 h.

Table 1a.Composition of the matrix expressed in percentages by weight.

Reference	A	B	C	D
Matrix composition	PP (100)	PP/MAPP (97/3)	PP/PET (95/5)	PP/MAPP/PET (92/3/5)

Table 1b. Silane treatments applied on the glass bead surfaces. Supplied by a) Dow Corning, b) Witco

Surface treatment reference	**Silane**	**Commercial name**
1	–	–
2	3-metacriloxipropyl trimethoxy silane	Z-6030$^{(a)}$
3	3-mercaptopropyl trimethoxy silane	A-189$^{(b)}$
4	N-(2-aminoethyl)-3-aminopropyl trimethoxy silane	Z-6020$^{(a)}$
5	N-(2-(vinylbencylamino)-ethyl)-3-aminopropyl trimethoxy silane	Z-6032$^{(a)}$

Experimental

Wide angle X-ray diffraction experiments (WAXD) were performed to analyze the PP crystalline orientation. The experiments were performed using a Phillips PW 1050/71 diffractometer. Radial scans of intensity (I) versus scattering angle (2θ) were recorded in the range 5-50 ° by using filtered Cu K_α radiation. The testing was carried out using prismatic bars, extracted from the dumb bell specimens (Figure 1), of nominal dimensions 25 x 5 x 3 mm^3.

Differential scanning calorimetry (DSC) measurements were performed using a Perkin-Elmer Pyris 7 calorimeter. Sample mass was between 8 and 9 mg, the samples were cut from dumb bell specimens as showed in Figure 1. After the erasing of the thermal history (200°C for 4 minutes) cooling measurements were conducted from 200 to 25 °C with several cooling rates: 5, 10, 15, 20, 25, 30, 40 and 60 °C/min. All runs were carried out in a stream of dried nitrogen. After each cooling experiment a heating run between 25 and 200 °C was performed at 10 °C/min.

The method developed by Dobreva and Gutzow [11] was applied to analyze the non-isothermal crystallization experiments. From this analysis, a nucleating activity parameter (ϕ) can be obtained for the filler. The value of ϕ decreases from 1 to 0 as the polymer crystallizes in the presence of more efficient nucleating particles. This approach has been successfully applied to evaluate the nucleating rate of PP filled with different mineral particles [12-14].

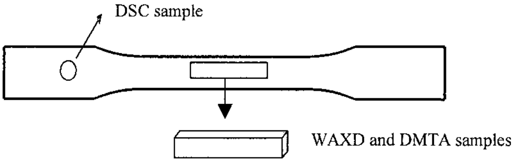

Figure 1. Injection-molded dumb bell specimen showing the sample extraction zone for DSC analysis and the machined prismatic specimen used in WAXD and DMTA analysis.

Dynamic mechanical thermal analysis (DMTA) was carried out using a Perkin-Elmer DMTA 7 and a Mettler DMA861-e equipments. The testing configuration was three-point bending with a span of 20 mm. The samples employed were the same used for WAXD measurements. A static stress of 6 MPa and a dynamic stress of ± 5 MPa were applied with a frequency of 1 Hz. For each material two kinds of tests were performed. First, experiments at 20 °C were performed to obtain quantitative results of the storage modulus (E') and the loss factor (tan δ). The values were collected 5 min after applying the stresses, i.e., once the initial fluctuations of the values had disappeared. Second, the study of the composites relaxations was carried out by tests performed in the temperature range from –40 to 130 °C at a heating rate of 5 °C/min.

Results

The orientation of the monoclinic α-phase PP crystals in the injection-molded samples has been studied by WAXD. The relationship between the orientation of PP a- and b-axes can be determined by calculating the ratio of the intensity of the PP (040) plane (peak at 2θ=16.7 ° in the diffraction pattern) to that of the (110) plane (peak at 2θ=13.9°). The results obtained are summarized in Table 2. Several values of this ratio can be found in the literature for filled polypropylene [12,14]. Moreover, several authors have reported values for an isotropic mixture of PP crystallites, for example 0.54 [15] and values comprised between 0.67 and 0.77 [16].

Table 2. WAXD results, activity parameter (Φ), storage modulus (E') and loss factor (tan δ), glass transition temperature (T_g) and α relaxation temperature (T_α).

Sample	$\frac{I(040)}{I(110)}$	Φ	E'(GPa)	tan δ	T_g (°C)	T_α (°C)
PP	1.44	1.00	1.6	0.054	-0.8	52.4
A1	0.98	0.72	3.0	0.041	-1.1	56.1
A2	1.06	0.77	3.5	0.040	-0.5	61.6
A3	1.00	0.62	3.2	0.039	-1.4	61.1
A4	0.97	0.71	2.9	0.035	0.5	61.1
A5	0.90	0.66	3.2	0.030	0.6	59.4
PP/MAPP	—	1.00	—	—	—	—
B1	1.17	0.53	2.8	0.040	0.2	57.6
B2	0.97	0.46	3.1	0.039	0.2	61.6
B3	1.10	0.55	3.2	0.035	0.2	62.5
B4	1.21	0.52	3.3	0.035	0.9	61.7
B5	1.07	0.55	3.0	0.032	0.9	61.7
PP/PET	1.17	0.52	1.7	0.046	0.3	52.1
C1	1.05	0.49	3.1	0.034	0.1	57.1
C2	1.01	0.56	3.1	0.032	0.0	59.6
C3	0.99	0.53	3.0	0.040	0.8	59.8
C4	0.95	0.46	3.0	0.031	1.0	65.0
C5	0.93	0.49	3.3	0.029	1.2	61.9
PP/MAPP/PET	1.35	0.51	1.9	0.042	0.7	54.6
D1	1.08	0.52	3.4	0.032	0.6	64.5
D2	1.20	0.46	3.2	0.031	0.6	64.3
D3	1.07	0.52	3.2	0.030	1.0	59.4
D4	1.06	0.36	3.4	0.028	1.3	62.6
D5	1.02	0.41	3.4	0.031	1.3	59.2

It is noticed that both PET and glass beads lead to intensity ratios close to 1, resulting in an homogenization of the polypropylene orientation due to these two components. The PET effect contrasts with that observed by Saujanya et al. [17] in PET fiber-reinforced PP composites in which the crystallite growth along b-axis is strongly affected by the presence of PET fibers. It should be mentioned that substrates with higher aspect ratio usually involve transcrystallinity structures in polypropylene [18, 19], allowing a preferential location of polypropylene chains. In previous investigations [12, 14] the anisotropy ratios for other PP systems were measured, the value was 6 for PP-talc composites, 21 for PP-silane treated talc materials, and 19 for PP-magnesium hydroxide materials. Therefore, as it was assumed in the introduction of this paper, glass beads particles, in comparison with other fillers, reduce the PP crystalline phase orientation of the composites.

On the other hand, it was appreciated that MAPP slightly promoted PP orientation, probably, due to the compatibilizing action of the copolymer. Finally, silane treatments does not have an obvious effect on the PP orientation.

The nucleating activity (ϕ) of glass beads is not to high (0.70) in comparison with that of other fillers (see DMTA results). The activity parameter is smaller (0.52) when PET was added to PP, indicating a higher nucleating rate. MAPP presence enhanced the nucleation activity of glass beads, leading to a significant reduction in ϕ values for all the composites with PP/MAPP matrix. On the other hand, glass beads addition into PP/PET and PP/MAPP/PET blends did not greatly change the values of ϕ when compared with unfilled blends.

With respect to the surface treatments applied on glass beads, although controversial opinions are found in the literature, in this work it was detected that the use of silanes with any aminofunctional group (silanes Z-6020 and Z-6032) enhanced slightly the nucleation activity of the glass beads.

Storage modulus values obtained from isothermal test (Table 2) showed, in unfilled samples, that the addition of PET increases slightly the stiffness. This increase is higher when MAPP was added, probably due the compatibilizing effect of MAPP in the PP/PET blend. The presence of glass beads in the PP matrix increases noticeably the stiffness of the compound, although there is no clear trend concerning the effect of the silane surface treatments applied.

It was observed a slight decrease (Table 2) in the value of the loss factor when PET was added to the polypropylene matrix. At room temperature, PET is under its glass transition temperature, therefore, a reduction of the viscoelastic character of the material is expected. A further reduction of the loss factor value was observed in the PP/MAPP/PET blend. This fact has been related to an enhanced interfacial adhesion between phases [10], which would hinder the molecular motion of polypropylene chains at the interface.

It is observed a remarkable reduction of the tan δ value when PP is filled with 50 wt% of untreated glass beads. This behavior is due, on the one hand, to the lower weight fraction of polymer in the composite, and on the other hand to the reduced mobility of the polymer phase close to the glass particles. Surface treatment of glass beads leads to a further reduction, in an extent that depends on the silane employed. Once again, this result should be understood in terms of the reduced mobility of the polymer molecular segments at the interface.

The loss modulus (E'') for all the samples has a maximum around 0 °C (Figure 2), which is associated with the glass transition of polypropylene (T_g). The obtained values for the glass transition temperature are collected in Table 2. Small differences between samples were established, as the values ranged between –1 and 1 °C. Moreover, there is no clear trend concerning the effect of glass beads. Nevertheless, as a general trend, it was observed that all the composites containing MAPP showed slightly higher T_g values than their homologous without copolymer. In addition, the highest values for each matrix composition were displayed by the samples with glass beads treated with silanes Z-6020 and Z-6032. This slight increase should be related with stronger interactions between matrix and filler promoted by silanes.

The shifting of the glass transition when PP is filled is an interesting subject in which a different behavior has been observed depending of the used filler. For instance, a reduction of the T_g value [12] (measured by DMTA) was observed for both PP-talc and PP-silane treated talc composites. The results for PP-Mg $(OH)_2$ or PP-Al $(OH)_3$ composites are similar to that for glass beads [13,14], the T_g remains constant. In our opinion, one of the main reasons for these differences is the different nucleating activity of each filler in the polymer crystallization. The nucleating activity of glass beads into PP (ϕ=0.70) is less effective than that displayed by crystalline mineral fillers like talc (ϕ=0.32 [12]), magnesium hydroxide (ϕ=0.52 [13]) or aluminum hydroxide (ϕ=0.54 [14]). Therefore, a very high nucleating activity seems to modify the PP morphology in an extend which shifts the glass transition temperature.

Both unfilled and filled samples displayed an additional maximum (T_α) located around 50-70 °C (Figure 2). Controversial opinions are found in the literature about this relaxation. McCrum [20] ascribes this relaxation to both mechanisms of lamellar slipping and rotation between crystalline entities. Jančář [21] supposes that this maximum is the consequence of a release of strongly hindered segmental mobility of molecules from the interface on the filler surface. This author also supposes that the relaxation is probably the glass transition peak of PP immobilized close to the filler surface, reporting the development of this relaxation with filler contents above 26 % vol., while it was no detected for unfilled PP. On the other hand, Stricker et al. [2] ascribe the existence of this transition to the quenching melts of glass bead filled PP, noticing that slow cooling and crystallization avoid this effect and discard the existence of the maximum due to presence of immobilized matrix.

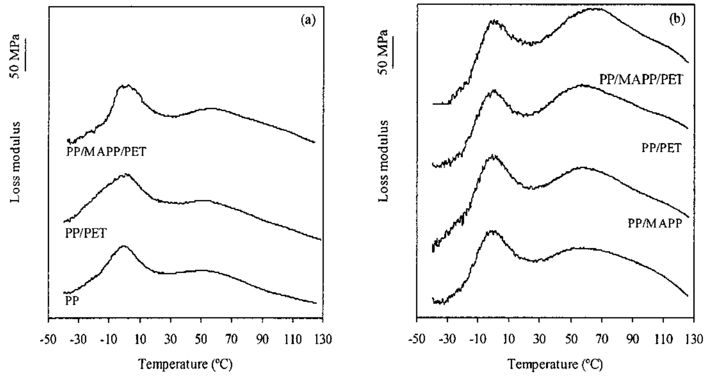

Figure 2. Loss modulus vs. temperature of a) unfilled samples and b) composites with untreated glass beads. Heating rate = 5 °C/min. Frequency = 1 Hz.

The values of the maximum of the α relaxation (T_α) are collected in Table 2. Contrary to the results observed by Jančář, we have observed this relaxation in the unfilled samples. Both its intensity and temperature have been very similar for the polypropylene and the PP/PET blend (Figure 2). On other hand, in the blend PP/MAPP/PET, the relaxation was more intense and shifted to higher temperatures, which might be a consequence of the compatibilizing effect exerted by MAPP. In the filled composites, the α relaxation showed the highest intensities, detecting that PET presence causes a build-up of the intensity. It is perceptible that in general terms silane surface treatments increased the T_α values.

From the obtained results it seems that this relaxation depends on the interactions between the PP and the other phases, increasing its intensity and shifting to higher temperatures when both glass beads and PET are added. Moreover, a similar trend was observed when MAPP and a glass bead surface-treated with silane were included in the formulation. Nevertheless, the existence of this relaxation in the unfilled PP involves a relationship with the PP crystalline phase, and may suggest that the special molding conditions (mould temperature 60 °C, cooling time 30 s, annealing at 110 °C for 24 h) applied to the produced materials could induce a particular crystalline structure which is able to develop into more stable states, under the DMTA testing conditions.

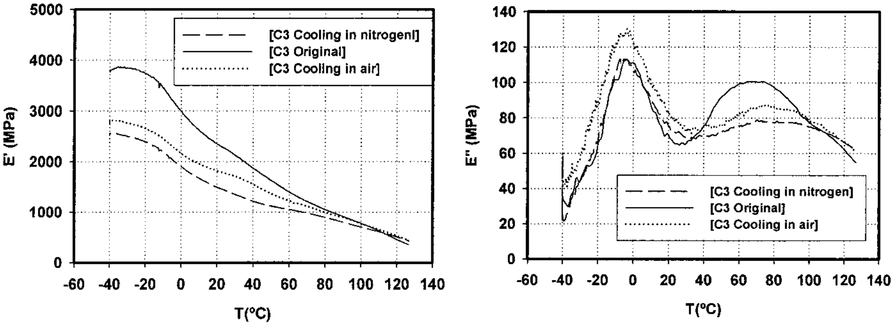

Figure 3. Dynamic Mechanical behaviour of sample C3 under different thermal treatments.

To check the previous hypothesis, the thermal history of several samples was modified by performing two different thermal treatments. First, annealing at 145° C for 1 hour and cooling in liquid nitrogen and second annealing at 145 °C for 1 hour and cooling in air. After these treatments, DMTA experiments in a Mettler 861-e equipment were carried out. A typical example of the results (C3 sample) is shown in Figure 3. As it can be observed, there is an obvious difference between the original material and the treated ones. Due to the treatments the storage modulus is clearly reduced, the alpha transition is shifted to higher temperatures and its intensity is also reduced. These two effects are more marked for the sample cooled in liquid nitrogen. Moreover, the glass transition temperature does not change by the treatments. Therefore, the treatments modify the crystalline structure of the polymer matrix and this modification is detected by DMA in a softer material, showing a less intense alpha relaxation.

Conclusion

Storage modulus of polypropylene increased slightly with the addition of PET, and considerably when glass beads were added, whereas the loss factor followed the opposite trend. Some of the DMTA trends seemed to be related to the compatibilizing effect of MAPP. Very small differences in the glass transition temperature of both unfilled and filled samples were found, probably due to the low activity of the filler. Under the applied processing conditions, it has been observed the α relaxation of PP at temperatures between 50-70 °C. This relaxation has been detected for all the materials under study, being its intensity and peak temperature determined by the presence of PET, MAPP and glass beads. It has also been observed that this relaxation is very sensitive to thermal treatments.

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