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Dynamic moduli of $CaCO_3$- and $Mg(OH)_2$-filled polypropylene

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Fillers suppressed the temperature dependence of storage modulus and caused the flattening of the temperature dependence of the loss modulus in the glass transition region of polypropylene (PP). The glass transition temperature (T_β) of PP did not change with filler content (v_f). This indicates that none of the fillers affect the mobility of PP in the bulk. A new loss maximum appeared at 50 °C for $v_f > 0.2$. This maximum became more prominent when increasing either the filler content or filler specific surface area. Interparticle interactions, leading to the space network of weakly bonded particles, affected PP mobility indirectly. The enhanced interfacial adhesion led to a further decrease of PP mobility near T_β and to the increase of the new loss maximum at 50 °C.

1. Introduction

The application range of compounds based on the high-volume produced thermoplastics, such as polypropylene (PP), filled with inorganic particles is increasing [1–3]. Effort is being exerted to substitute engineering plastics by compounds with the low price/volume ratio which would possess appropriate mechanical properties. Nevertheless, the introduction of filled PP brings problems such as flammability, toughness and strength.

One possible means of solving the problem of nonflammability of PP is seen in the use of a flame-retardant filler such as $Mg(OH)_2$ [4]. It is a new noble particulate filler, advantageously affecting both mechanical properties and flammability, suppressing smoke production during the combustion. The combustion products of PP filled with $Mg(OH)_2$ are neither toxic nor corrosive. As $Mg(OH)_2$ consists of platelet-shaped particles, the mechanical behaviour of PP/$Mg(OH)_2$ compounds differs significantly from that for PP filled with common $CaCO_3$ [5].

Polypropylene, whose surface energy is inherently low, interacts with the surface of none of the common fillers [6]. Thus, the shift of the glass transition temperature, T_β, with increasing filler volume fraction is negligible for $CaCO_3$-filled PP. There are, however, no data for $Mg(OH)_2$-filled PP. The relationship between dynamic moduli and molecular mobility is not so straightforward for multicomponent materials as in the case of a pure matrix. Despite this, conclusions can be drawn about the influence of filler on molecular mobility, judging from the relative changes in relaxations in the matrix and in the blend [7].

2. Experimental procedure

Commercial polypropylene Mosten 58.412, melt index 4 g/10 min (230 °C, 21.6N), was used as a matrix. Maleated PP (MPP) was prepared by grafting the maleic anhydride (MA) on to PP in the melt. The MPP grade used for the interphase modification contained 0.76 wt % reactive–COOH groups (Table I). It is assumed, that the grafting procedure used probably leads to the "fence-like" molecular structure. Consequently, MPP is a blend of relatively short molecules containing grafted MA and long non-grafted molecules.

Calcium carbonate Durcal 2, magnesium hydroxide Kisuma 5B, Kisuma 7B and Reachim were used as fillers. The fillers are characterized in Table II. $CaCO_3$ with irregular, approximately spherical particles, was surface treated with a blend of stearic acid and calcium stearate. $Mg(OH)_2$ was used surface treated by the producer with about 2% wt/wt oleates. Particles of $Mg(OH)_2$ (Kisuma 5B, Reachim) were either in the form of hexagonal plates or (Kisuma 7B) of needles (Figs 1–3).

The components were mixed in the PLE 651 Brabender Plasticorder (chamber W-50-H, charge 48 ml, 200 °C, 50 r.p.m., 10 min). Compounded materials were compression moulded at 210 °C. The specimens, cut from the sheets, were annealed for 1.5 h at 114 °C and then slowly cooled, 0.5 °C min^{-1}.

The measurements were performed using a Dynamical Mechanical Thermal Analyser (PL DMTA, Polymer Laboratories, GB) and on a freely oscillating torsion pendulum with automatic data acquisition. The experiments were carried out within the temperature range −100 to +100 °C, the exciting frequency of PL DMTA being 1 Hz. The torsion pendulum oscillated in the interval 2.0–0.5 Hz over the temperature region.

3. Results and discussion

3.1. Unfilled PP

The shape of the temperature dependences of the

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TABLE I Characteristics of PP, MPP and their blends after Brabender treatment

Sample	Composition	MA content[a] (% wt/wt)	M_w[b] (10^{-3} g mol^{-1})	Melt index (g/10 min)	Crystallinity (%)[c]
PP	iPP	0	472 ± 16	4	54
M1	iPP + MPP	3×10^{-3}	470 ∓ 21	4	55
M2	iPP + MPP	3×10^{-2}	465 ∓ 16	4	55
M3	iPP + MPP	10^{-1}	415 ∓ 20	6	55
M4	iPP + MPP	4×10^{-1}	359 ∓ 16	8	56
M7	MPP	0.92	271 ∓ 20	20	32

[a] By IR spectrometry and titration.
[b] By light scattering.
[c] From X-ray diffraction.

TABLE II Characteristics of fillers used

Composition	Grade	Specific surface area ($m^2 g^{-1}$)	Density (g cm^{-3})	Young's modulus, E (GPa)	Shear modulus, G (GPa)	Average aspect ratio
$CaCO_3$	Durcal 2	3.3	2.71	72 [13]	28 [13]	Irregular approximately spherical p = 1
$Mg(OH)_2$	Kisuma 5B	7	2.36	64[a]	25[a]	Hexagonal lamellae p = 5
	Reachim	6.8	2.36	64	25	Hexagonal lamellae p = 5
	Kisuma 7B	37	2.36	64	25	Needles p = 25

[a] The values E and G moduli of $Mg(OH)_2$ were estimated from the relation between elastic moduli and hardness of materials.

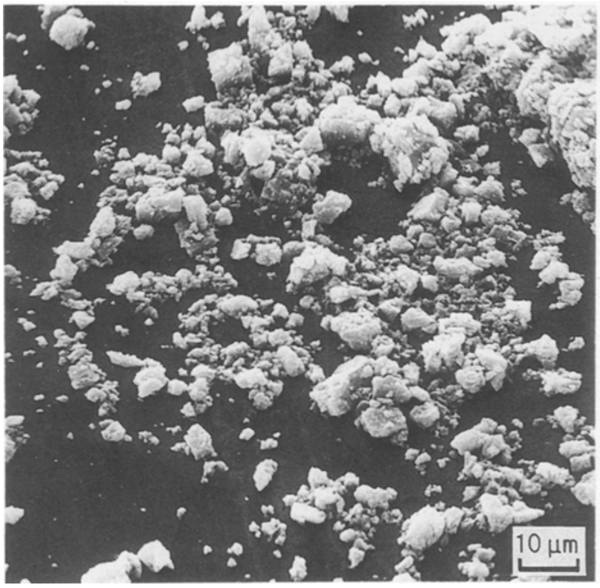

Figure 1 Scanning electron micrograph of Durcal 2, $CaCO_3$ (Omya, Switzerland).

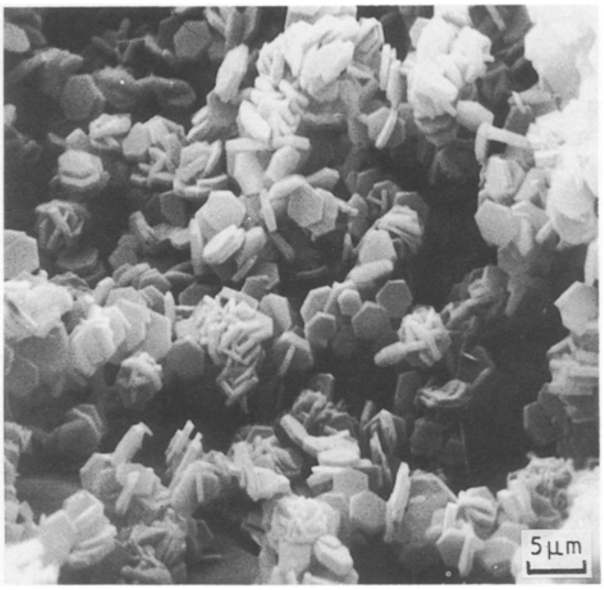

Figure 2 Scanning electron micrograph of platelet $Mg(OH)_2$ Kisuma 5B (Kyowa, Japan).

dynamic moduli does not depend on the MA content in a monotonic manner for the unfilled PP (Fig. 4). This must be the consequence of at least two contradictory competitive processes. We assume that the increase of the G' modulus is connected with the increasing crystallinity (Table I) and the changing crystallite morphology (Fig. 5). On the other hand, a consequent lowering of both molecular weight, M_w, and crystallinity leads to a reduction in G'. To analyse PP relaxations, a relaxation strength S_G [8, 9]

$$S_G = [G_u/G'_r] - 1 \qquad (1)$$

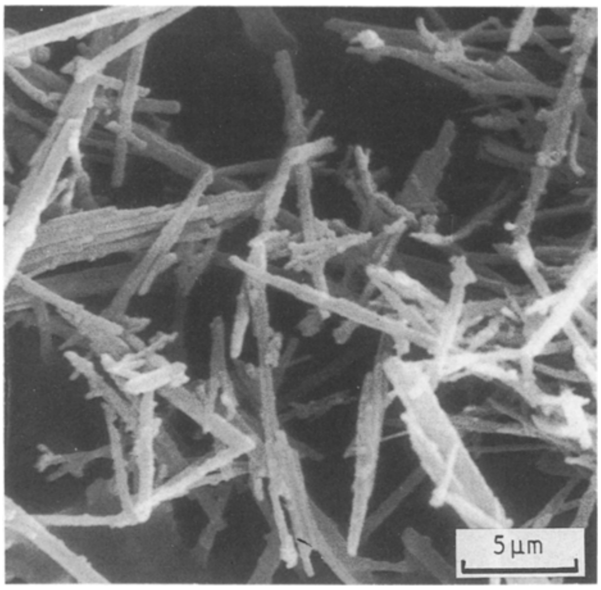

Figure 3 Scanning electron micrograph of needle-shaped $Mg(OH)_2$ Kisuma 7B (Kyowa, Japan).

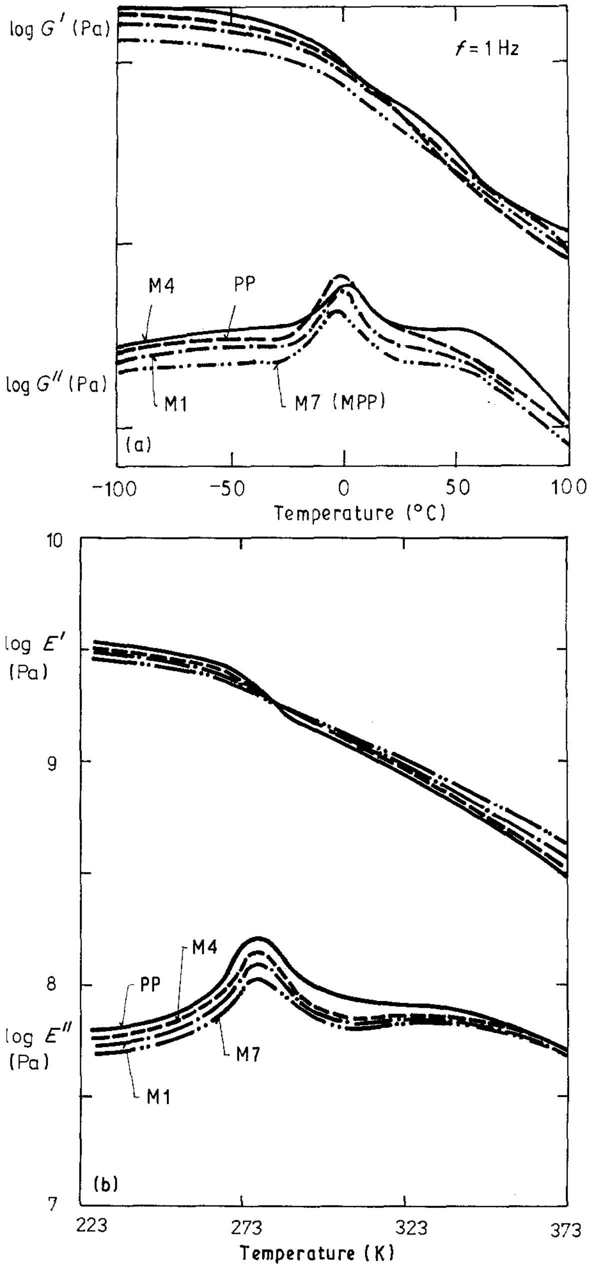

Figure 4 Temperature dependences of the tensile and shear moduli of PP with different MA contents.

was used (G'_u is the unrelaxed and G'_r is the relaxed modulus). Two significantly pronounced relaxation regions were considered to be the β relaxations (glass transition) and the α relaxation (high-temperature region). As a reduction in PP mobility is expected, the strength, S_G, for both β and α relaxations decreases with MA content (Fig. 6). Consequently, the loss of G' modulus decreases with MA concentration, but the position of the relaxations does not change significantly.

3.2. Filled PP–zero adhesion

The presence of fillers offsets the temperature dependence of the storage E' and G' moduli and causes a flattening of the loss maxima on $E''(T)$ and $G''(T)$ curves near T_β (Figs 7–9). These effects are accounted for by the decrease of the amount of amorphous fraction

3.2.1. Temperature region below glass transition temperature, T_β

The decrease of the storage $E'(T)$ and $G'(T)$ moduli, above $Mg(OH)_2$ volume fraction 0.3, is partly due to the mechanical destruction of the filler in the course of compounding and partly due to the formation of a hyperstructure of physically bonded particles. The hyperstructure [10] consists of bundles of needles, acting as reinforcing elements possessing an aspect ratio which is lower than that of individual needles. The created bundles have lower effective moduli than the $Mg(OH)_2$ needles as they contain low-modulus PP. The formation of the bundles is attributed to the interpenetration of immobilized interlayers on the surface of $Mg(OH)_2$ particles. However, the subsegmental motions below the T_β temperature are probably uninfluenced by the presence of the hyperstructure and by the immobilization effects. Thus the formation of the hyperstructure is manifested only as an apparent decrease of the storage moduli.

3.2.2. The glass transition region

The glass temperature, T_β, of PP changed neither with the volume fraction of the filler nor with its shape and chemical nature. Hence we introduced the term relaxation strength, S, for the discussion of filler influence on the molecular mobility of the matrix in the same way as for the unfilled PP (Equation 1). The values of unrelaxed and relaxed moduli were determined at − 40 and + 30 °C, respectively. The relaxation strength, S, is reduced with increasing filler volume fraction, regardless of its nature. In all cases, the shear relaxation strength was higher than the tensile one. The decrease in the relaxation strengths is the consequence of a molecular mobility reduction. This reduction is due to a decrease of PP volume fraction and, additionally, to an increasing amount of PP immobilized on the filler surface. The lower sensitivity of tensile measurements to the matrix immobilization is probably the consequence of a different loading pattern.

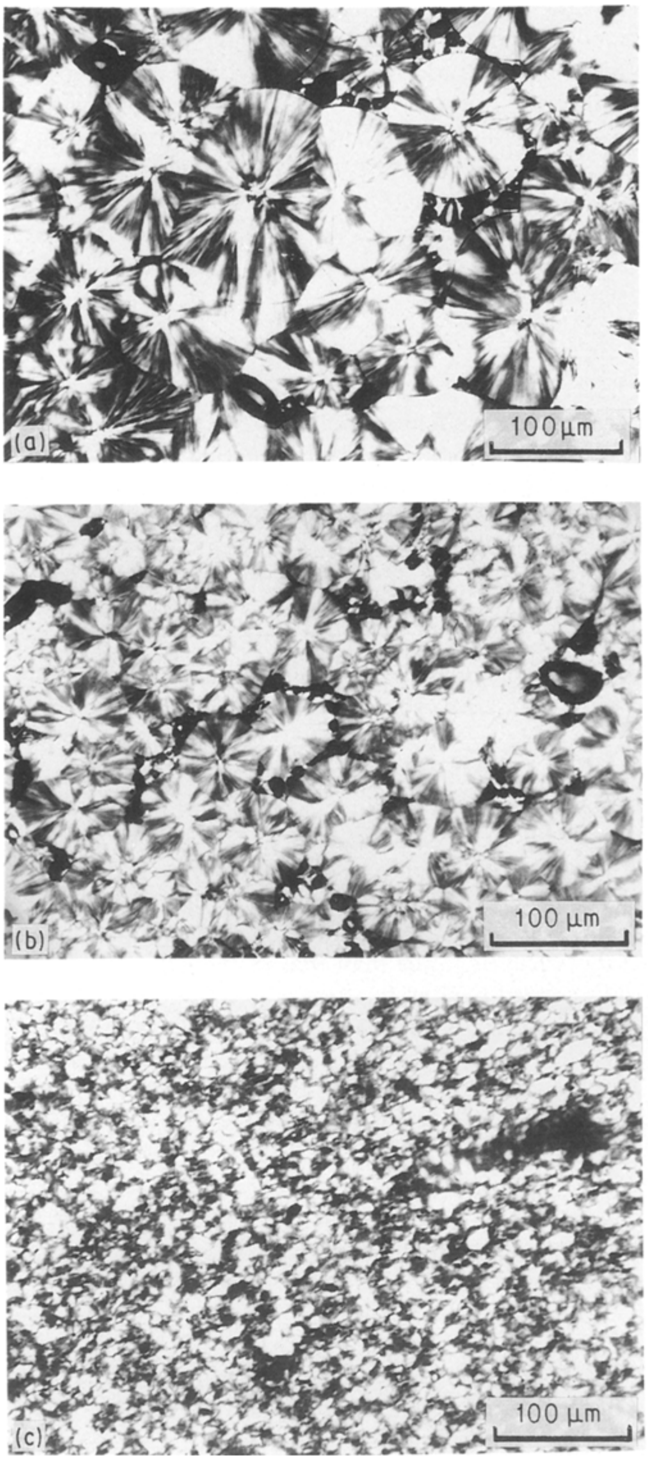

Figure 5 Micrographs of the spherulitic structure of PP with different contents of grafted MA: (a) iPP, (b) 3×10^{-3}% wt/wt, (c) 0.92% wt/wt MA.

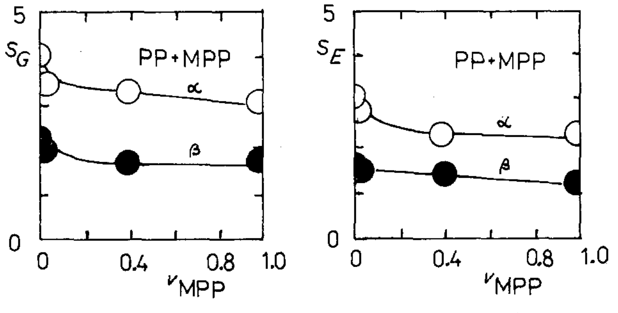

Figure 6 Dependence of relaxation strength on MA content for PP. Added MPP contained 0.92% wt/wt grafted MA.

3.2.3. Temperature region above the glass transition temperature, T_β

A characteristic feature is the origin of a new α′ loss maximum for the filler volume fraction higher than 0.25 at about 50 °C (Figs 7–9). This maximum is more significant for shear loading and it increases with filler content. We suppose that this maximum is the consequence of a release of strongly hindered segmental mobility of molecules from the interphase on the filler surface [10]. Because the peak position is independent of both filler volume fraction and filler nature, it can be concluded that the molecular mobility pattern is not influenced by any of the fillers used. This can lead to the statement that the α′ peak is probably the glass transition peak of PP immobilized on the filler surface. In general, the molecular mobility of PP is higher than in the glass transition region and it is more influenced by the presence of the filler (Figs 10–12).

3.3. Filled PP – effect of adhesion

3.3.1. The region below T_β

At the constant filler content ($v_f = 0.18$), MPP, promoting interfacial adhesion, has reduced both storage and loss moduli (Figs 13–15). This is partly due to the changes in the PP bulk morphology [11] and partly due to the "effective interlayer thickness" increasing. Further effects can be assigned to the hyperstructure origin in PP filled with $Mg(OH)_2$. The hyperstructure formation causes an apparent increase in the amount of immobilized matrix and an apparent reduction of the particle average aspect ratio [12].

3.3.2. The glass transition region

The PP glass transition temperature does not change with the enhancement of interfacial adhesion. At the same time, the temperature dependences of both storage and loss moduli are weakened (Figs 16–18). We suppose that the segmental mobility of PP in the bulk remains uninfluenced by the adhesion enhancement and only its extent is reduced. Hence, a conclusion can be drawn assuming the presence of MPP preferably in the interlayer on the filler surface, as was expected.

3.3.3. The region above the glass transition

The enhancement of adhesion decelerates the decrease in storage modulus with increasing temperature. This is most significant for $Mg(OH)_2$-filled PP, which supports our previous idea about the role of immobilization and hyperstructure origin. As the "effective interlayer thickness" increases with increasing amount of MPP, the conditions are created for the appearance of α′ loss maximum at lower filler content than in systems with "zero" adhesion. The assumed coherence between the existence of α′ maximum and the large amount of molecular mobility release from the interlayer is supported by the appearance of this peak only for $Mg(OH)_2$ needle-filled PP. This is due to the high

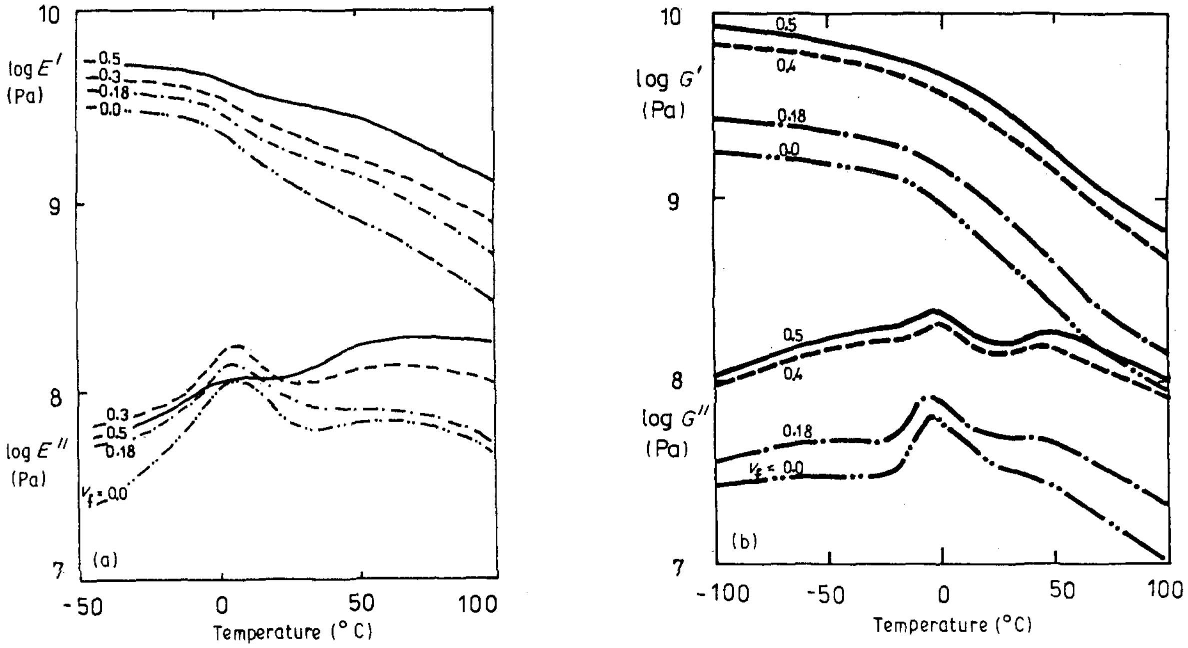

Figure 7 Temperature dependences of (a) Young's and (b) shear moduli of PP filled with different $CaCO_3$ volume fractions (1 Hz).

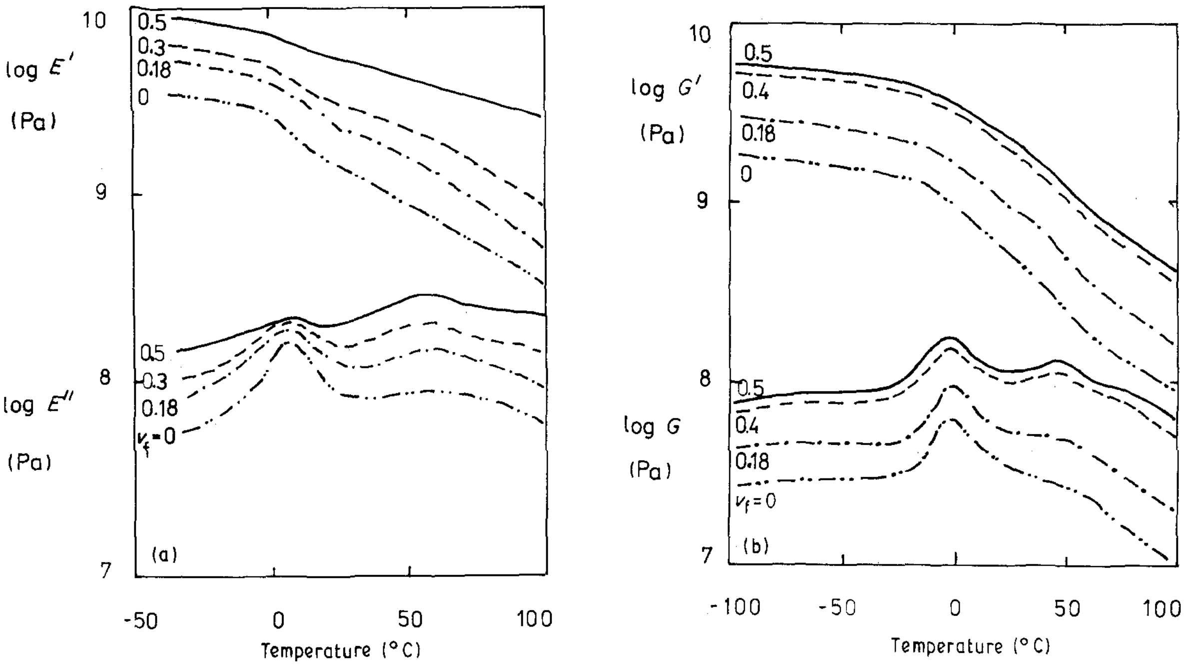

Figure 8 Temperature dependences of (a) Young's and (b) shear moduli of PP filled with different $Mg(OH)_2$ platelet volume fractions (1 Hz).

specific surface area of this filler (37 $m^2 g^{-1}$) compared to the others (3.3 $m^2 g^{-1}$ for $CaCO_3$, 7 $m^2 g^{-1}$ for $Mg(OH)_2$ platelets). The enhancement of adhesion due to the interactions between carboxyl groups from MPP and basic hydroxyl groups from the filler surface causes a much more significant reduction of molecular mobility in comparison with the systems with only weak physical interfacial interactions.

4. Conclusions

None of the fillers used changed the PP molecular mobility pattern in the glass transition region; only the extent of segmental motion was reduced due to the presence of the filler. A new significant loss maximum was found around 50 °C for filler content higher than 25 vol %. This maximum is probably connected with the retarded release of the segmental mobility of PP molecules immobilized on the filler surface. The position of this maximum on the temperature axis was independent of either filler volume fraction or its nature.

The enhancement of the interfacial adhesion did not change the PP mobility pattern in the glass temperature region. The proposed explanation is based on the assumption of a preferable presence on MPP molecules in the interphase on the particle surface.

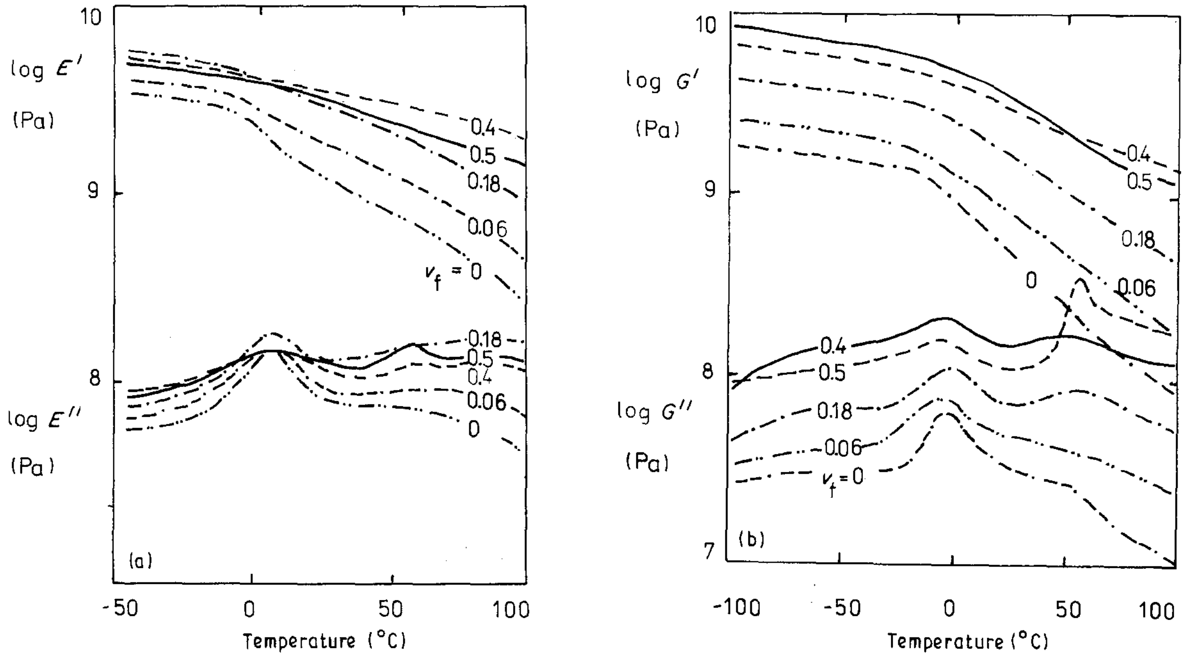

Figure 9 Temperature dependences of (a) Young's and (b) shear moduli of PP filled with different $Mg(OH)_2$ needle volume fractions (1 Hz).

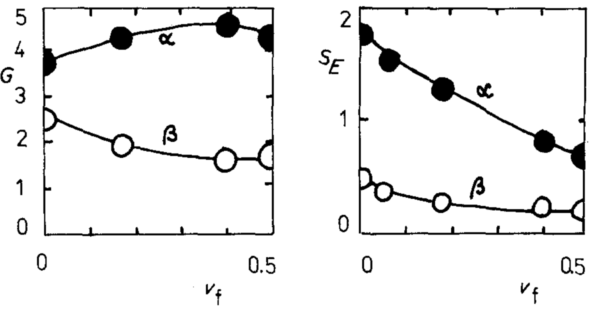

Figure 10 Concentration dependence of relaxation strength *S* for β- and α-relaxations of PP filled with $CaCO_3$.

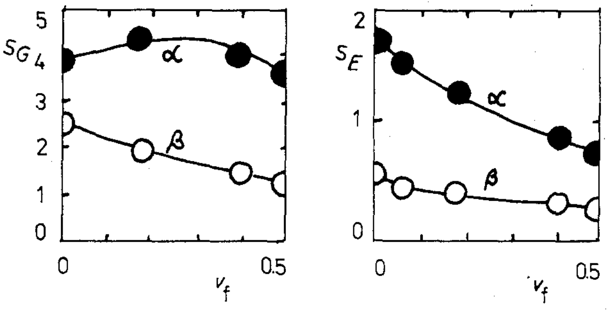

Figure 11 As Fig. 10 for $Mg(OH)_2$ platelet-filled PP.

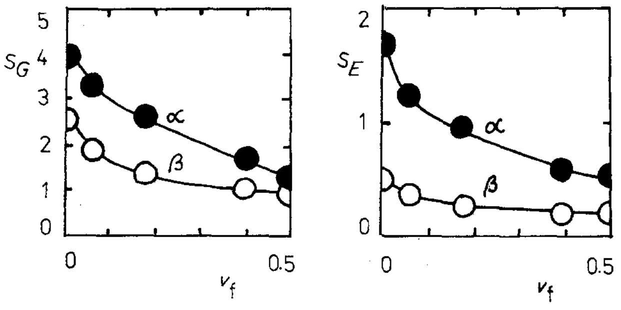

Figure 12 As Fig. 10 for $Mg(OH)_2$ needle-filled PP.

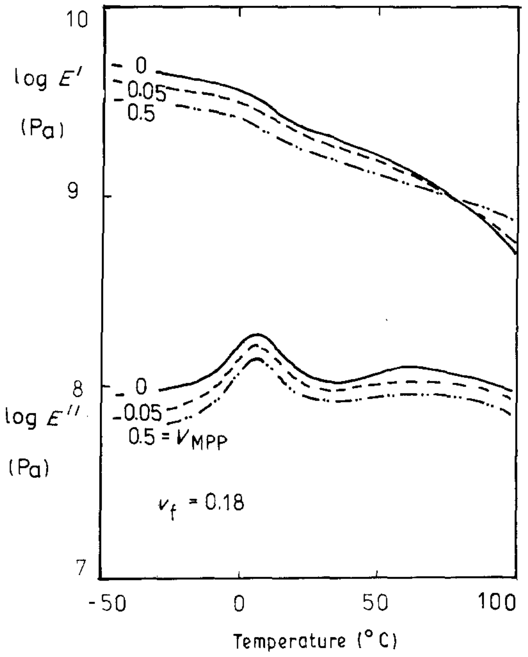

Figure 13 Temperature dependence of Young's modulus of PP filled with 18% vol/vol $CaCO_3$ and containing different MA contents (1 Hz).

The "effective interlayer thickness" increased with adhesion enhancement. This caused the appearance of new loss maximum at 50 °C for compounds containing less filler; however, this feature was observed only for the needle-shaped $Mg(OH)_2$ which had the largest specific surface area and, hence, the highest content of immobilized matrix.

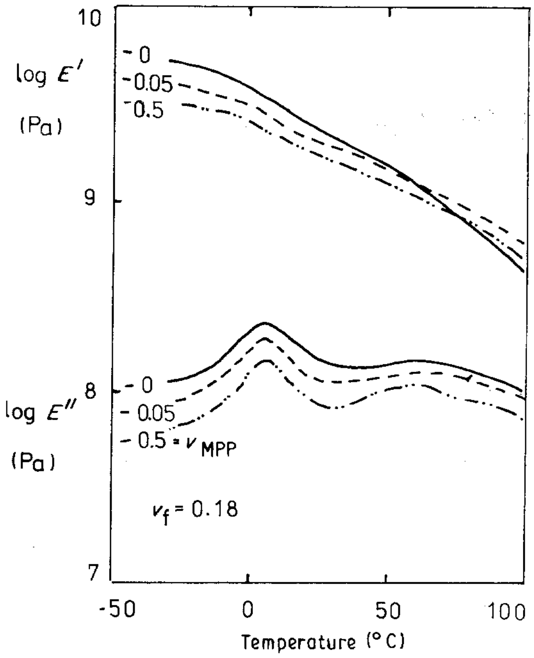

Figure 14 As Fig. 13 for $Mg(OH)_2$ platelet-filled PP.

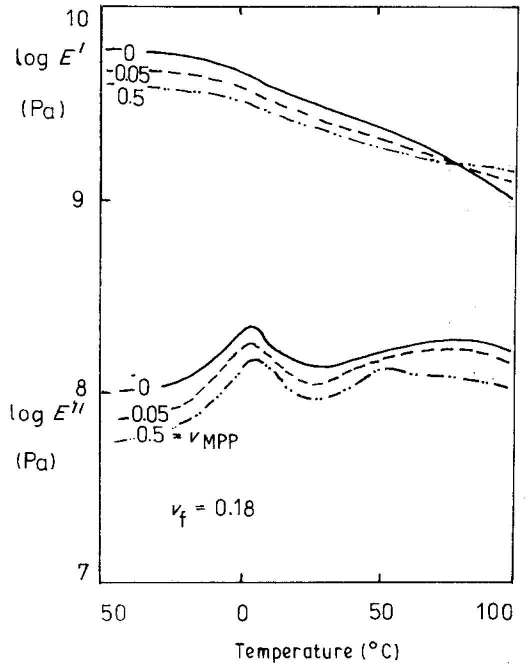

Figure 15 As Fig. 13 for $Mg(OH)_2$ needle-filled PP.

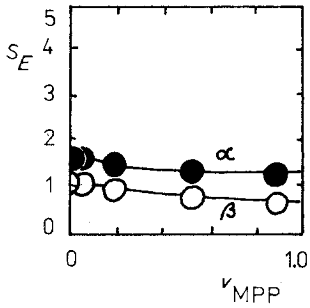

Figure 16 Dependences of β- and α-relaxation strengths of PP filled with 18% vol/vol $CaCO_3$ on the MA content.

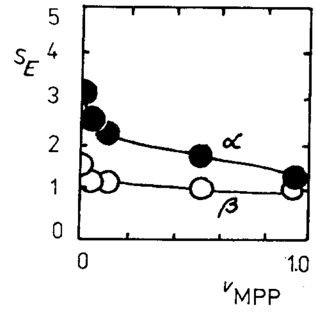

Figure 17 As Fig. 16 for $Mg(OH)_2$ platelet-filled PP.

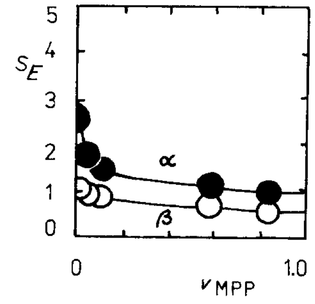

Figure 18 As Fig. 16 for $Mg(OH)_2$ needle-filled PP.

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