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Dynamic properties in aluminum filled PMMA

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Abstract

The dynamic mechanical properties of polymethyl methacrylate reinforced with different amounts of aluminum filler were investigated. The internal friction and the shear storage modulus were measured with an automated damped torsional pendulum in the temperature range between 200 and 375 K in an argon atmosphere. An increase in the glass transition temperature occurred at higher filler contents. The amount of filler in the matrix seems to modify the β relaxation of the composite. The dynamic modulus increases with the aluminum percentages for low filler content. These results were explained in terms of a model presented in the literature for the elastic modulus.

Keywords: Dynamic mechanical properties; Filled PMMA; Main and secondary relaxation

1. Introduction

In recent years, the conductive polymer field has increased. One of the methods used to attain these materials is adding rather large amounts of a conductive filler in a polymer matrix [1,2]. This kind of material was prepared by Yang and Schruben [2] who investigated several metal filled composites made of polymethyl methacrylate (PMMA) with aluminum and nickel powder.

Besides the importance from the point of view of electrical properties, it is interesting to analyze this class of material in terms of its dynamic mechanical properties. As it is known, the mechanical properties depended on the type, concentration, size, and shape of the filler. Other important factors that affect the mechanical behavior of filled systems are the strength of the adhesive bond between different phases, the type of dispersion and the kind of agglomeration.

Several researchers studied different mechanical properties of metal filler composite but the interest was focused mainly on tensile properties [3–6]. Using a method analogous to the theory of the dependence of Young's modulus of the composites with the filler content [4,7,8], a relationship for the dynamic modulus can be given as

$$\frac{G_c^*}{G_p^*} = (1 + k\phi) \tag{1}$$

where G_c^* and G_p^* are the dynamic modulus of the composite and the polymer matrix respectively, ϕ is the volume fraction of filler and k is an adhesion factor. $k = 2.5$ represents perfect adhesion between the filler and the polymer matrix while $k = 1$ indicates a weak adhesion [4]. G^* is calculated as $G^* = \sqrt{G'^2 + G''^2}$ with G' and G' the shear storage and shear loss modulus, respectively. The loss tangent or internal friction is defined as the ratio between G'' and G', i.e.

$$IF = \tan\delta = \frac{G''}{G'} \tag{2}$$

The objective of this paper is to study the dynamic properties of a composite made of PMMA with several contents of aluminum powder and to analyze its associated relaxation in the range of temperatures between 200 and 375 K.

2. Experimental procedure

2.1. Materials

The material used in this investigation was PMMA as a matrix and aluminum powder of a mean diameter between 10 μm and 40 μm. Aluminum powder was pre-dried into vacuum chamber at 393 K during 1 h before incorporation into PMMA matrix. Test samples were prepared by dissolving the polymer using 350 ml of methylene chloride as a solvent for each 70 g of solid PMMA. Then, certain amounts of aluminum powder were added to the solution,

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stirred and mixed well. The solution was cast in a mold. The specimen was put into a drying chamber in order to make the solvent evaporation slow enough to avoid the bubbles from appearing in the material [9]. The dimension of the composite sheet was 120 mm × 120 mm × 4 mm.

Samples with volume fractions of filler (ϕ) of 0, 0.03, 0.10, 0.15, 0.20 and 0.30 were prepared.

In order to characterize the molecular weight distribution of the matrix and the commercial PMMA used in the fabrication, gel permeation chromatograms (GPC) of PMMA were obtained by using a Shimadzu L-6A liquid chromatogram system with a RID-6A refractive index detector and a Shimpack GPC 802-803-804-805-807 as the columns at 303 K. THF was used as the eluate. The measured values of number and weight average molecular weight were $M_n = 809.900\ g\ mol^{-1}$, $M_w = 2.212.613\ g\ mol^{-1}$, and $M_n = 576.700\ g\ mol^{-1}$, $M_w = 1.591.500\ g\ mol^{-1}$ for the commercial and fabricated PMMA respectively.

NMR measurement on the commercial and fabricated PMMA were made. The ^1H spectra of the samples was recorded on a Bruker AC-200 spectrometer using ca. 7% (w/v) solution in chloroform at 300 K.

The distribution of particles and the agglomeration size were determined by using a scanning electron microscope Philips type PW 6700/01.

2.2. Mechanical tests

The internal friction, *IF*, and shear storage modulus, G', were measured with an automated damped torsion pendulum in Ar atmosphere at 40 Torr between 200 and 375 K with a temperature ramp of 0.4 K min^{-1}. This pendulum is completely instrumented both in its control and data acquisition systems, and it is commanded by a PC-AT [10]. The maximum shear strain in the dynamic measurements was always less than 10^{-5}, thus ensuring linear viscoelastic behavior. Samples were cut into strips of 40 mm × 3 mm from the central part of the composite sheet. The final thickness was obtained (2 mm) by polishing with alumina powder. The dimensions of the samples were according to ASTM D 4065.

3. Results

Measurements of internal friction and G' as a function of temperature were performed in the as-received commercial PMMA and the unfilled prepared material. These behaviors are shown in Fig. 1. Two peaks are clearly shown in the unfilled sample, which are associated to the main (α) and secondary (β) relaxation in PMMA [11–13]. The primary main chain motion is identified with the glass transition which marks the onset of the long range main chain wriggling motions [14]. The location of this peak can be defined as the glass transition temperature (T_g). The β relaxation in PMMA is related to the partial rotation of the ester group about the C–C bond linking the group to the main chain.

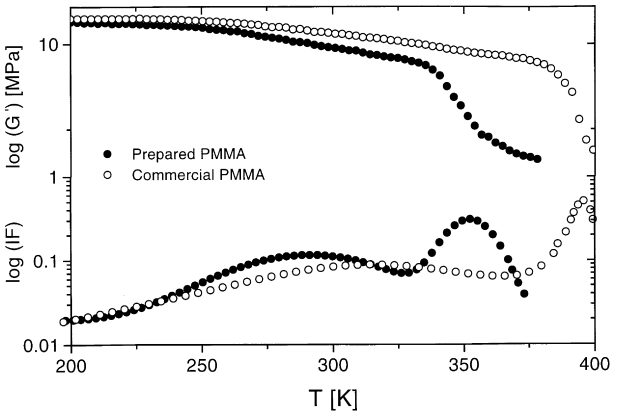

Fig. 1. Internal friction (*IF*) and storage modulus G' curves as a function of temperature for sample A (commercial PMMA) and sample B (prepared PMMA).

In Fig. 1, two relevant facts can be noticed: first, a strong shift to lower temperature in the values of the T_g and to a small extent in the case of T_β; secondly, the value of the storage modulus decreases in the prepared specimen. The T_g value obtained in the commercial sample is similar to those generally reported in atactic PMMA [11–13].

The effect observed in the shift of the relaxation peaks can be attributed to the presence of plasticizer [15–18] in the polymer and the difference in the molecular weight between the samples. The last statement leads to a small shift in the value of T_g considering the difference in molecular weight measured in our samples. In order to verify the presence of solvent in the prepared PMMA sample NMR spectra were made in both samples before to dynamic mechanical measurements. Fig. 2(a) and 2(b) shows the ^1H spectra of the as-received PMMA (sample A) and the prepared PMMA in the laboratory (sample B) respectively. Upon comparing both spectra, it can be observed that one anomalous peak appears around 5.3 ppm in sample B. This fact is associated to the presence of solvent used in the fabrication of the samples. On analyzing this spectrum, a solvent percentage of 9% was calculated. After the mechanical dynamic measurement, the NMR spectrum for sample B was made and no changes were observed comparing with Fig. 2(b).

In Fig. 3(a)–3(c), the microscopic photographs of the samples with $\phi = 0.03$, 0.10 and 0.3 are shown. A homogeneous distribution of particles can be noticed in the sample with 0.03 filler (Fig. 3(a)) while in the case of $\phi = 0.10$ (Fig. 3(b)) the presence of aluminum particles agglomeration was observed. This effect is larger in the sample with $\phi = 0.30$ (Fig. 3(c)).

In Fig. 4, the *IF* experimental curves of all the prepared samples are given as a function of temperature. As can be seen, the two relaxation peaks (α and β) appear in the *IF* curves of the filled samples too. An increase in the temperature of the α peak with filler contained in the sample was observed. On the other hand, the location of the temperature

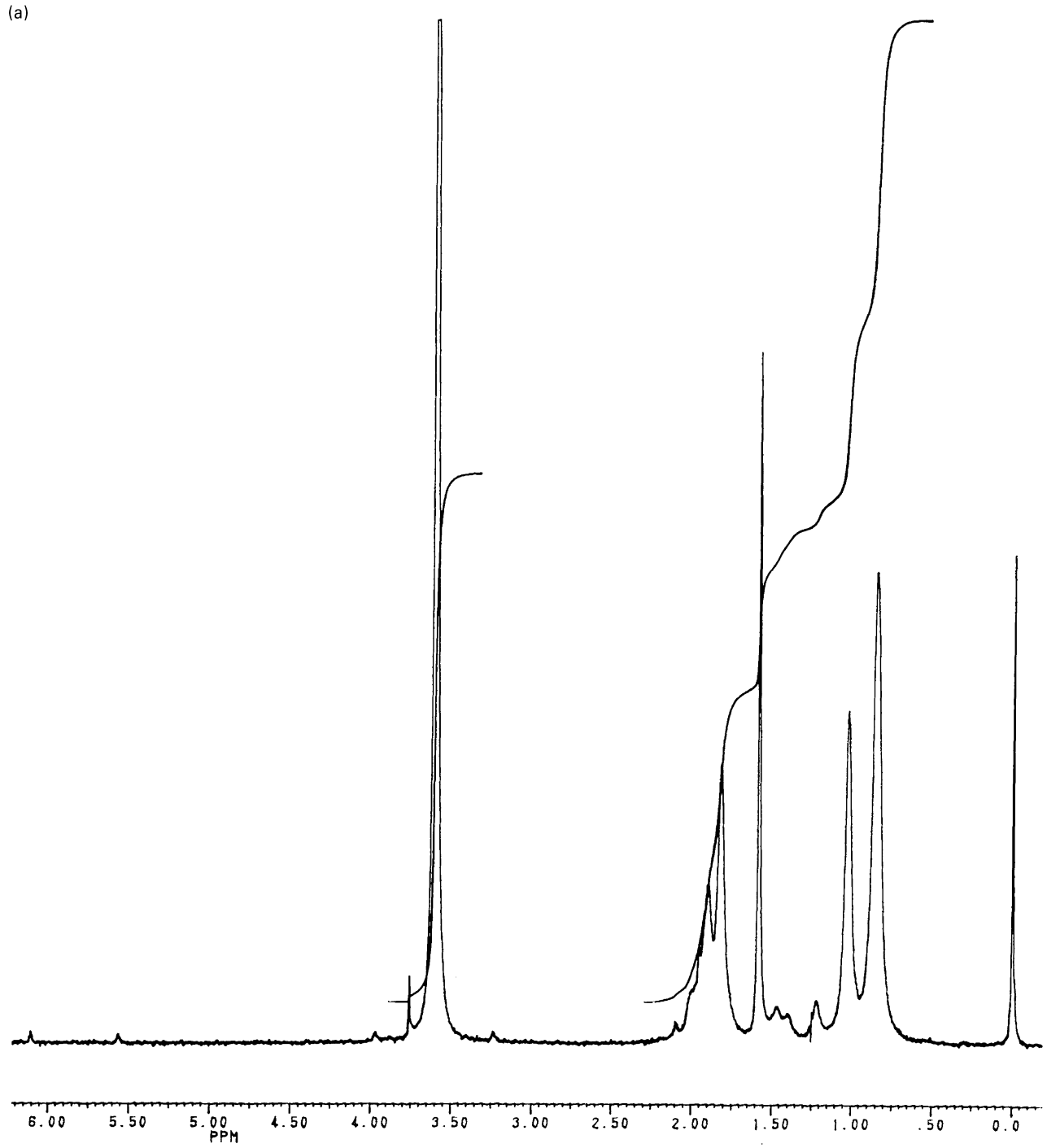

Fig. 2. ^{1}H spectra of PMMA at 300 K: (a) commercial, (b) fabricated.

of the β peak (T_β) in all the analyzed samples seemed to remain at the same temperature, independent of the percentage of filler in the composite.

Fig. 5 shows the dependence of G^* with volume fraction of filler at three different temperatures. It is interesting to note that the behavior of G^* is similar in every case. Furthermore, an increase in the value of G^* can be noted to reach a maximum value at $\phi = 0.15$ after which this value drops.

4. Discussion

The curves of Fig. 4 can be adjusted by the contribution of two Gaussian curves. Then it is easy to obtain the temperature of each peak. The T_g and T_β values are shown in Table 1, where it can be appreciated that the T_g value increases with the percentage of aluminum powder. This result is in good agreement with those usually reported in the literature [19–21] for particle–polymer matrix compounds.

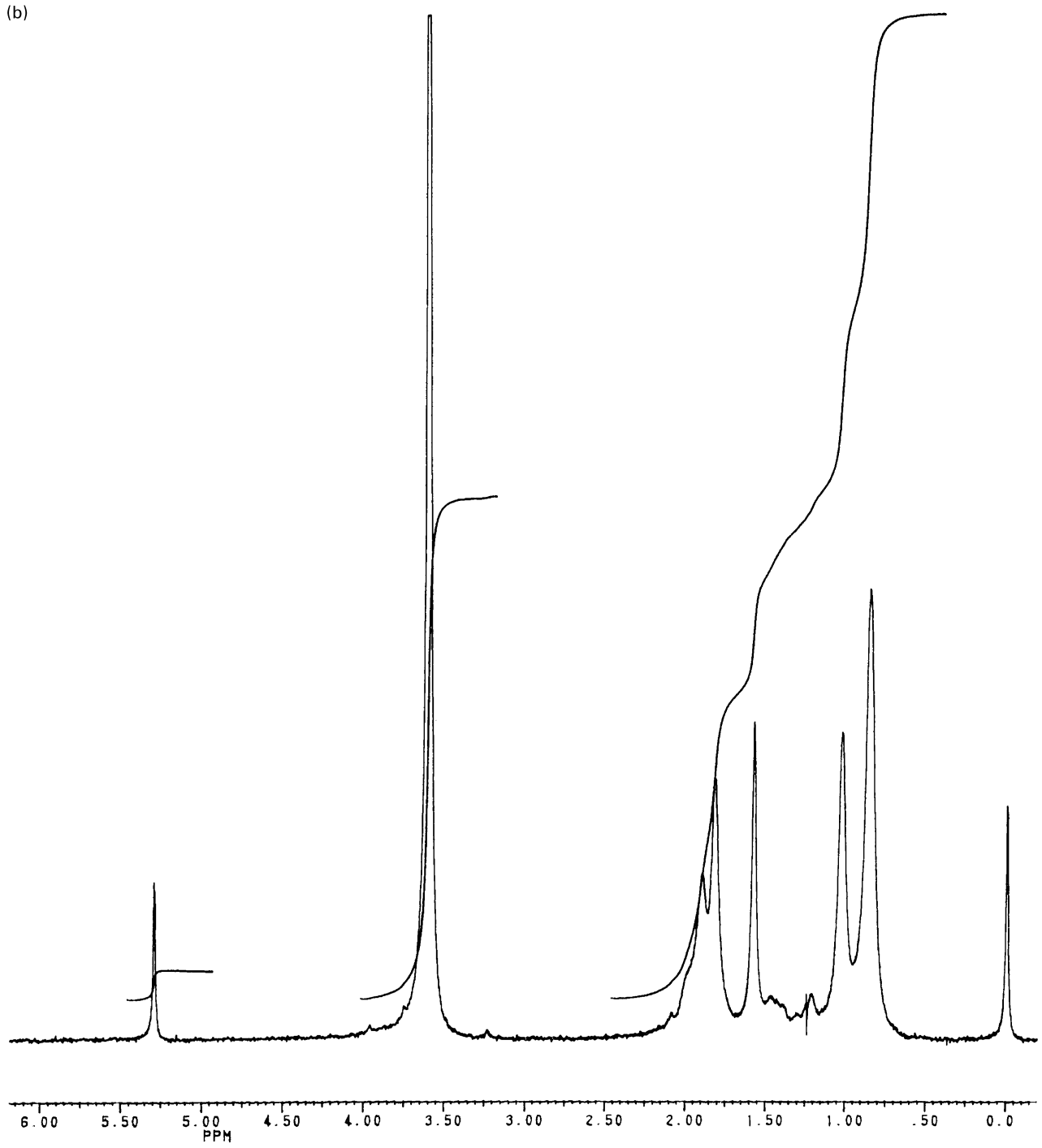

Fig. 2. *continued*

An interesting point to be discussed refers to the filler percentage dependence of the β relaxation temperature. In Table 1 it can be seen that T_β is not related to ϕ. According to Heijboer [13], the location of the β maximum in PMMA is determined by the local intramolecular barrier. The fact that this temperature does not change with the aluminum percentage leads us to the idea that the intramolecular barrier could not be affected by the filler. However it must be mentioned that modifications in the intensity of the β peak can be observed in Fig. 4.

As is known, the β relaxation in PMMA is associated with the partial rotation of the ester group ($COOCH_3$) about the C–C bond linking of the main chain [13], and the intensity of this relaxation depends on the number of lateral groups for which the rotation is possible.

The intensity of the β relaxation, I_β, is influenced by the α

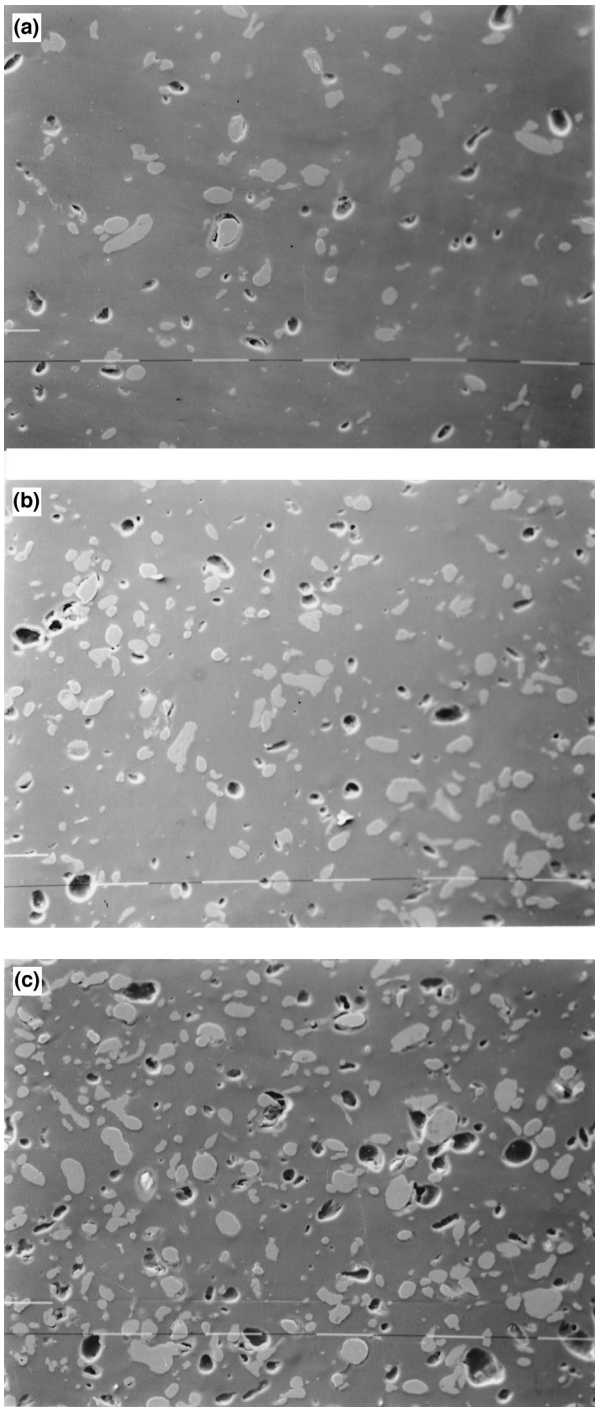

Fig. 3. Scanning electron micrographs of aluminum filler composite for three different volume fraction of filler. (a) $\phi = 0.03$, (b) $\phi = 0.10$ (c) $\phi = 0.3$. Magnification, 100 × . Scale bar, 100 μm.

transition and the *IF* background. Then, in order to obtain the value of I_β it is necessary to subtract the two effects mentioned previously. Therefore, the I_β value was determined as the integrate of the curve resulting from the subtraction of a baseline to the measured *IF* curve. This baseline was taken between the beginning of β and α transitions. The intensity of β relaxation is shown as a function of the filler volume fraction in Fig. 6. There is an evident

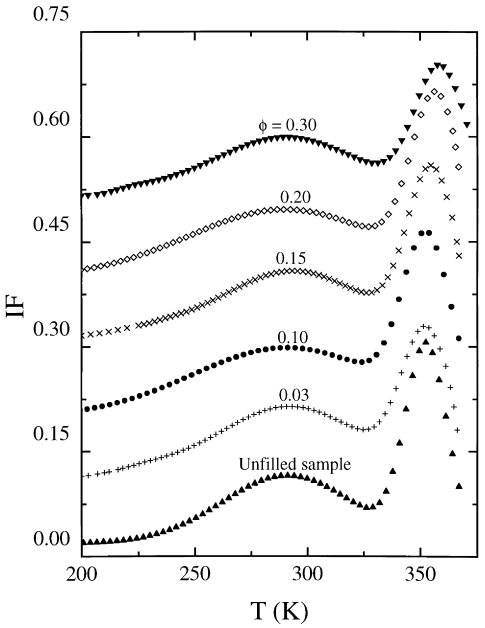

Fig. 4. Internal friction (*IF*) curves obtained from the free oscillation test. Curves are shifted along the *y* axis by 0.1 per each level of ϕ, beginning at $\phi = 0$.

decrease in the contribution of this intensity to the *IF* of the compound at higher volume fraction of filler.

We believe that the decrease in the intensity of the β relaxation at higher level of filler is due to the change in the polymer volume fraction instead of a physical bonding interaction between the ester group and the Al filler surface.

The dependence of the dynamic modulus with ϕ, shown in Fig. 5, is very close to that measured by Tavman [4] in a composite of polyethylene filled with aluminum powder. This author observed a change in the behavior of the Young's modulus for a 0.15 volume fraction of aluminum.

Our results, for low volume fraction of aluminum particles (up to about 0.15), can be fit by Einstein's equation considering $k = 1.54$. This value is an intermediate

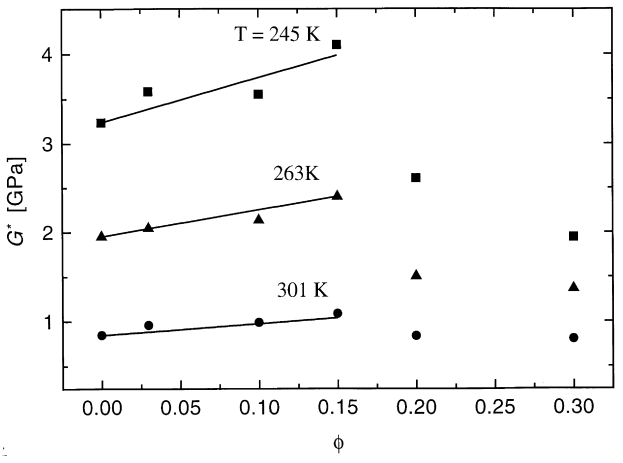

Fig. 5. Dependence of G' with the volume fraction of filler at three different temperatures.

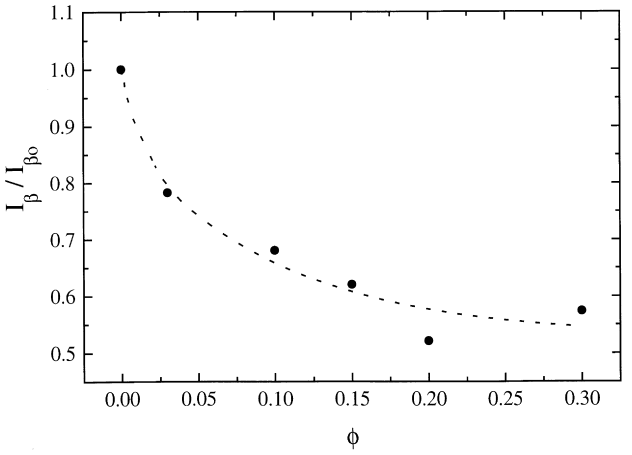

Fig. 6. Dependence of the intensity of the *IF* at the β peak with the volume fraction of filler normalized to the intensity for the unfilled sample ($I_{\beta 0}$).

Table 1
Variation of T_g and T_β with the volume fraction of filler, ϕ

ϕ	T_g (K)	T_β (K)
0	352.5	291.0
0.03	352.5	292.0
0.10	352.2	291.0
0.15	354.9	293.7
0.20	357.0	290.1
0.30	358.6	290.1

condition between perfect adhesion, $k = 2.5$, and weak adhesion $k = 1$.

Finally, it is interesting to note that, for $\phi > 0.15$, Einstein's model does not fit our results. In this situation, the particles begin to form aggregates in the composite. This was revealed by the microscopic studies (Fig. 3). The bond between the filler particles is not as strong as that between the matrix and the particles. By the application of a shear stress, voids can be formed which explains the decrease of the dynamic modulus of high particle content.

5. Conclusions

In this paper, dynamic mechanical properties of PMMA filled with aluminum powder were studied. An increase in the value of T_g was obtained for volume fraction of filler higher than 0.15. The behavior of the β peak temperature is not modified in the range of filler content used in our experiences. However, the intensity of the β relaxation shows an important fall as the filler content increases.

Finally, the dynamic modulus increases up to 0.15 volume content of aluminum particles. An estimation of the matrix filler adhesion level coefficient was calculated using Einstein's equation.

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