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Abstract: Poly(ethylene terephthalate) (PET) composites containing muscovite mica as reinforcing filler were prepared by melt mixing, and their molecular dynamics were investigated by low-field NMR. Spin-lattice and proton spin–spin relaxation times of composites containing different amounts of the filler from 2 to 15 wt% were evaluated and the results compared with pure PET. DSC showed that for systems containing muscovite mica in percentages above 2 wt% a high level of crystallinity is achieved. By proton spin-lattice relaxation studies, a slight decrease in the T_1H is observed for the composites with filler content up to 8 wt% and a drastic decrease at the higher filler content (15 wt%). Changes in T_1H were associated with the content of amorphous phase in the composite.

Keywords: Low-field NMR; Molecular dynamics; Muscovite mica; Poly(ethylene terephthalate)

INTRODUCTION

Mica-reinforced thermoplastics are becoming increasingly important.[1,2] When used as reinforcing filler in plastics, mica offers many advantages including planar reinforcement, reduced creep, and reduced wear of processing equipment.[3] The incorporation of mica into plastics is also known to increase the stiffness and to reduce the elongation at yield and at break,[4] resulting in apparently brittle materials. However, in practice, as the propagation of cracks originates from flaws that exist in most structures, the performance of mica-based composites is also dependent upon the filler degree of dispersion, morphology, and degree of interaction between mica surface and the polymer matrix.[5]

Poly(ethylene terephthalate) (PET) reinforced with mica has received particular attention due to its high stiffness, low cost, good dimensional stability, and adequate temperature performance.[6] In Brazil, rock-formed muscovite mica is readily available and reasonably cheap.[7] Therefore, PET/muscovite mica composites may result in low-cost composites.

Muscovite mica $(KAl_2(AlSi_3O_{10})(OH_2))$ is a 2:1 aluminosilicate of the mica class.[8] It is a normal constituent of magmatic rocks, especially granites, and can show different colors like white, gray, brown, and green. Muscovite mica is rich in aluminum and presents a double lamellae structure composed by siloxane tetrahedral layers based on Si_2O_5 and an aluminum-containing octahedral layer. Hydroxyl groups are distributed on the material buried about 0.4 nm from the layered surface. The layers are linked by potassium ions.[9–11]

Although the structure of this mineral is close to that of other aluminosilicates like montmorillonite, exfoliation is rather difficult due to its low cation exchange capacity. Nevertheless, the flat external surface of mica particles may change the crystalline morphology of these composites and the molecular dynamics of the polymer phase.[12]

High-field nuclear magnetic resonance (NMR) is a powerful technique to investigate polymer structure; it has been used for decades for this purpose.[13] Less commonly used is low-field NMR. This technique can analyze samples in the solid state, and it enables identifying the molecular domains in an organic material due to changes in proton relaxation times. This feature makes the technique a good tool to analyze the molecular dynamics of polymer systems.[14,15]

In this work the preparation of PET/muscovite mica composites and the effect of the degree of dispersion on their properties were investigated. The results obtained from the investigation of the molecular dynamics of these composites, determining the proton spin-lattice relaxation time by using a low-field NMR spectrometer, are reported.

EXPERIMENTAL SECTION

Materials

PET with a melting temperature of 250°C and intrinsic viscosity of 0.77 dL/g was supplied by Braskem (Brazil). Muscovite mica (composition: Al_2O_3, 37.27%; SiO_2, 53.00%; K_2O, 7.53%; Fe_2O_3, 0.67%; and CaO, TiO_2, MgO, Na_2O, and $P_2O_5 < 1\%$) with a surface area of $3.78\,m^2/g$, specific density of $2.64\,g/cm^3$, and average particle size of 54.8 μm was supplied by Brasilminas (Brazil).

Composite Preparation

Both PET and muscovite mica were dried at 120°C for 16 h prior to composite preparation to remove moisture. Composites were prepared by melt mixing PET and the mica in a Haake twin-screw extruder, with four heating zones set at 265°, 270°, 280°, and 285°C and screw speed of 90 rpm. The melt was cooled in a cold-water bath. Several compositions were prepared, ranging from 2 to 15 wt% of muscovite mica. Composites were then pelletized and ground in a knife mill, generating a powder that was used for the NMR analyses. PET/mica composites in the ratios of 98/2, 96/4, 95/5, 92/8, 90/10, and 85/15 were prepared and designated as PET1, PET2, PET3, PET4, PET5, and PET6, respectively. PET without any filler (PET0) and amorphous and highly crystalline PET commercial samples were processed at the same conditions and used for comparison.

DSC Analysis

The degree of crystallinity of the composites was measured using a differential scanning calorimeter (DSC) by Perkin-Elmer, DSC-7. Samples were heated from 40° to 300°C at a scanning rate of 10°C/min. Only a first run was considered. The melting temperature (T_m) was considered to be the maximum of the endothermic melting peak. The degree of crystallinity (X_c) was calculated from the ratio of the melting endotherm (ΔH_m) and the standard melt enthalpy of 100% crystalline PET (ΔH^o_m), previously reported as 136 J/g.[16]

Low-Field NMR Analysis

Powder PET and PET/mica samples were analyzed in a low-field NMR MARAN ultra 23 spectrometer, operating at 23 MHz (for protons) and

equipped with an 18 mm variable temperature probe. The equipment was used for the determination of relaxation measurements. Proton spin-lattice relaxation times (T_1H) were determined directly by the traditional inversion recovery pulse sequence ($180° - \tau - 90°$). The 90° pulse of 4.6 μs was calibrated automatically by the instrument software. The conditions used were 27°C, 10 s of recycle delay, τ ranging from 10 to 10.000.000 μs, 32 scans for each τ value, 1 h total acquisition duration, and gain 30. The measurements were repeated four times. The relaxation values and relative intensities were obtained by fitting the exponential data with the aid of WINFIT software. Distributed exponential fittings as a plot of relaxation amplitude versus relaxation time were performed by using WINDXP software. Both are commercial programs furnished with the equipment. DXP software was used to separate magnetic domains, and WINFIT software was used for proton spin-lattice relaxation time. Separation of different T_1 values was done by two-exponential splitting.

The traces of magnetic minerals present as impurities do not affect the T_1 measurements of the organic polymer phase.

RESULTS AND DISCUSSION

Crystallinity of PET and Composites

Figure 1 and Table I summarize the results of DSC analyses of PET and PET/muscovite mica composites. Although all samples were obtained by
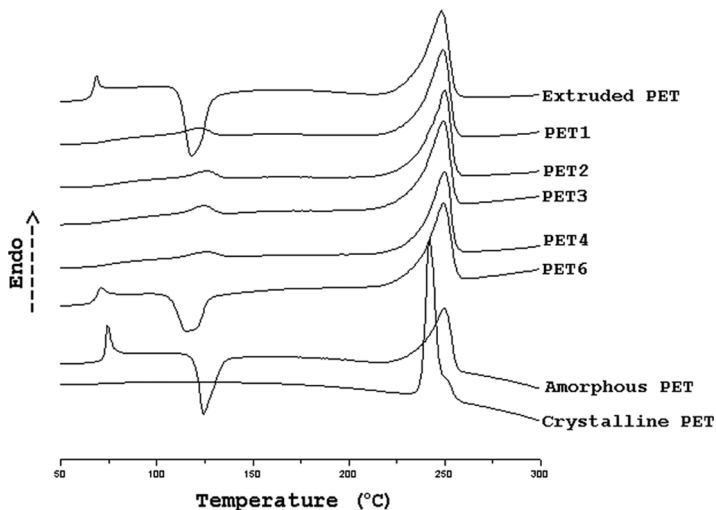

Figure 1. DSC traces of PET and PET/muscovite mica.

Table I.   Thermal properties of PET/muscovite mica samples

Sample name	Composition (PET/mica)	T_{ch} (°C)	ΔH_{ch} (J/g)	T_m (°C)	ΔH_m (J/g)	X_C^a (%)
PET0	100/0	117.87	−29.224	248.50	41.587	9.0
PET1	98/2	—	—	121.83	4.910	34.4
				249.23	42.578	
PET2	96/4	—	—	125.46	4.067	32.4
				249.93	40.692	
PET3	95/5	—	—	123.90	4.731	33.5
				249.26	41.470	
PET4	92/8	—	—	130.39	4.115	30.7
				249.80	38.251	
PET5	90/10	—	—	125.90	3.316	30.5
				249.80	38.780	
PET6	85/15	115.46	−20.413	249.43	36.385	11.6

[a]Crystalline fraction is given by $X_c = \Delta H_M / \Delta H_M^0 \times 100$, where $\Delta H_M^0 = 136 \, J/g$ for PET samples.

quenching the molten polymer material in a water bath at room temperature, all of them presented some crystallinity. The composites presented a degree of crystallinity (X_c) higher than the neat PET, indicating that the filler acts as a nucleating agent. The nucleation effect is, however, lower for the composite with 15 wt% of muscovite mica, suggesting a different degree of filler dispersion/agglomeration in this composite. Composites with 2, 4, 5, 8, and 10 wt% of mica showed also two melting peaks, while the 15 wt% mica composite showed only one and a profile similar to that of the neat PET, which can indicate domain separation. In both cases (PET and 15 wt% mica composite), the curves showed a crystallization on heating, which indicates that the materials are more amorphous.

The effect of a high amount of mica in avoiding crystallization to a large extent is probably due to mica agglomeration in the matrix and reduction of the surface area available for nucleating crystallization.

Molecular Dynamics by Low-Field NMR

The ^1H NMR spectra of PET/muscovite mica composites with at least 2 wt% of filler recorded in low field presented significant differences from the neat PET, suggesting changes in the molecular mobility of PET chains. The T_1H data acquired by low-field NMR are shown in Table II and Figure 2 for all samples. Changes in this parameter were detected for all PET/mica ratios. T_1H values for composites with

Table II. T_1H and magnetic domains

Composite name	PET/muscovite mica (wt%)	Global T_1 (ms)	T_1 (ms)
Amorphous PET	—	477	0.8
			477
Crystalline PET	—	750	1
			750
PET0	100/0	848	6
			865
PET1	98/2	611	2
			629
PET2	96/4	610	4
			617
PET3	95/5	585	4
			596
PET4	92/8	578	2
			597
PET5	90/10	590	0.7
			611
PET6	85/15	429	4
			440

2–10 wt% of muscovite mica were between the values of the amorphous and crystalline neat PET, slightly decreasing as the content of mica increased in the polymer matrix. The decrease of T_1H with increasing quantities of mica followed the tendency observed for the degree of crystallinity, which also slightly decreased with the increase of mica content. These changes in the proton relaxation value could come from the differences in the molecular mobility of domains with different molecular arrangements and/or ordinations, probably induced by interaction with the filler surfaces.

The addition of higher quantities of muscovite mica leads to a drastic decrease in the T_1H, as observed for PET/mica 85:15 (PET6), which was below the value of even the amorphous polymer. This behavior could be due to a lower degree of dispersion of mica particles in the PET matrix, which causes a decrease of filler surface area and a lower level of polymer chain/surface particle interaction. This may increase the amount of amorphous phase whose protons have lower relaxation times.

Magnetic domain evaluation showed a free water peak at lower relaxation values, a small peak due to the amorphous phase, and a higher peak that is a mixture of crystalline and constricted amorphous phase.

Global T_1H values, obtained by processing the data with one exponential value, are presented in Figure 3 for PET0, PET1, PET3, and PET6
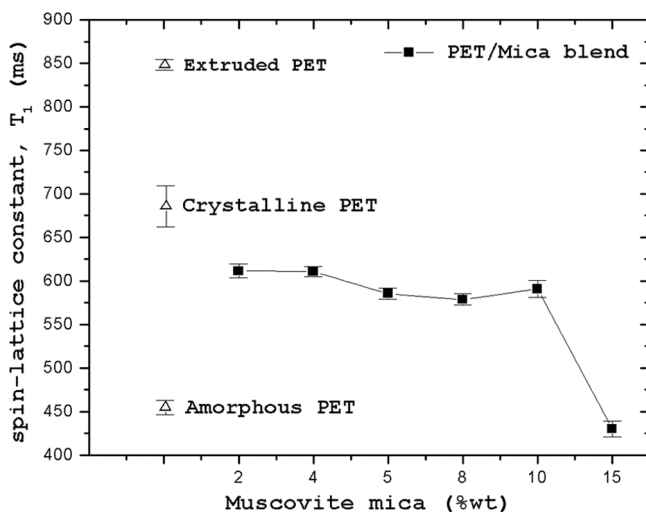
Figure 2. Proton spin-lattice time constant for PET and PET/mica muscovite composites.

composites. The figure shows that the increase in muscovite mica concentration actually lowers global T_1H values, compared to extruded PET.

Global T_1H values are also plotted against muscovite mica concentration (Figure 4). The results reported suggest that T_1H relaxation is
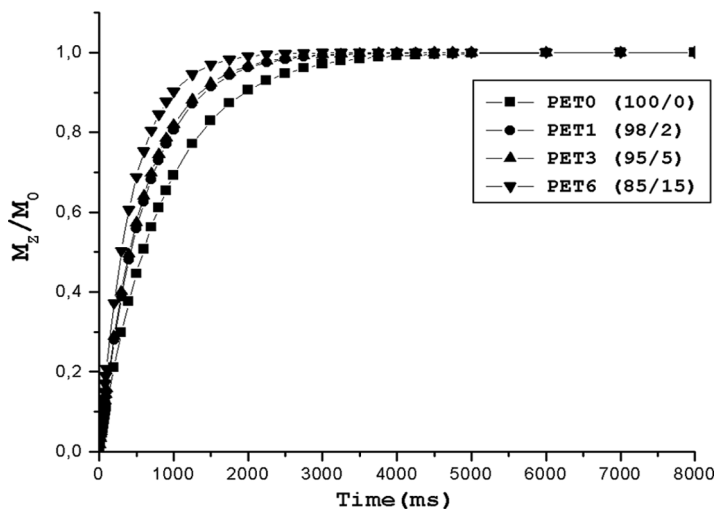

Figure 3. Global T_1H values for PET0, PET1, PET3, and PET6 samples. Increasing muscovite mica concentration decreases global T_1 constant.
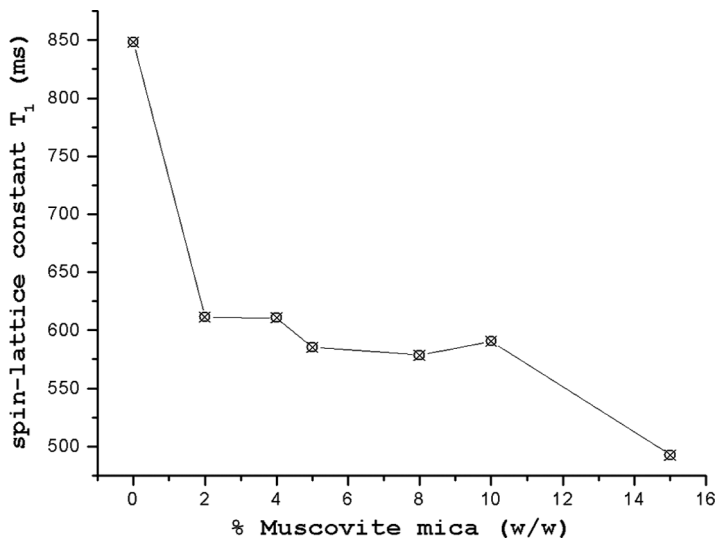
Figure 4. T_1H values versus muscovite mica concentration.

strongly influenced by muscovite mica dispersion in the semicrystalline PET structure.

Analyzing the T_1H domain values obtained by two-exponential data, a decrease in the T_1H values following the increase of mica content can also be seen. Two levels of responses seem evident: (1) for 2 to 8 wt% of mica, which is probably related to better mica dispersion with a decrease in its nucleation effect on crystallization and increase of amorphous phase content, which promotes a decrease in the relaxation values due to an increase in the molecular mobility, because the intermolecular interactions are less strong than before, promoting chain freedom; and (2) for 15 wt% of mica, an abrupt change in the T_1H relaxation value, probably due to the filler ratio between agglomeration/dispersion causing domain separation.

CONCLUSIONS

Low-field NMR technique was successfully applied to investigate changes in the dynamics of chains in PET/muscovite mica composites, considering the different molecular domains detected. DSC and proton spin-lattice relaxation studies showed that for the systems containing filler percentages as low as 2 and 10 wt% development of a high level of crystallinity takes place. A slight decrease in the T_1H is observed for

the composites with filler content up to 8 wt%, and a drastic decrease at the higher filler content (15 wt%) is due to filler agglomeration. These changes are highly associated with the content of amorphous phase in the composite, as well as with its distribution.

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