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Temperature dependence of the mechanical properties of EPDM rubber–polyethylene blends filled with aluminium hydrate particles

Part 1 *Characterization and dynamic mechanical behaviour*

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New flame-retardant electrical cables producing no toxic or corrosive gases and smokes when they are exposed to fire are now developed, in particular EPDM rubber–polyethylene blends filled with large amounts of aluminium hydrate particles. The aim of the present work is to study the mechanical behaviour of different filled EPDM–polyethylene blends as a function of temperature. In this first part, the characterization of the initial polymers (EPDM, polyethylene, silane-modified polyethylene) and their corresponding filled blends is presented. Electron microscopical observations reveal that the inorganic particles are embedded in the elastomer phase and consequently are well dispersed within the matrix. Thermal analysis performed by differential scanning calorimetry shows that the characteristics (melting temperatures, degree of crystallinity) of the initial polymers are only slightly affected either when they are mixed together or by the presence of filler. Finally, the variations of the dynamic mechanical moduli of filled blends with the filler volume fraction are in good agreement with the predictions of classical models. The main object of the second paper will be to describe the variation of the static mechanical properties of the blends with temperature and to evidence the causes of an unexpected phenomenon of brittleness which appears at about 70° C.

1. Introduction

Flame-retardant electrical cables made of chlorine-containing polymers, such as chloroprene rubber, polyvinylchloride or chlorosulphonated polyethylene, produce large amounts of corrosive and toxic gases (HCl, CO etc.) and smoke when they are exposed to fire. These combustion smokes and gases cause serious personal injuries and contribute to amplifying the disaster due to a fire, especially in crowded areas. Consequently, since a few years ago, new non-halogen flame-retardant cables producing no hydrogen halide gas like HCl have been developed. Recently, use has been made of blends of EPDM rubber–polyethylene filled with large amounts of aluminium hydrate (up to about 50 vol %). In a fire, aluminium hydrate absorbs a large part of the combustion heat which is necessary for its endothermal dehydration. The pyrolysis of the matrix is thus delayed and later the velocity of the combustion is decreased. Furthermore, the water vapour produced by the dehydration of the aluminium hydrate dilutes the combustion gases, accompanied again by a slow-down of the combustion rate. However, the use of large amounts of inorganic filler generally alters some important mechanical properties of the materials. To solve this difficulty it is possible to crosslink the matrix, for instance by using a silane-modified polyethylene which is effective even at room temperature. This polymer, in the presence of water vapour which causes at room temperature the hydrolysis of the grafted silane, is progressively crosslinked without using any other chemical additives such as peroxides. Thus, suitable tensile strengths of the final composites are obtained, but the elongations at break of the crosslinked materials are reduced. Moreover, such materials are expensive. When employing blends of polyethylenes and elastomers for manufacturing the new type of electrical cables, due to the existence in the mixture of a rubbery phase, the mechanical properties are strongly dependent on temperature. Further, it was noticed that the filled blends presented

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a ductile–brittle transition at about 70° C, i.e. at the working temperature of electrical cables having similar compositions.

The aim of the present work is to study the mechanical behaviour of different filled EPDM rubber–polyethylene blends at various temperatures, from about 20 to 120° C.

In this first part, the characterization of EPDM rubber, polyethylenes and their unfilled and filled blends is considered. The morphology of the blends and, in particular, the distribution of aluminium hydrate particles within the matrix, are studied by optical and electron microscopies. The thermal analysis of all these materials is then performed by differential scanning calorimetry. Finally, their dynamic mechanical behaviour is studied in relation to the temperature.

A following paper [1] will describe the variation of the static mechanical properties of the blends with temperature and, particularly, the phenomenon of brittleness which appears at about 70° C.

2. Experimental procedure

2.1. Materials

Poly(ethylene–propylene-diene monomer), EPDM rubber (Vistalon 3708, Essochem) contained (5-ethylene 2-norbornene) and about 65% of ethylene.

The thermoplastic polymeric phase used initially was a low-density ($0.92\,\mathrm{g\,cm^{-3}}$) polyethylene (PE) (DFDG 2142, BP Chemicals). Later, this same PE was modified by grafting using trimethoxyvinyl silane as the reagent. About 2 wt % of silane groups are fixed on the polymer. This silane-modified polyethylene (SMPE) was then mixed with an equivalent weight amount of unmodified PE to obtain the polymeric phase.

Aluminium hydrate (AH) (Apyral 120-VAW) with α-crystalline structure was employed. The AH particles looked like hexagonal flakes with an aspect ratio equal to about 10 (mean diameter $\simeq 0.5\,\mu\mathrm{m}$ and mean thickness $\simeq 0.06\,\mu\mathrm{m}$). The specific surface area, measured by nitrogen adsorption (BET) was equal to $13 \pm 1\,\mathrm{m^2\,g^{-1}}$. Their density was $2.4\,\mathrm{g\,cm^{-3}}$. Differential scanning calorimetry (DSC) showed that the dehydration of AH particles began at about 180° C. The total weight loss during this heating was equal to about 35%.

The unfilled blends were prepared by mixing the components in a Brabender Plasti-Corder PLE 651 device for 15 min at 140° C and at a shear rate of $60\,\mathrm{min^{-1}}$. The mixture was then moulded at 160° C to obtain panels with $\simeq 2$ mm thickness. Two types of matrix were then obtained with the following composition (by weight):

EPDM rubber 60%–PE 40%

EPDM rubber 60%–PE 20%–SMPE 20%

The filled composites made from these two matrices were obtained by mixing in a Banbury apparatus 100 parts of blends and 50, 100, 150 or 200 parts by weight of AH, corresponding to volume fractions of filler respectively equal to 0.17, 0.29, 0.38 and 0.45.

2.2. Measurements

The scanning electron (SEM) or transmission electron (TEM) micrographs were taken with a Jeol JEM 100 B apparatus.

In order to study the morphological aspects of unfilled and filled blends, especially the distribution of the AH particles in the matrix, thin slices of the different materials were obtained by means of a microtome. On the one hand, for optical microscopy, slices (thickness $\simeq 3$ to $5\,\mu\mathrm{m}$) were cut at room temperature and directly recovered. On the other hand, for electron microscopy, very thin slices (thickness less than 100 nm) were made in the same way but recovered on water. To visualize the localization of phases, either in the unfilled or filled blends, the EPDM elastomer was etched off prior to microscopical observations by immersing the samples in toluene for 20 days at room temperature. They were then dried for 2 days under vacuum at room temperature.

The thermal analysis of the starting polymers and their unfilled and filled blends was carried out by DSC with a Mettler TA 3000 apparatus. The samples (10 mg) were analysed under a constant nitrogen gas flow ($0.5\,\mathrm{ml\,min^{-1}}$). To put the different materials in the same thermal state and, consequently, to obtain reproducible and comparable results, all samples were submitted to the following thermal conditions prior to DSC analysis:

(i) heating from -100 to $+140°$ C with an increasing rate of $10°\,\mathrm{C\,min^{-1}}$,

(ii) quenching from $+140$ to $+25°$ C with a decreasing rate of about $50°\,\mathrm{C\,min^{-1}}$,

(iii) isothermal treatment at $+25°$ C for 20 min.

The DSC spectra were then recorded from room temperature to $+140°$ C with an increasing rate of $10°\,\mathrm{C\,min^{-1}}$. The melting temperature and the melting enthalpy of EPDM rubber and polyethylenes were noted in each case. The degree of crystallinity C of PE phases was calculated using the relationship

$$C(\%) = (\Delta H/\Delta H_c) \times 100$$

where ΔH and ΔH_c are respectively the measured melting enthalpy and that of a pure crystal of the same PE. For a low-density polyethylene, ΔH_c was taken equal to $270.0\,\mathrm{J\,g^{-1}}$ according to Aggarwal [2]. For EPDM rubber, the same calculation using the same value of ΔH_c was also made to obtain an estimate of its degree of crystallinity, although the choice of this ΔH_c value is open to criticism.

Dynamic mechanical measurements were performed with a Metravib apparatus on samples having a cylindrical shape (base diameter $\simeq 9$ mm and height $\simeq 15$ mm), which had been moulded at 150° C. The samples were glued on the plates of the apparatus and submitted to sinusoidal compression–elongation forces at frequencies (ω) varying from 7.8 to 62.5 Hz. Their storage modulus E' and loss modulus E'' were determined as functions of temperature from 20 to 120° C, at intervals of 10° C.

3. Results and discussion

SEM and TEM micrographs (Figs 1a and b) confirm

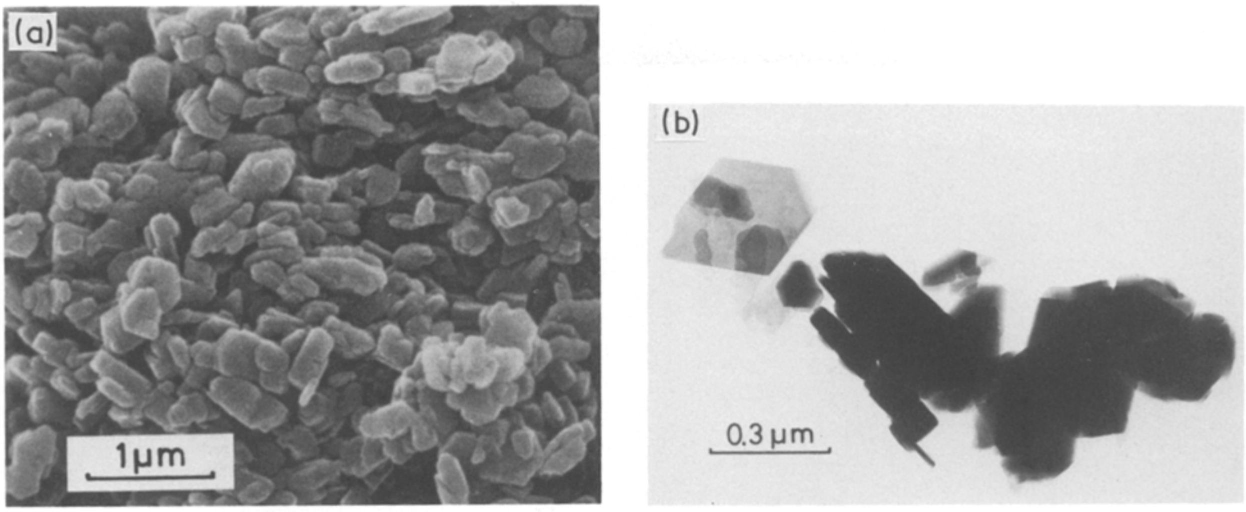

Figure 1 (a) SEM and (b) TEM micrographs of aluminium hydrate particles.

that the shapes of aluminium hydrate particles are irregular flakes with an apparent mean diameter equal to about 0.5 μm.

The dispersion of a large amount (volume fraction = 0.45) of these particles in EPDM rubber–PE blends is shown in Fig. 2. Sometimes, the presence of a few small aggregates can be seen. Nevertheless, the AH flakes are remarkably well dispersed in the matrix, even for such a large volume fraction.

Fig. 3 presents the surface aspect of an unfilled blend after dissolution of the EPDM rubber phase in toluene. As observed elsewhere [3], both components certainly form an interpenetrating network, but it is difficult to distinguish this kind of structural detail on the micrograph. It appears that the mean size of the domains occupied by the rubber phase is in the order of 0.2 to 0.5 μm.

Concerning the filled blends before and after etching treatment of EPDM rubber, Fig. 4 clearly shows that the aluminium hydrate particles are very easily extracted from the matrix after immersion in toluene. In particular, in Figs 4b and c there is no evidence of flakes bound to the PE phase. Consequently, it seems that the EPDM elastomer phase preferentially covers all the aluminium hydrate particles. This observation could explain the good dispersion of the filler, already coated by an EPDM skin during mixing, in the matrix.

All the photographs in Figs 2 to 4 concern only EPDM–PE–AH blends, but identical observations have been made on EPDM–PE–SMPE–AH systems.

The results concerning the thermal analysis by DSC of EPDM rubber, polyethylenes and their unfilled and filled blends are given in Tables I, II and III. There are no particular comments on the characteristics of EPDM elastomer. The melting temperature and the degree of crystallinity of silane-modified PE are somewhat lower, about 2° C and 3% respectively, than those of unmodified PE. By comparison of Table I with the first line of Tables II and III, it can be observed that both EPDM rubber — or PE — melting points and degrees of crystallinity decrease when they are blended together.

The thermal characteristics of the two phases which constitute the matrix are also dependent on the volume fraction of the filler (Tables II and III). The melting temperature of the EPDM elastomer is kept constant or lightly decreases, while its degree of crystallinity increases continuously with volume fraction of AH particles. On the other hand, either the melting points

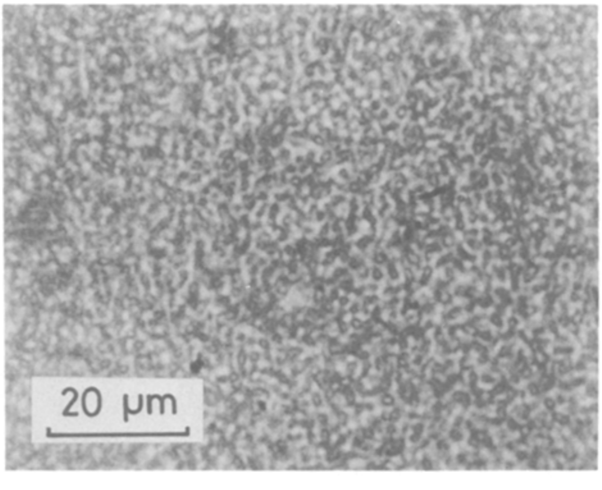

Figure 2 SEM micrograph of filled (ϕ = 0.45) EPDM–PE blend.

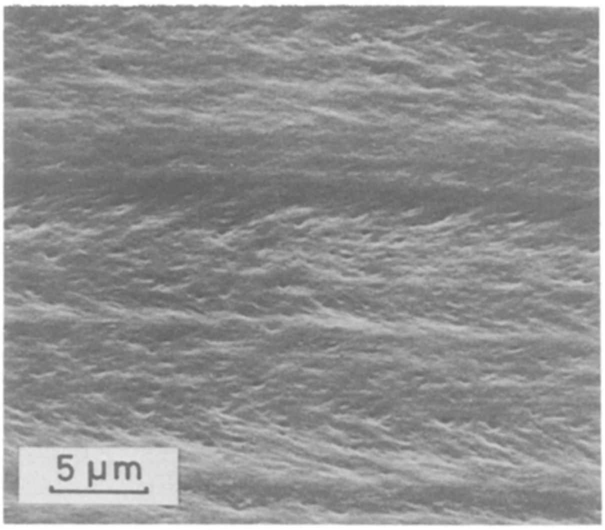

Figure 3 SEM micrograph of unfilled EPDM–PE blend, after dissolution of the EPDM rubber phase in toluene.

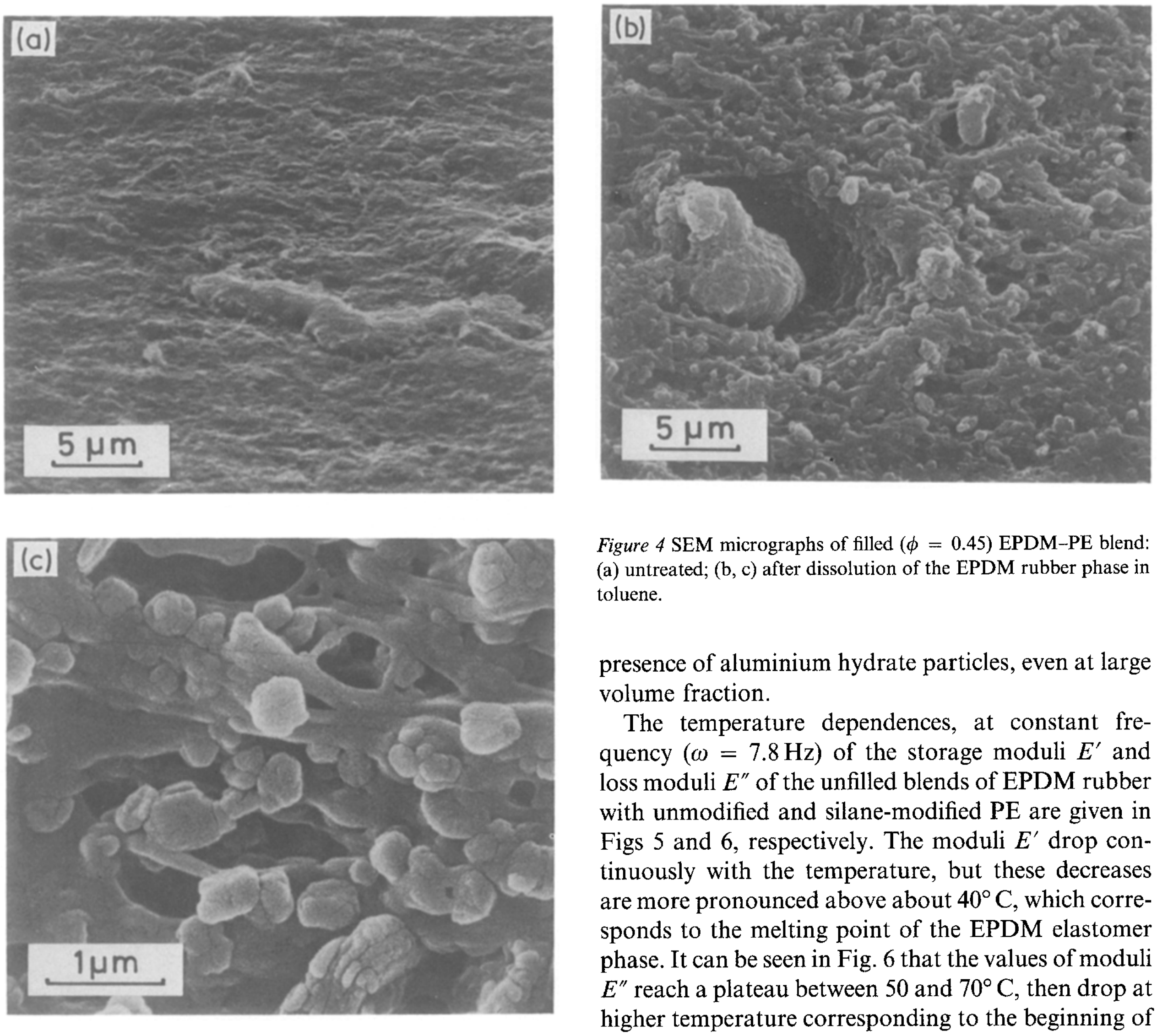

Figure 4 SEM micrographs of filled ($\phi = 0.45$) EPDM–PE blend: (a) untreated; (b, c) after dissolution of the EPDM rubber phase in toluene.

or the degrees of crystallinity of PE phases slightly decrease with volume fraction of filler, on the whole uniformly. As previously observed, the filler seems to be totally coated by EPDM rubber and so the increase of the degree of crystallinity of this phase could be explained by the epitaxial growth of crystals near the aluminium hydrate surface in agreement with other observations [4, 5] concerning polypropylene–mica systems. On the other hand, since the PE phase is never in contact with the filler, the presence in the blend of the latter should not influence the crystalline structure of the former. The observed decrease of the degree of crystallinity of the PE phase could then be explained by a morphological hindrance of crystal growth, due to the increasing volume fraction of filler.

Nevertheless, we can conclude that the thermal properties and the crystalline structure of the starting materials are only very slightly affected by the presence of aluminium hydrate particles, even at large volume fraction.

TABLE I Melting temperature (T_f) and degree of crystallinity (C) of the initial polymers

Polymer	T_f (°C)	ΔH (J g^{-1})	C (%)
EPDM	50.3	21.8	8.1
PE	118.3	113.2	41.9
SMPE	116.3	105.7	39.2

The temperature dependences, at constant frequency ($\omega = 7.8$ Hz) of the storage moduli E' and loss moduli E'' of the unfilled blends of EPDM rubber with unmodified and silane-modified PE are given in Figs 5 and 6, respectively. The moduli E' drop continuously with the temperature, but these decreases are more pronounced above about 40° C, which corresponds to the melting point of the EPDM elastomer phase. It can be seen in Fig. 6 that the values of moduli E'' reach a plateau between 50 and 70° C, then drop at higher temperature corresponding to the beginning of the PE crystals melting. The variation of the moduli E' and E'', for the unfilled blend EPDM–unmodified PE, against frequency ω at different temperatures are shown in Figs 7a and b, respectively. It can be observed that all the curves have the same shape whatever the temperature and are simply vertically shifted. Such a result indicates that this polymeric system follows the William–Landel and Ferry time–temperature equivalence principle [6].

The influence of temperature, at various volume fractions (ϕ) of filler, on the moduli E' and E'' of the two kinds of blend used in this study is respectively described in Figs 8 and 9 at constant frequency $\omega = 7.8$ Hz. As expected, whatever the temperature and the nature of the matrix, these moduli increase with the volume fraction of aluminium hydrate particles. However, in each case the values of the moduli for the matrix containing silane-modified PE are lower than those concerning the blend EPDM–unmodified PE. A comparison between the dynamic mechanical behaviours of both filled blends at 20° C and 7.8 Hz is shown in Fig. 10, where E' and E'' are plotted against ϕ.

Considerable theoretical and experimental work has been devoted to the problem of predicting the dynamic moduli of filled polymers from pure-component data [7, 8]. In particular, the observed increases of E' and E'' with the volume fraction ϕ of

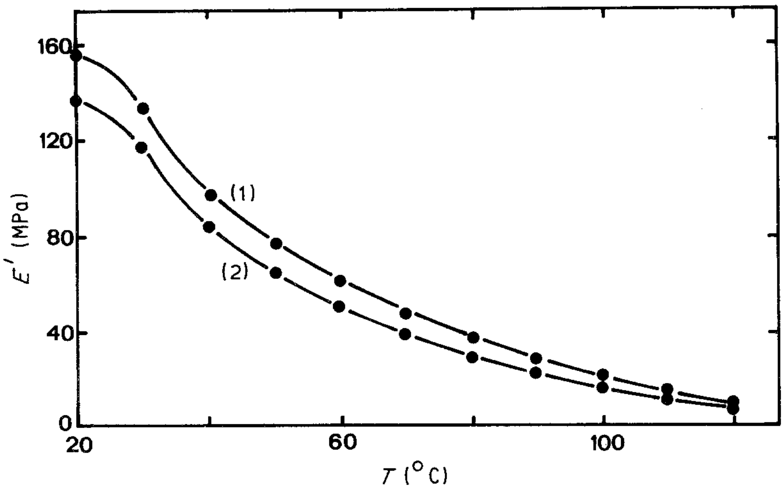

Figure 5 Temperature dependence of the storage moduli E' of unfilled (1) EPDM–PE and (2) EPDM–PE–SMPE blends (frequency = 7.8 Hz).

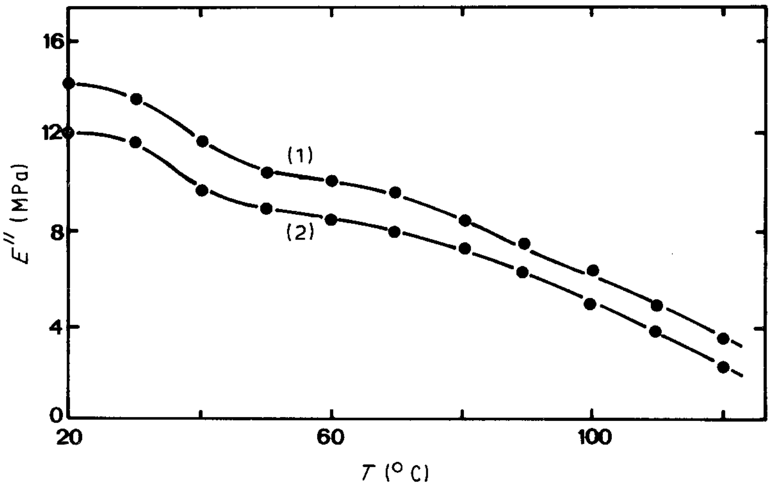

Figure 6 Temperature dependence of the loss moduli E'' of unfilled (1) EPDM–PE and (2) EPDM–PE–SMPE blends (frequency = 7.8 Hz).

aluminium hydrate can be compared, for example in the case of the filled EPDM–PE–SMPE blend at 20° C, with the values obtained from classical semi-empirical relationships like those proposed by Guth [9] and Smallwood [10] and Eilers [11]. In the first case, the relative moduli E_r' and E_r'', defined as the ratios E'/E_0' and E''/E_0'', where E_0' and E_0'' are the moduli of the unfilled blend, are given by

$$E_r' = E_r'' = 1 + 2.5\phi + 14.1\phi^2 \qquad (1)$$

Equation 1 is a modification of the relationship for relative viscosity, valid for suspensions of a small volume fraction of rigid spheres, and proposed by Einstein; the last term in the right-hand side takes into account interparticle interactions. The Eilers relationship takes the form

$$E_r' = E_r'' = \left(1 + \frac{k\phi}{1 - S\phi}\right)^2 \qquad (2)$$

TABLE II Melting temperature (T_f) and degree of crystallinity (C) of EPDM rubber and PE phases in unfilled and filled blends EPDM–PE

Volume fraction of filler, ϕ	EPDM			PE		
	T_f (°C)	ΔH (J g^{-1})	C (%)	T_f (°C)	ΔH (J g^{-1})	C (%)
0	44.0	10.2	3.8	115.3	107.5	40
0.29	43.5	13.2	4.9	114.5	105.2	39
0.38	43.4	12.7	4.7	113.6	103.1	38
0.45	41.2	13.0	4.8	113.3	102.9	38

TABLE III Melting temperature (T_f) and degree of crystallinity (C) of EPDM rubber and PE phases in unfilled and filled blends EPDM–PE–SMPE

Volume fraction of filler, ϕ	EPDM			PE–SMPE		
	T_f (°C)	ΔH (J g^{-1})	C (%)	T_f (°C)	ΔH (J g^{-1})	C (%)
0	41.9	11.6	4.4	113.0	99.8	37
0.29	42.3	11.9	4.4	112.2	94.3	35
0.38	42.0	13.3	4.9	111.8	92.7	34
0.45	42.5	14.6	5.4	111.3	90.5	34

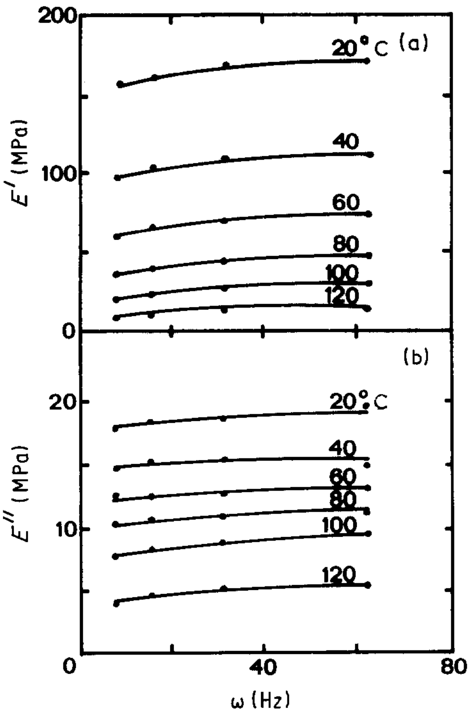

Figure 7 Frequency dependence of (a) storage moduli E' and (b) loss moduli E'' of unfilled EPDM–PE blend at different temperatures.

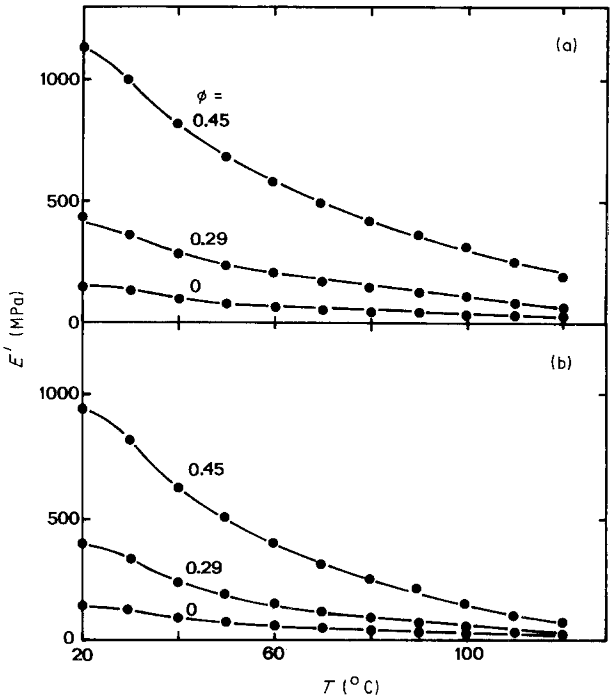

Figure 8 Temperature dependence of the storage moduli E' of filled (a) EPDM–PE and (b) EPDM–PE–SMPE blends at different volume fractions ϕ of aluminium hydrate particles (frequency = 7.8 Hz).

where k and S are empirical constants equal to about 1.25 and 1.5, respectively. Equation 2 has the same mathematical form as that proposed by Maron and Belner [12] to describe the relationship between viscosity and the spherical particle concentration of a suspension. Robinson [13] has shown that $2k = 2.5$, Einstein's viscosity constant, and that S^{-1} is equivalent to the solid volume fraction of a dense packing of spheres. It must be noted that the slope of the tangent at the origin for Equation 1 as well as for Equation 2 is equal to 2.5.

In Fig. 11, the measured values of the relative moduli E_r' and E_r'', at 20° C and 7.8 Hz, are compared as functions of ϕ with the theoretical variations from Equations 1 and 2. It can be seen that these experimental values are in good agreement with Guth and Smallwood's model for low volume fractions, less than about 0.35, while the Eilers model becomes well

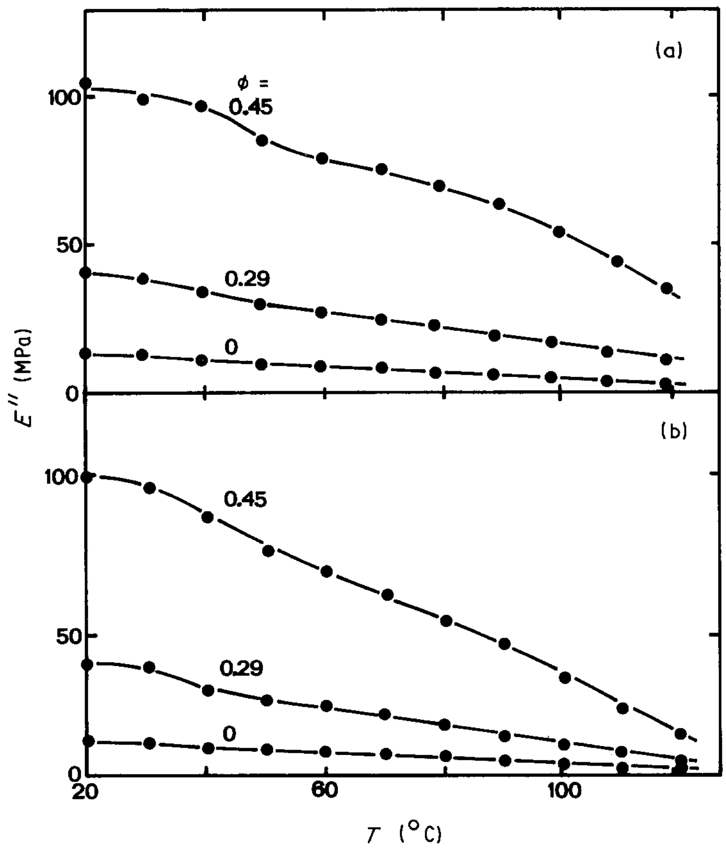

Figure 9 Temperature dependence of the loss moduli E'' of filled (a) EPDM–PE and (b) EPDM–PE–SMPE blends at different volume fractions ϕ of aluminium hydrate particles (frequency = 7.8 Hz).

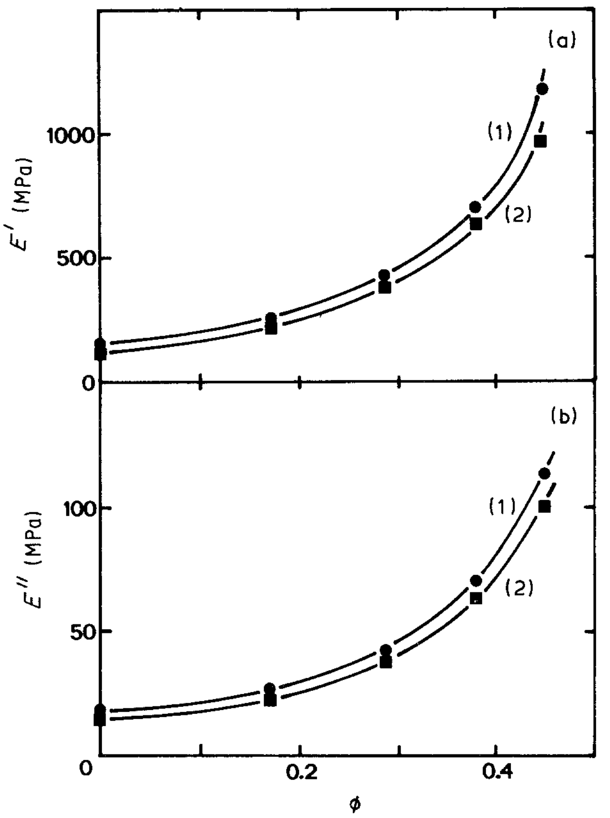

Figure 10 Variations of (a) storage moduli E' and (b) loss moduli E'' against the filler volume fraction ϕ (frequency = 7.8 Hz and temperature = 20° C): (1) EPDM–PE blend, (2) EPDM–PE–SMPE blend.

adapted to describe the results at higher volume fractions. Hence, these two very simple models seem valid for our systems, although no account is taken of the thermal stresses developed at the filler–matrix interface. This is not always the case for other filled blend systems [14], where it is necessary to use more sophisticated models, like Kerner's or the Halpin–Tsai–Nielsen generalized equations [8, 15].

4. Conclusion

In this part of our study the characterization of EPDM rubber, unmodified and silane-modified polyethylenes and their corresponding blends filled with aluminium hydrate flakes was presented.

It was shown that the inorganic particles are totally embedded in the EPDM elastomer phase. This explains the good dispersion of filler in the matrix, observed by electron microscopy, even at high loadings.

The thermal characteristics of the starting polymers are only slightly affected either when they are mixed together or by the presence of filler: the melting temperatures of EPDM rubber and PE are somewhat reduced. The degree of crystallinity of the elastomer phase increases in contact with the filler, while it decreases for PE–$Al(OH)_3$ mixtures. These results may be accounted for by, in the first case, an epitaxial crystal growth of EPDM in the vicinity of aluminium hydrate and, in the second case, by a spatial hindrance of PE crystal growth.

Finally, the dynamic mechanical properties of unfilled and filled blends were studied as functions of temperature and frequency. Classical models such as those proposed by Guth, Smallwood and Eilers describe well the influence of the filler volume fraction on the storage and loss moduli of the filled systems.

The second part of this paper will be devoted to the static mechanical behaviour of the filled blends in relation with temperature, since preliminary observations of the fracture facies of these materials have shown that they present a ductile–brittle transition phenomenon at about 70° C. The main object of the following paper will be to evidence the causes of this unexpected phenomenon.

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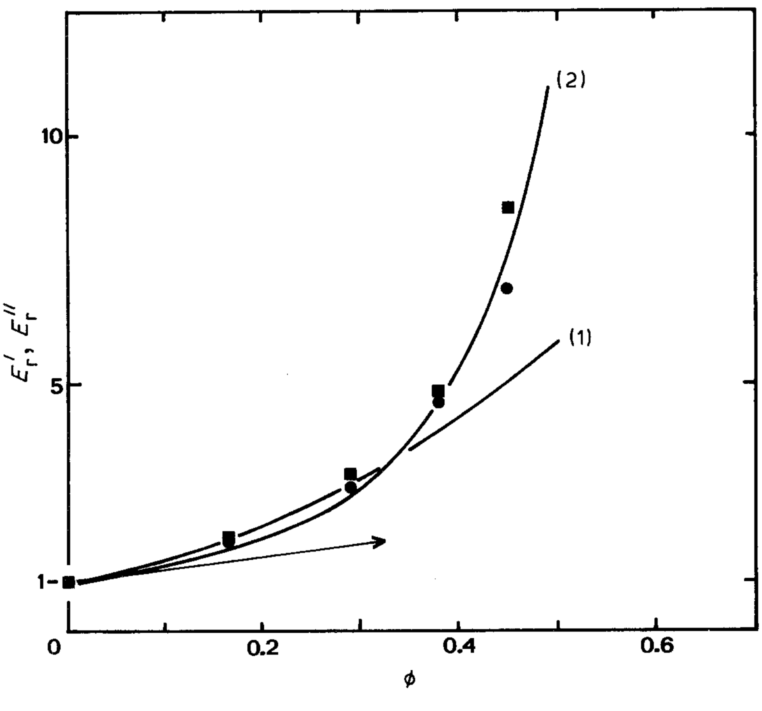

Figure 11 Variations of the relative moduli (●) E_r' and (■) E_r'' against the filler volume fraction ϕ, the curves corresponding to (1) Equation 1 and (2) Equation 2 (frequency ≐ 7.8 Hz and temperature = 20° C).

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