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Thermal and dynamic mechanical properties of polypropylene and short organic fiber composites

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Abstract

The effect of unmodified (nat) and azide modified (mod) short organic polyethylene terephtalate (PET) and Nylon 66 (PA) fibers on the thermal behavior and dynamic mechanical properties of an isotactic polypropylene (iPP) has been investigated. The study has been carried out by means of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The results have shown that both fibers behave as nucleant agents for the crystallization of polypropylene. A noticeable increase of the PP crystallization temperature in the presence of both fibers has been observed. This effect is more sensible with the incorporation of azide groups on the chemical structure of the fibers. On the other hand, the percentage of PP crystallinity (X_c) decreases in the presence of PET fibers and hardly varies with the incorporation of PA fibers. The fibers give rise to a sensible increase of the polypropylene stiffness (storage modulus), whereas a slight decrease of the damping factor (tan δ) has been observed. Furthermore, the PP glass transition temperature (T_g) decreases in the presence of the PET fibers and remains nearly unchanged with the incorporation of the PA fibers. The chemical modification of both fibers gives rise to an additional decrease of T_g as compared with the T_g of the plain PP. The activation energies for the relaxation process increase with the incorporation of both fibers, and this increment is more sensible in the case of the azide treated fibers. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: PP composites; Short PET and PA fibers; Thermal behavior and dynamic mechanical properties

1. Introduction

Thermoplastic-based composites are becoming more popular in many application fields due to the possibility of combining the toughness of thermoplastic polymers with the stiffness and strength of reinforcing fibers, and their ultimate properties depend on the characteristics of the matrix and fibers, as well as on the adhesion strength at the interface. In addition, these composites can be easily processed by common techniques such as injection- and compression-molding. In order to be applicable for a massive and economic production the matrices have to be economic, easily available and well established. For this reason, polypropylene (PP) is one of the most used polymers for short fiber-reinforced composite, especially due to economic reasons, ease of processing, environmental and working security, and recyclability. In addition, it is well known that organic textile fibers can be used to prepare polymer composites, but due to their relatively low stiffness, they are used as reinforcements of polymer matrices with even lower mechanical characteristics, such as rubbers and thermoplastics [1]. It is, in fact, possible to obtain good composites using PP with short organic fibers.

In order to improve the physical performance of fiber-reinforced polymers, different coupling agents have been used in the last few years, those based on titanate and silane chemistry being the most utilized [2]. However, coupling agents based on azide chemistry have been recently used. The main characteristic of the azide group is to allow the covalent reaction to any available carbon–hydrogen bond through a highly reactive intermediate singlet nitrene [3–6], coming up from its thermal decomposition. Thus, the treatment of mica and glass fiber with azidosilane coupling agents has shown to improve the reinforcing effect of these filler/reinforcement filled polyolefins, without the breaking or crosslinking side reactions of peroxide grafting systems [7–10]. In the present work, the *p*-sulphonyl–carbonyl diazide of benzoic acid previously synthesized in our laboratories was employed as coupling agent between the short organic fibers and polypropylene matrix. Likewise, the use of diazides as crosslink agents in diene and saturated elastomers has also been investigated [11,12].

It is well known that the physical and mechanical properties of a polymeric material are strongly dependent on its structure, morphology and relaxation processes [13].

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Table 1
Physical and mechanical characteristics of PET and PA short fibers

Characteristic	PET	PA
Density (g/cm^3)	1.38	1.14
T_m (°C)	250–260	250–260
Tensile strength (MPa)	890–1100	620–820
Modulus of elasticity (MPa)	2830	2800
Elongation at break (%)	85–105	60–300
Water absorption (%)	0.4	4–6

Furthermore, the properties of composite materials are determined by the characteristics of the polymer matrices themselves, together with reinforcements, and the adhesion fiber/matrix interface that mainly depends on voids and the bonding strength at the interface [14,15].

Dynamic mechanical analysis over a wide range of temperatures and frequencies permits the determination of the viscoelastic behavior of molten polymers and provides valuable insights into the relationship between structure, morphology and proportional properties of polymeric matrices and composites materials. Moreover, the stress–strain response curves reveal the mechanical nature of the material. Several studies on fiber-reinforced PP composites based on structure–property relationship by means of a dynamic mechanical analysis [16–19] were reported in the literature.

The main goal of the present work is to analyze the effect of polyethylene terephthalate (PET) and Nylon 66 (PA) short fibers, and their surface modification with *p*-sulphonyl–carbonyl diazide of benzoic acid on the thermal and dynamic mechanical behavior of thermoplastic composites based on polypropylene (PP). In a previous study [20], a significant increase of the tensile and flexural strength and stiffness as well as the toughness of the PP composites with the incorporation of this coupling agent was observed. Moreover, this agent significantly modifies the adhesion at the fiber/matrix interface, which could explain the improvements of some characteristics.

2. Experimental

2.1. Materials and blend preparation

Isotactic PP (iPP) (melt flow index 2.9, at 190°C and 5 kg and density 0.905 g cm^{-3}) supplied by Repsol Química S.A., under the trade name PP-051, and short textile PET and PA fibers (both 6 mm long), supplied by Velutex Flock S.A., were used in the present study. The *p*-sulphonyl–carbonyl diazide of benzoic acid was utilized as the coupling agent. The physical and mechanical properties of the fibers used are compiled in Table 1.

In order to avoid any orientation of the fibers, two-rolls mill and compression molding have been used to prepare the materials. So, it can be considered that the materials show an isotropic behavior. In any case, the materials have been prepared following the same procedure which will give rise to materials with a similar morphology. Anyway, the isotropic behavior of the materials was previously confirmed by testing specimens which were cut in different directions from the compression molded plaques.

The compounding was carried out in a roll-mill, equipped with a pair of high shear roller-type rotors. The temperature was set at 190°C and the blending time was 20 min. The rotors rate was set at 60 rpm. Once the polymer was melted, the appropriate percentage of fiber was added (20% by weight). The obtained compounds were compression molded at 200°C in a parallel plate press for 15 min. Specimens about 0.6 mm in thickness were cut from the plaques for the different measurements realized in the present study.

2.2. Measurements

Dynamic mechanical analysis was carried out by means of stress–strain oscillation measurements using a Metravib dynamic mechanical thermoanalyzer. Samples of dimension $10 \times 6\ \mathrm{mm}^2$ and 6 mm thickness were cut from the compression molded plaques. Tests were performed over a wide frequency range (5, 10, 25 and 50 Hz) and the temperature programs were run from −40 to 60°C under a controlled sinusoidal strain, at a heating rate of 2°C/min under a flow of nitrogen. An oscillating dynamic strain of 0.15% was used. The viscoelastic properties, such as, the storage modulus (E') and the mechanical loss factor, damping ($\tan\delta = E'/E''$), were recorded as a function of temperature and frequency. The activation energies were also calculated.

Thermal analysis measurements were performed using a DSC-7 Perkin–Elmer differential scanning calorimeter coupled with a data station PE 7700. Crystallization tests were carried out in dynamic condition with the following standard procedure: samples of about 8 mg were heated from 30 to 200°C at a heating rate of 10°C/min and then held for 10 min in order to eliminate any thermal history in the material. Then, the samples were cooled to 25°C at a rate of 10°C/min. After the dynamic crystallization a scan at 10°C/min was performed, in order to check the presence of residual crystallinity. The percentage crystallinity (X_c), the average values of apparent melting temperatures (T_m), crystallization temperature (T_c), and the heat evolved during the isothermal crystallization (ΔH_c) as a function of time, were calculated for all investigated materials.

2.3. Chemical treatment of the fibers

In order to promote chemical bonding between the fibers and the polymer matrix, a coupling agent based on azide chemistry (*p*-sulphonyl–carbonyl diazide of the benzoic acid) was incorporated into the chemical structure of the fibers. The synthesis of this diazide was previously described [11].

Azide fiber modification was carried out following a process previously developed in our laboratories [21]. The fiber modification takes place through the isocyanate groups coming from the Curtius transposition of the carbonyl azide groups, and the free hydroxyl and amino groups of the

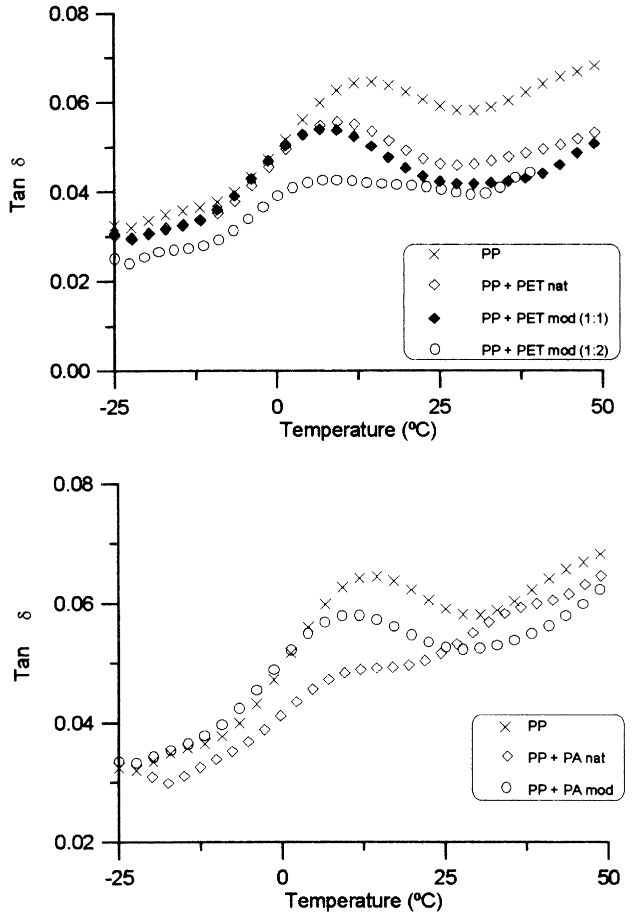

Fig. 1. Tan δ of neat PP and PET (top) and PA (bottom) fiber-reinforced composites as a function of temperature.

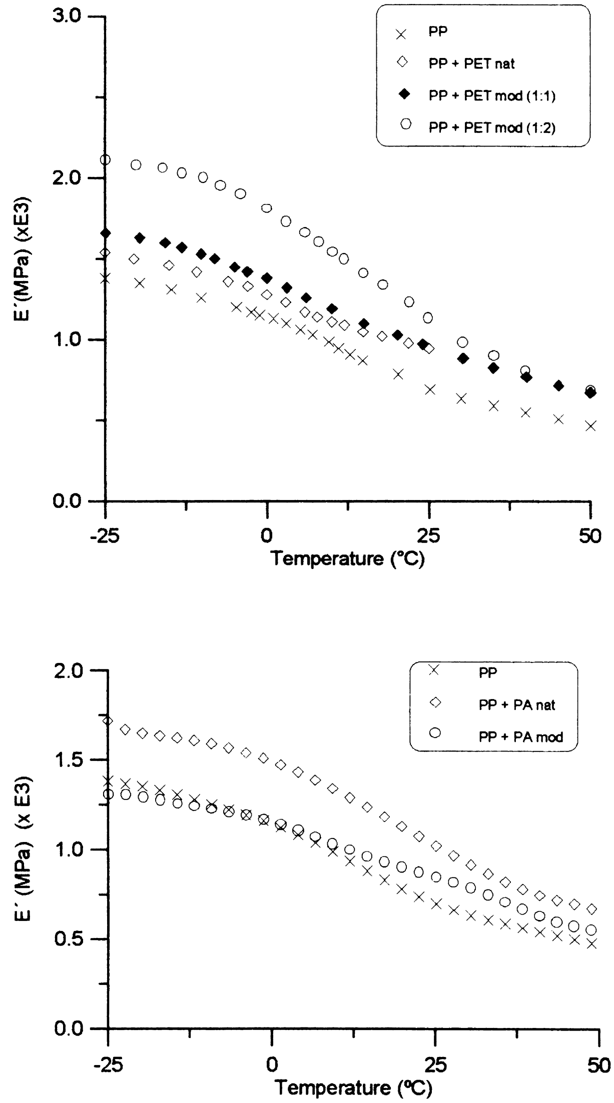

Fig. 2. E' of neat PP and PET (top) and PA (botton) fiber-reinforced composites as a function of temperature.

chains ends of PET and PA fibers, respectively. The reaction can be controlled by the IR spectra of the reactant solution, following the continuous decrease of the band at 2105 cm^{-1} that corresponds to the azide group. The reaction was performed at 80°C and completed in about 6 h. The fibers were then filtered off, washed with toluene and dried in an oven at 60°C. The chemical structure of PET fibers presents two hydroxyl final groups capable of reaction with the azide derivative. For this reason, PET/azide molar ratios of 1:1 and 1:2 were used, thus one or two sulphonyl azide groups, respectively were present on the PET structure. In the case of the PA fiber, only a PP/azide molar ratio of 1:1 was used, due to the preferential reaction of the isocyanate groups with the amine groups of the PA fibers.

Table 2
Dynamic mechanical properties of the studied materials at 5 Hz

Material	E' (MPa)/tan δ at		T_g (°C)/tan δ at peak
	−20°C	25°C	
PP homopolymer	1300/0.033	690/0.058	13.9/0.065
PP–unmodified PET	1600/0.030	970/0.045	10.1/0.055
PP–modified PET (1:1)	1500/0.030	940/0.042	7.9/0.054
PP-modified PET (1:2)	2000/0.026	1100/0.042	8.1/0.043
PP–unmodified PA	1600/0.030	1000/0.052	15.9/0.049
PP–modified PA	1200/0.034	860/0.052	10.9/0.059

The azide-modified fibers were characterized by chemical analysis, DSC and thermogravimetric measurements. The hydroxyl number of the modified PET fibers was negligible and a depression in the DSC curve was observed at about 185°C, which corresponds to the decomposition of the sulphonyl azide group that was present in the fibers. The thermogravimetric curve showed that almost all the azide percentage was incorporated to the fibers.

3. Results and discussion

3.1. DMA measurements

Pure polymer and their composites were subjected to a

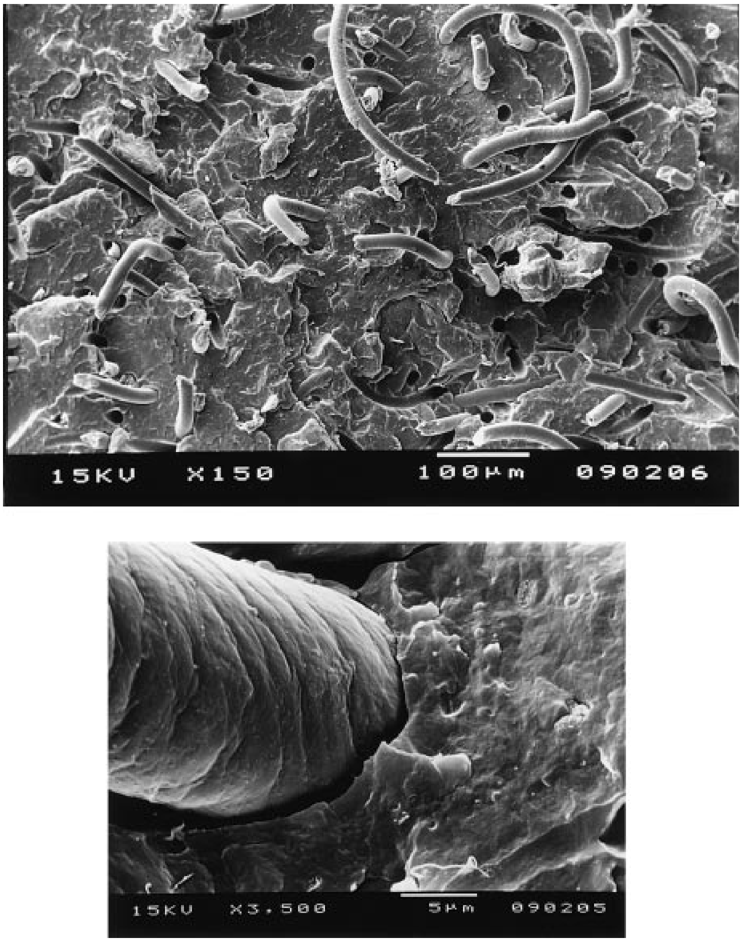

Fig. 3. Fracture surface of unmodified PET fiber composites.

controlled sinusoidal strain and the resultant displacement was measured. The mechanical loss factor (tan δ) versus temperature curves, at 5 Hz, for the PP homopolymer and their composites with unmodified and azide modified PET and PA fibers are graphically represented in Fig. 1. McGrum and colleagues [22] have demonstrated that the tan δ curve of PP exhibits three relaxations localized in the vicinity of -80 (γ), 100C (α) and 10°C (β). In the present work, the study was focused on the β-relaxation of polypropylene that correspond to the glass–rubber transition of the amorphous portions and the temperature of the maximum peak is assigned to the glass transition temperature (T_g).

Fig. 1 reveals the presence of a peak at about 10°C corresponding to the glass transition of the polypropylene. Although PET and PA fibers are viscoelastic materials, their glass transition temperatures are above 60 and 50°C, respectively, which has permitted to analyze the effect of the fibers on this relaxation of the polymer matrix. From this figure, it can be deduced that the intensity and magnitude of the peak sensibly decrease in the presence of both fibers. In addition, a displacement of the T_g peak to lower temperatures is observed when PET fibers are incorporated, being this effect more evident when the azide derivative is incorporated on the chemical structure of the fiber. These results seem to indicate that other mechanisms of dissipation of energy, such as the effects of sliding fiber/fiber that could exceed to those produced by fiber/matrix interactions are simultaneously taken place. In the case of the unmodified PA fibers, the transition is very broad and does not show a clear peak. However, it can be observed that the position of the relaxation remains nearly unchanged in relation to that of the plain polypropylene. On the other hand, the chemical modification of the PA fibers gives rise to a displacement of the T_g peak to lower temperatures, as can be observed in Fig. 1.

The glass transition temperature (T_g) and the tan δ values at T_g peak, -20 and 25°C are reported in Table 2.

In the same manner and to evaluate the effect of both unmodified and azide modified fibers on mechanical properties of PP, the storage modulus (E') as a function of temperature is graphically represented in Fig. 2 for PET and PA fibers. As can be observed, the incorporation of both fibers gives rise to a considerable increase of the PP stiffness. Moreover, in the case of the PET fibers the composite stiffness increases as the sulphonyl azide groups introduced in the chemical structure of the fibers increase. However, the chemical modification of the PA fibers tends

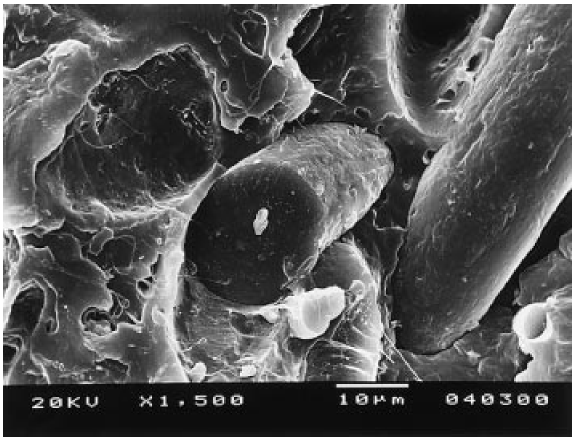

Fig. 4. Fracture surface of azide modified PET fiber composites.

to decrease this characteristic. The storage moduli (E') of the studied composites at -20 and 25°C are reported in Table 2. These results are in agreement with the microphotographs taken in the scanning electron microscope (SEM) and reported in Figs. 3–5. Unmodified PET fiber composites are shown in Fig. 3, and as can be observed, there is hardly any adhesion at the fiber/matrix interface since the fibers are pulled out from the polymer matrix without leaving any sign and the fibers themselves show a very clean surface. In Fig. 3 (bottom) it can be clearly seen that there does not exist any interaction at all at the fiber/matrix interface. However, as deduced from Fig. 4, in the case of the azide modified PET fibers a considerable improvement of the adhesion at the interface is observed and there are hardly any voids on the fracture surface which indicates that the fibers are so well trapped by the polymer that fiber pull-out considerably decreases. So, in general, the fibers broke level with the polymer surface and due to the better bonding promoted by the azide treatment, fibers protruding from the polymer matrix are covered with a polymer layer. In the case of the

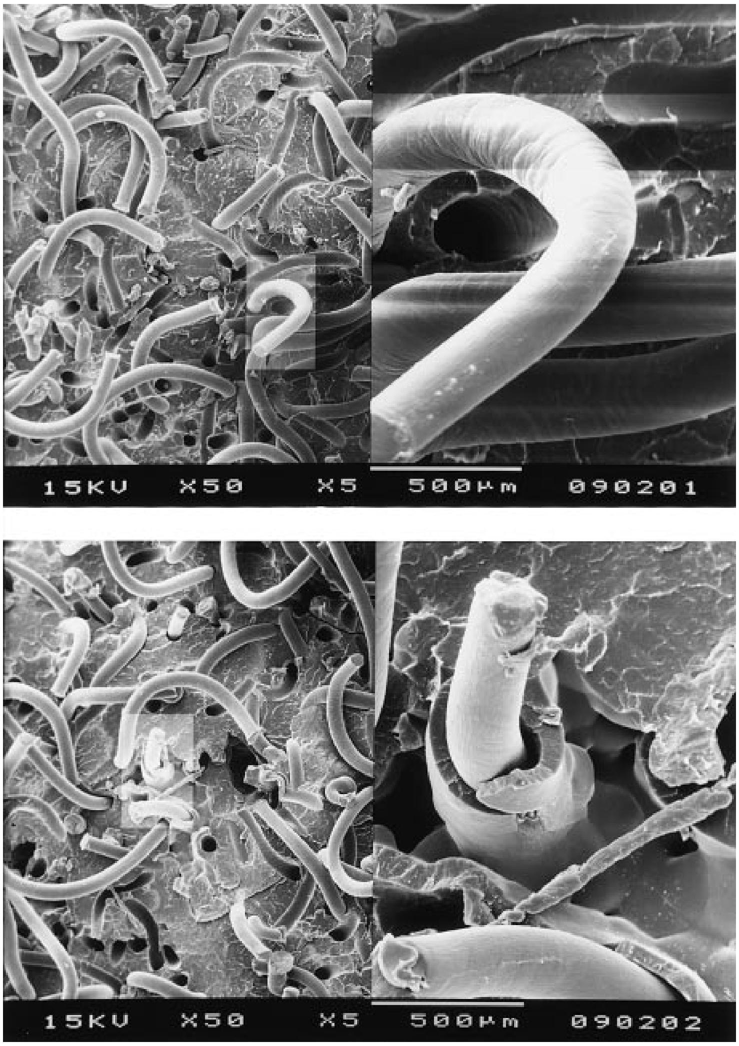

Fig. 5. Fracture surface of unmodified (top) and modified (bottom) PA fiber composites.

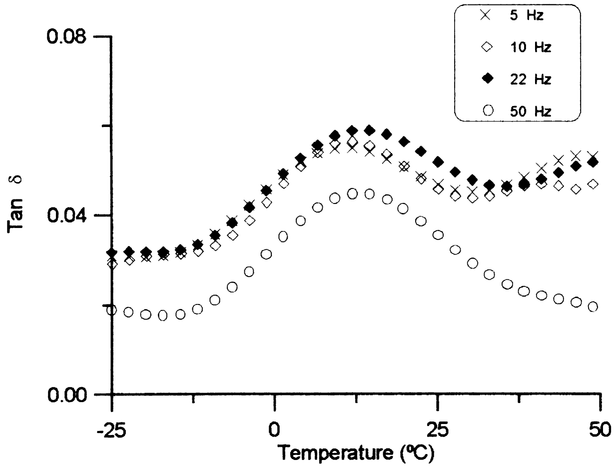

Fig. 6. Effect of the frequency on DMA spectra of PP unmodified PET fiber composites.

PA fibers, the aspect of the fiber/matrix hardly varies in the unmodified and azide modified fiber composites (Fig. 5), and in both cases there is not any adhesion at the fiber/polymer interface and fibers are easily pulled out from the matrix as can be seen in the fracture surfaces of the composites with unmodified (top) and azide modified PA fibers (bottom). This study carried out by SEM seems to explain the results obtained by dynamic mechanical analysis of the studied composites. It is well known that the mechanical properties are strongly dependent on the composites composition and the adhesion or interaction at the fiber/matrix interface.

3.2. Calculation of the activation energy

In order to analyze the effect of frequency on the dynamic mechanical properties of the investigated materials, DMA tests were performed over a temperature range of −40 to 60°C and at four different frequencies (5, 10, 20 and 50 Hz). In Fig. 6, the temperature dependence of tan δ for PP composites with PET fibers is represented at the four frequencies studied. From this figure, it can be deduced that the effect of the frequency on peak magnitude does not show a clear tendency, however the relaxation peak temperature is increased by about 5°C when frequency goes from 5 to 50 Hz, being this effect more sensible with PA fibers (about 8°C).

It has been suggested that is possible to interrelate the temperature at which a relaxation process is observed (f) with the frequency of excitation (f) by the Arrhenius equation [23]:

$$f = f_0 \exp \frac{-E_a}{RT} \tag{1}$$

where f_0 is a constant, f the frequency of the test, R, the gas constant and E_a, the activation energy for the relaxation process.

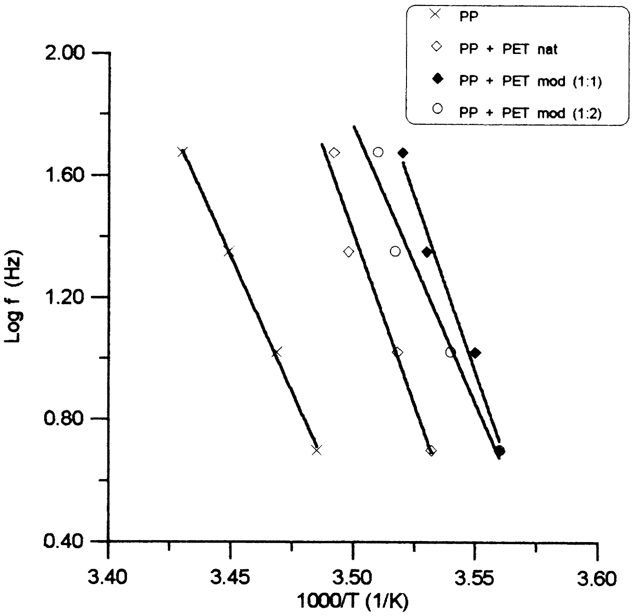

Fig. 7. Calculation of the activation energies.

According to this equation, a plot of log f versus $1000/T$ (Fig. 7), should give a straight line with a slope that is proportional to the apparent activation energy for relaxation process of PP and their composites. Calculated activation energies according to the Eq. (1) are shown in Table 3. As can be deduced, the activation energy of the polypropylene increases in the presence of PET and PA fibers. This increase of the activation energy value is more evident when the fibers are chemically treated with the azide derivative.

3.3. DSC measurements

The effect of the fibers on the thermal properties of PP has also been analyzed in non-isothermal DSC experiments. Thermal parameters such as melting temperature (T_m), crystallization temperature (T_c), heat of fusion (ΔH_f) and the percentage of crystallinity (X_c), of the studied samples, were analyzed by non-isothermal crystallization experiments. The results are reported in Table 4. Crystallinities (X_c) of the different composites were calculated utilizing the

Table 3
Activation energies of the investigated materials

Material	Activation energy (kJ/mol)
PP homopolymer	383
PP–unmodified PET	424
PP–modified PET (1:1)	459
PP–modified PET (1:2)	468
PP–unmodified PA	431
PP–modified PA	472

Table 4
Thermal properties of the studied materials utilizing differential scanning calorimetry at 10°C/min

Material	T_m (°C)	T_c (°C)	ΔH_f (J/g)	X_c (%)
PP homopolymer	169.5	116.2	78.4	56.8
PP–unmodified PET	168.8	118.6	56.2	40.7
PP–modified PET (1:1)	170.0	120.2	57.0	41.3
PP–modified PET (1:2)	170.1	121.3	61.3	44.5
PP–unmodified PA	169.9	119.0	75.5	54.8
PP–modified PA	169.0	120.5	76.0	55.3

following expression:

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \times 100 \qquad (2)$$

using an extrapolated value of enthalpy corresponding to the melting of 100% crystalline PP homopolymer: $\Delta H_f =$ 137.9 J/g [24].

The dynamic crystallization behavior shows the positive effect of the fibers on the crystallization kinetic of PP. A marked increase of the crystallization peak temperature can be observed when the fibers are incorporated in the homopolymer matrix and this increment is more sensible when the fibers are chemically treated. These results can be explained by the strong nucleation ability of the PET and PA fibers on PP crystallization. Furthermore, these results are in agreement with those obtained in a previous study [25], where the nucleating effect of both fibers on the crystallization rate of polypropylene was demonstrated.

However, no changes in the final absolute crystallinity fraction are detected. In fact, the decrease in the values of the crystallinity content observed in Table 4 with the addition of PET fiber is directly associated to the dilution effect of the fiber. Furthermore, no changes in the melting point of the PP phase were detected in the composites.

4. Conclusions

- The effect of unmodified and azide modified PET and PA short fibers on the thermal properties of iPP has been analyzed by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC).
- The incorporation of the fibers gives rise to a considerable increase of the storage modulus (stiffness) and a decrease of the tan δ values. These results demonstrate the reinforcing effect of both fibers on PP matrix.
- The efficiency of the *p*-sulphonyl–carbonyl diazide of the benzoic acid as coupling agent between organic fibers and polypropylene was verified. An increase of the properties with the chemical treatment of fibers was observed. Moreover, with increasing diazide content on the PET fiber, the E' modulus increases and tan δ decreases in a regular manner. These results suggest that a much better interaction between the fibers and the matrix exists, when the azide derivative is incorporated.
- The study performed by DSC, revealed strong nucleation ability of the PET and PA fibers on PP crystallization. An increment of the crystallization temperature with the introduction of the fibers is observed. This increase is more noticeable when the sulphonyl azide group is incorporated in the chemical structure of these fibers.
- From the above, the reinforcing effect of both PET and PA fibers for polypropylene matrices and the efficiency of *p*-sulphonyl–carbonyl diazide of the benzoic acid as coupling agent between polypropylene and the fibers has been demonstrated, with a significant increment of the studied properties.

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