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

Part 2 *Static mechanical behaviour*

M. T. CHANLIAU-BLANOT, M. NARDIN, J. B. DONNET, E. PAPIRER
Centre de Recherches sur la Physico-Chimie des Surfaces Solides,
24, Avenue du Président Kennedy, 68200 Mulhouse, France
G. ROCHE, P. LAURENSON
Société Anonyme de Télécommunications – Câblerie de Riom, Route de Maréchat, BP 153,
63203 Riom Cedex, France
G. ROSSIGNOL
Société Industrielle de Liaisons Electriques, Rue de Varennes Prolongée, 77130 Montereau,
France

In this second part of the study concerning the characterization of new flame-retardant materials, special attention has been paid to a ductile–brittle transition which occurs at about 70° C. In order to evidence the causes of this unexpected phenomenon of brittleness, all the tensile mechanical properties (tensile strength, strain at break and modulus of elasticity) of filled and unfilled EPDM–polyethylene blends are systematically studied in relation to thermal conditions. Examination of the fracture facies of broken samples, at different temperatures, clearly points out this transition. It is shown that the presence of a rubber phase within the matrix is solely responsible for this type of behaviour. The fracture energy of the blends, as a function of filler volume fraction and temperature, is also determined. Finally, a very simple test on folded samples, allowing a precise determination of the critical temperature at which the ductile–brittle transition occurs, is developed.

1. Introduction

In a previous paper [1], the properties of new non-halogen flame-retardant materials were determined as a function of the temperature. These materials are constituted by an EPDM rubber–polyethylene blend filled with a large amount of aluminium hydrate particles. Firstly, the morphological aspects of these blends and the distribution of the filler particles in the matrix were studied. It was shown that the filler particles, totally coated by the EPDM phase, were very well dispersed in the blend. Secondly, the thermal characteristics of the pure polymers, analysed by differential scanning calorimetry (DSC), were not or only slightly affected when they were mixed together or filled with aluminium hydrate flakes. Finally, a dynamic mechanical study of unfilled and filled blends showed that classical models describe well the influence of the filler volume fraction on storage and loss moduli.

The second part of this study deals with the static mechanical behaviour of these materials in relation to the temperature. In fact, it was noticed by observation of their fracture surfaces that, surprisingly, filled blends presented a ductile–brittle transition around 70° C. The aim of the present paper is to find an explanation of the phenomenon of brittleness which appears on increasing the temperature of a deformed sample. Consequently, all the tensile mechanical properties (tensile strength, strain at break and Young's modulus) of the blends are systematically studied in relation to thermal conditions. The fracture energy, as a function of filler volume fraction and temperature, is also determined. Fracture facies of broken samples, at different temperatures, are observed by electron microscopy. Finally, a simple test allowing a precise measurement of the critical temperature at which the brittleness occurs is developed.

Actually, the purpose of all these experiments is to find out which constituent of the filled blends is responsible for the initially unexpected phenomenon of fragilization by temperature increase of the stressed polymer blends.

2. Experimental procedure

2.1. Materials

Thermoplastic polymeric phases of the blends, comprising unmodified low-density polyethylene (PE) and silane-modified polyethylene (SMPE), were used in the same conditions as previously described [1]. In addition to the EPDM elastomer fully characterized in the previous paper and now denoted EPDM-1, two other

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TABLE I Melting temperature T_f and degree of crystallinity C of the elastomers

Polymer	T_f (°C)	ΔH (J g^{-1})	C (%)
EPDM-1	50.3	21.8	8.1
EPDM-2	–	0	0
EPDM-3	48.1	10.6	3.9
EPR	54.1	49.4	18.3

types of EPDM rubber (EPDM-2 and EPDM-3) (Vistalon, from Essochem) and ethylene–propylene–rubber (EPR) were also employed. Their thermal properties (melting temperature T_f, melting enthalpy ΔH and degree of crystallinity C) determined by DSC [1] and their ethylene content are gathered in Table I. All three kinds of EPDM rubber contain 5-ethylidene-2-norbornene as diene monomer.

Two types of filler were used: on the one hand, the well-characterized aluminium hydrate flakes of the previous study and, on the other hand, a thermal carbon black (Sterling MT, Cabot, USA) with a density of 2 g cm^{-3} and a specific surface area equal to 8.5 m^2 g^{-1}. Thus, the influence of the nature of the filler on the mechanical behaviour of filled blends can be then determined.

The unfilled and filled blends were made under the same experimental conditions as previously described. In each case, and independently of the nature of the constituents, the composition of the blends was always, by weight, 60% of elastomer phase and 40% of thermoplastic polymeric phase (40% PE or 20% PE + 20% SMPE). The volume fraction ϕ of aluminium hydrate particles varied from 0 to 0.45, while that of carbon black was constant and equal to 0.50.

2.2. Measurements

To study the static mechanical behaviour of our unfilled and filled blends, stress–strain curves were obtained on an Instron 1195 H tensile testing machine, at a constant crosshead speed of 10 mm min^{-1}. The testing machine was equipped with an environmental chamber enabling the temperature to be varied from room temperature to about 100° C. The elongation was measured by an optical extensometer. Each sample, with the standard ISO 1/2 shape, was held in the chamber for 30 min before testing in order to reach thermal equilibrium at the chosen temperature. Tensile strength (σ_t), strain at failure (ε_r) and Young's modulus (E) at 0.2% strain were then measured on five samples for each system.

Measurements of fracture energy were also carried out with the same mechanical and thermal conditions using a "trouser tear" test, described elsewhere [2]. The tear test pieces consisted of rectangular strips, about 2 mm thick, partially precut with a razor blade on each side along a central line so that only about 0.6 mm of the thickness remained to be torn through. The fracture energy G was calculated from the tear force F by the equation

$$G = \frac{2F}{t}$$

where t is the width of the tear path. No correction is made concerning the experimental value of t, since in our case notches have been made on the two sides of our samples.

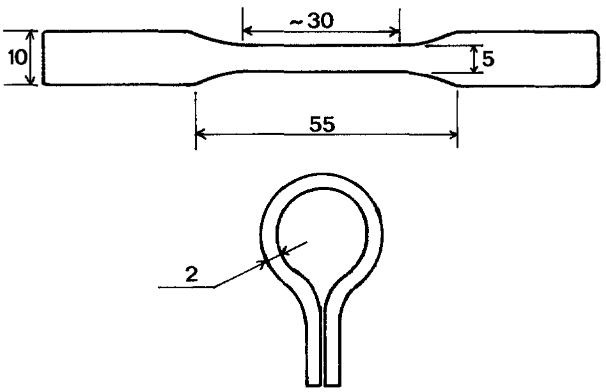


Figure 1 Unfolded and folded ISO 1/2 samples (dimensions in millimetres).

To study the phenomenon of brittleness of filled blends in the temperature range 60 to 80° C, a very simple test was specially developed. Samples (ISO 1/2) were folded as shown in Fig. 1 and put in the environmental chamber. The temperature inside this chamber was then gradually increased from 20 to 120° C with an increasing rate of 1° C min^{-1} and under constant nitrogen gas flow. The behaviour of each sample was continuously followed and recorded by means of a video system provided with a timer. Consequently, one was able to measure precisely at which critical temperature θ_c failure of the folded samples occurred. Three samples in each case were tested by this method.

Finally, fracture surface micrographs of filled blends were obtained by scanning electron microscopy (SEM) using a Jeol JEM 100 B.

3. Results and discussion

The values of tensile strength σ_t, strain at failure ε_r and modulus of elasticity E (at 0.2% strain) of unfilled and filled blends (EPDM-1–PE or PE–SMPE) are gathered in Tables II and III. The scatter of the results is equal

TABLE II Tensile strength, strain at failure and Young's modulus of unfilled and filled EPDM-1–PE blends at different temperatures

T	Temperature (° C)				
ϕ	20	40	60	80	100
Tensile strength, σ_t (MPa)					
0	> 11.0	> 2.3	> 1.5	1.2	0.5
0.17	> 14.6	> 2.9	> 2.0	1.3	0.6
0.29	8.8	> 4.3	1.9	1.1	0.6
0.38	6.2	> 3.7	2.3	1.5	0.8
0.45	6.8	4.3	2.9	1.6	1.1
Strain at failure, ε_r (%)					
0	> 800	–	–	83	31
0.17	> 800	–	–	138	45
0.29	737	–	126	63	40
0.38	663	–	79	26	35
0.45	76	50	15	9	16
Young's modulus, E (MPa)					
0	0.9	0.8	0.6	0.4	0.2
0.17	1.3	0.8	0.3	0.2	0.1
0.29	2.0	0.9	0.6	0.3	0.1
0.38	4.3	2.4	1.1	0.7	0.3
0.45	4.6	2.6	1.4	0.8	0.5

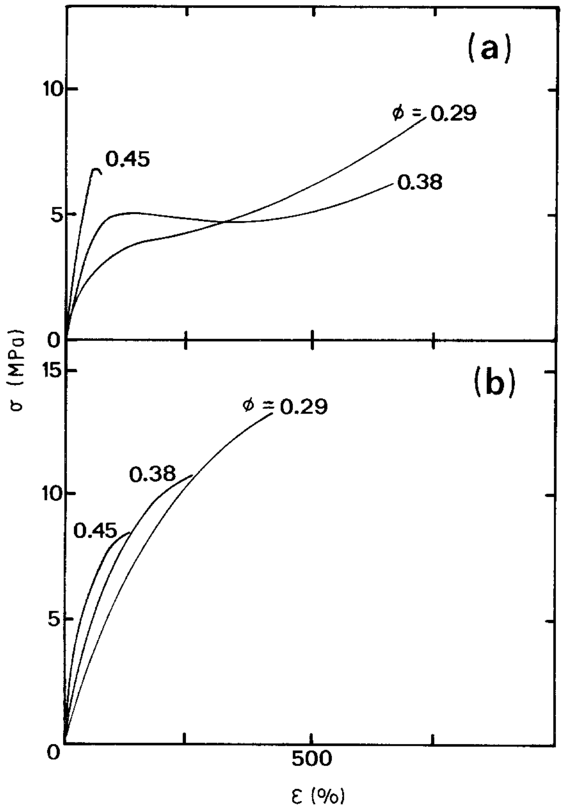


Figure 2 Stress–strain curves of (a) EPDM-1–PE blend and (b) EPDM-1–PE–SMPE blend at different filler volume fractions ϕ.

TABLE III Tensile strength, strain at failure and Young's modulus of unfilled and filled EPDM-1–PE–SMPE blends at different temperatures

T ϕ	Temperature (° C)				
	20	40	60	80	100
Tensile strength, σ_t (MPa)					
0	> 13.3	> 4.0	> 2.0	1.3	0.6
0.17	> 15.3	> 5.5	2.6	1.4	0.5
0.29	13.1	6.1	2.7	1.4	0.7
0.38	10.8	5.5	2.8	1.5	0.7
0.45	8.5	5.8	3.3	1.9	1.0
Strain at failure, ε_r (%)					
0	> 800	–	–	75	39
0.17	> 640	–	200	56	33
0.29	417	–	81	31	32
0.38	255	170	28	16	22
0.45	128	79	15	11	14
Young's modulus, E (MPa)					
0	1.4	1.0	0.8	0.4	0.2
0.17	1.9	0.9	0.2	0.1	0.1
0.29	2.5	1.0	0.3	0.2	0.1
0.38	4.6	2.1	1.0	0.5	0.2
0.45	5.0	2.4	1.2	0.5	0.4

to about 5 to 10%. For temperatures higher than or equal to 40° C, some ε_r values could not be measured since the corresponding values exceed 250%, which is the maximum strain measurable in our environmental chamber.

Firstly, it can be observed from Tables II and III that the use of silane-modified PE increases the tensile strength σ_t of the blends, at least for temperatures lower than 60° C, whatever the filler volume fraction ϕ. At the same time, the strain at break (ε_r) is in each case strongly reduced, except for the highest value of ϕ (0.45) especially at 20 and 40° C.

For example, stress–strain curves for both kinds of matrix employed in this study, at different filler loadings, are shown in Fig. 2. It is obvious that yielding and plastic deformation disappear when SMPE is present in the matrix. Such an effect is equivalent to a crosslinking of the PE network. As expected, the moduli of elasticity, whatever the nature of the blend, increase with the filler volume fraction at a given temperature, whereas they decrease with temperature at constant loading.

The most important results in this domain are the variations of strain at break ε_r, in relation to the temperature. In fact, it appears that for high values of ϕ, in particular $\phi = 0.38$ and 0.45, ε_r values, which uniformly decrease from 20 to 80° C, reach a minimum at about 80° C. The decrease with temperature of both σ_t and ε_r is illustrated in Fig. 3 at constant ϕ, while Fig. 4 gives the variations of ε_r with temperature at different loadings. In this last figure, the minimum values of ε_r at about 80° C are clearly shown.

Before analysing more precisely these results, it is interesting to observe some fracture facies of our composites at different temperatures. Figs 5 and 6 show macrographs of top and side views of the fracture zone of, respectively, EPDM-1–PE and EPDM-1–PE–SMPE blends filled with 45 vol % of aluminium hydrate at 20, 60 and 100° C in each case. At 20° C, classical ductile fracture exhibiting fibrillar structure can be seen for the EPDM-1–PE blend, this behaviour being less pronounced when SMPE is present in the matrix. At 60° C, whatever the composition of the blends, typical brittle fracture occurs. This fact constitutes what we now call the phenomenon of brittleness at temperature. Another mode of failure, equivalent to a ductile one, appears at higher temperature (100° C) and seems to be related to the beginning of PE crystals melting. A more detailed examination can be made on SEM micrographs (Figs 7 and 8) corresponding to fracture facies at 20 and 60° C, respectively, of filled ($\phi = 0.45$) EPDM-1–PE blend. For the lowest temperature, ductile fracture with polymeric fibres oriented along the stress direction is clearly shown. On the other hand, at 60° C this fibre structure does not exist and the tri-dimensional polymeric network seems to be simply broken up. For SMPE-containing blends, such differences between both temperatures are not so clearly observed, since, as described above, the presence of the silane-modified polymer reduced considerably the plastic deformation of the blend even at room temperature.

Before attempting an interpretation of this brittleness at temperature, it is interesting to consider a few results concerning the fracture energy G of the blends in relation to the filler volume fraction ϕ and temperature. Typical variations of G against ϕ at constant temperature are given in Fig. 9. It is generally accepted [3–5] that a crack front travelling through a material will be slowed down when it meets a filler particle and becomes temporarily pinned at that point. Then, the crack front bows forward between pinning points until it forms semicircular segments which will overlap

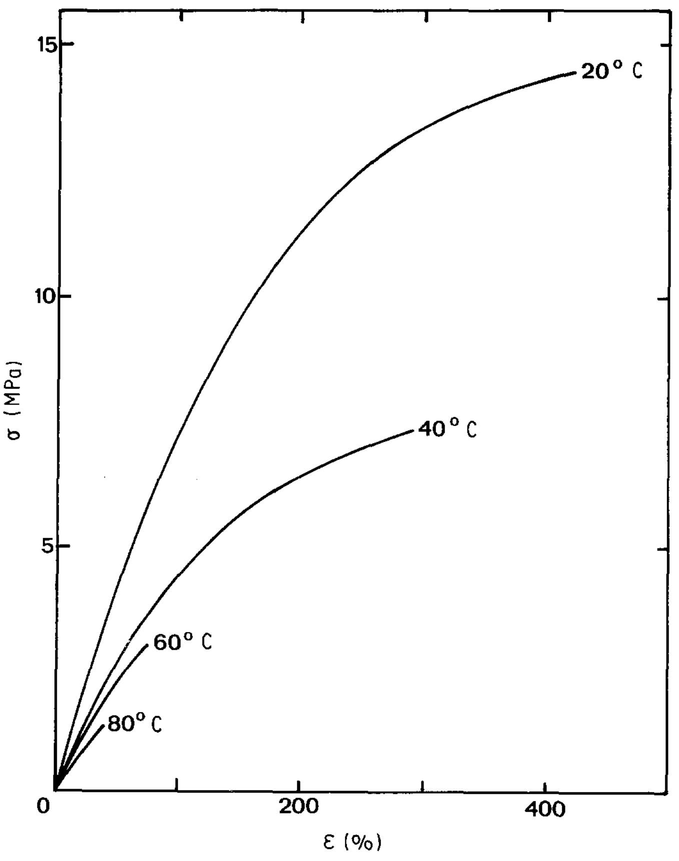


Figure 3 Stess–strain curves, at different temperatures, of EPDM-1-PE-SMPE blend (ϕ = 0.29).

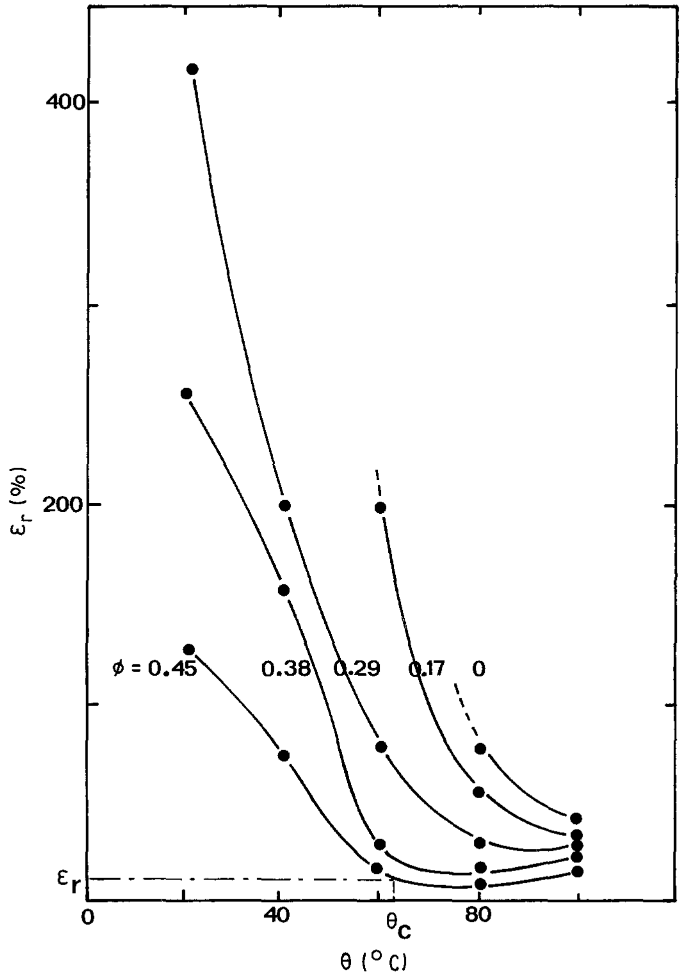
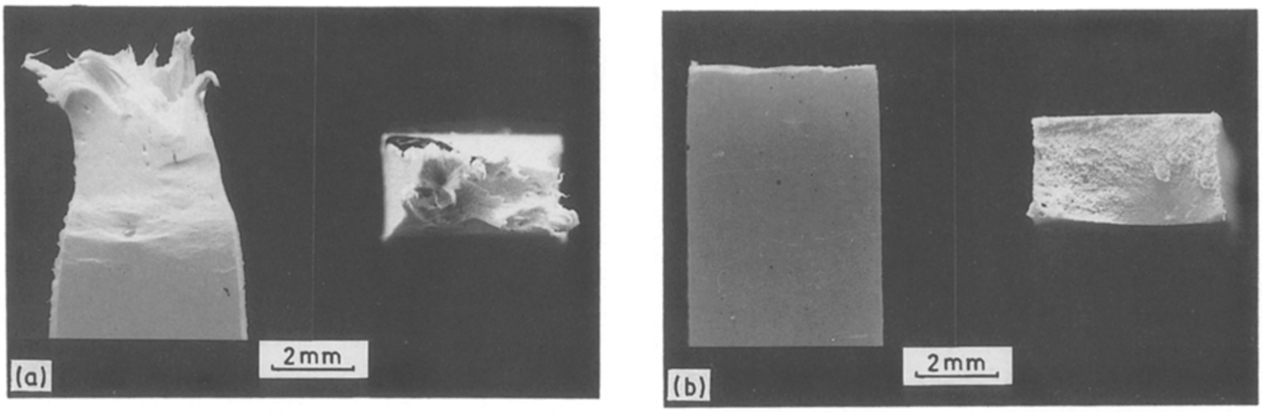


Figure 4 Strain at failure ε_r against temperature θ for EPDM-1-PE-SMPE blends at different filler volume fractions ϕ.



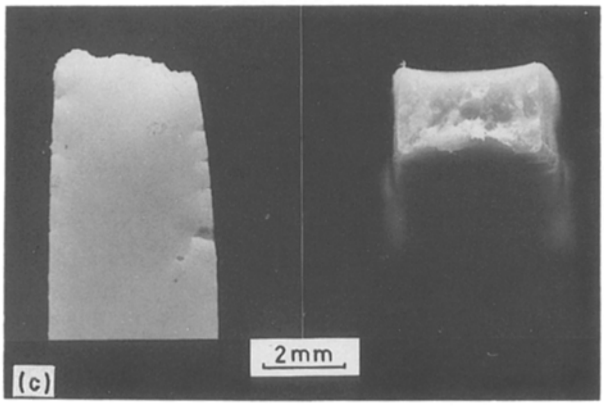
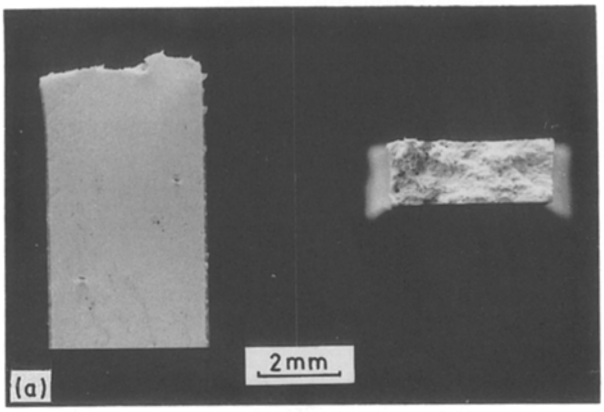


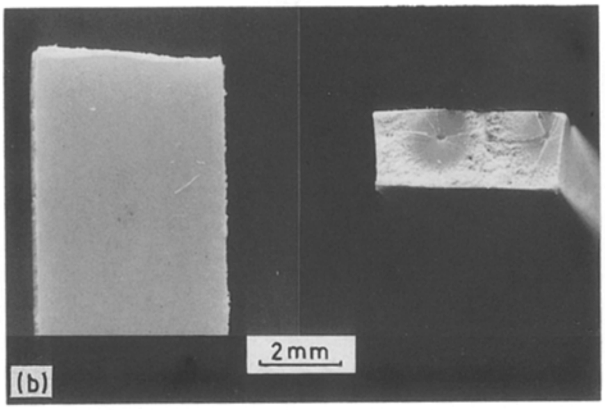
Figure 5 Macrophotographs of fracture facies of filled EPDM-1-PE blend ($\phi = 0.45$) at different temperatures: (a) 20, (b) 60 and (c) 100° C.

behind the pinning points so that the crack front will break away. This behaviour leads to an increase of the fracture energy, at least for low filler loadings. As expected, this increase is observed in Fig. 9 until the filler volume fraction is equal to about 15 to 20%, for which G reaches an optimum value. Afterwards, G suddenly drops and tends towards a constant value for $\phi > 35\%$. This type of variation is similar to those observed [4, 5] for other systems. Fracture energy–temperature curves at constant filler loading are shown in Fig. 10. It can be observed that G decreases linearly with temperature up to 40° C, then strongly drops to reach very low values for temperature higher than about 60° C. It seems that the temperature (40 to 50° C) corresponding to the beginning of this sudden decrease of G is related to the melting point of the elastomer phase (see Table I and [1]). Such a melting behaviour certainly plays a role in the brittleness phenomenon, which appears at about the same temperature.

We can then assume that the rubber phase is largely responsible for the brittleness at temperature of our blends.

So far, we have also seen that the presence of silane-modified PE did not influence this particular behaviour. Consequently, it is now necessary to check whether the nature of the filler plays a particular role. However, by using carbon black, at $\phi = 0.50$, instead of aluminium hydrate particles, the same behaviour as a function of the temperature is again observed, although the interactions between the filler and the matrix are certainly completely different. Hence the nature of the filler is not the predominant factor of fragilization.





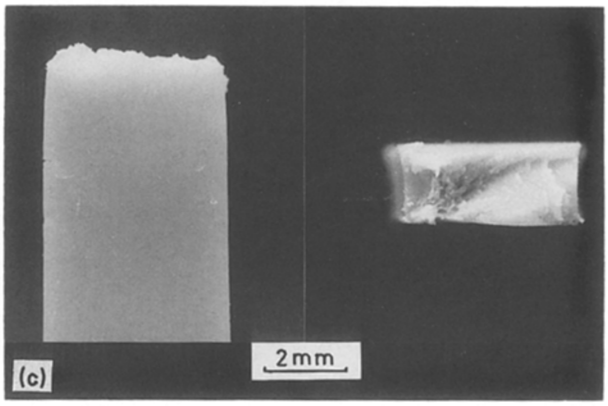


Figure 6 Macrophotographs of fracture facies of filled EPDM-1-PE–SMPE blend ($\phi = 0.45$) at different temperatures: (a) 20, (b) 60 and (c) 100° C.

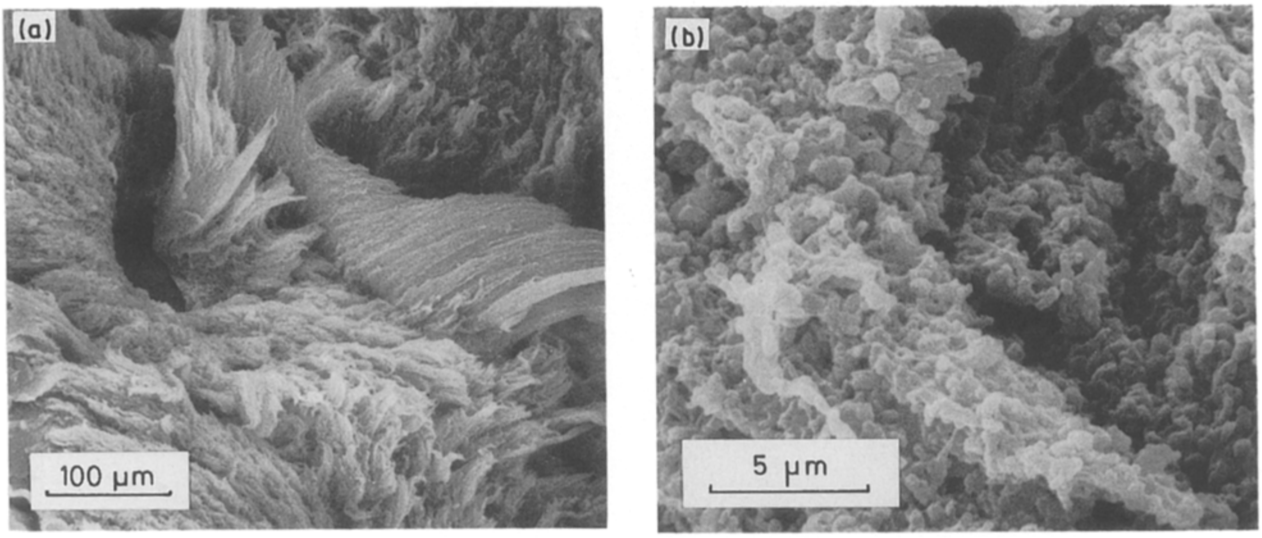


Figure 7 (a, b) SEM micrographs of the fracture surface of filled EPDM-1–PE blend (ϕ = 0.45) at 20° C.

Finally, it appears that the rubber phase is solely responsible for the brittleness at temperature of the filled polymers. Of course, the other constituents of the blends are able to modify the magnitude of this phenomenon, in particular the toughness of the polymeric phase. Further, the volume fraction of filler probably plays also an important role.

A more detailed examination of this brittleness can now be undertaken by studying the ultimate tensile properties of the blends in order to define a failure envelope in each case according to Smith and coworkers [6–11]. Certain important aspects of the ultimate tensile properties of elastomers can be considered in terms of the schematic diagram shown in Fig. 11, where stress–strain curves determined at various strain rates v and temperatures θ are represented. The envelope ABC connects the rupture points. The rupture point moves clockwise around this failure envelope, either as the strain rate is decreased or as the test temperature is increased. Point B corresponds to the maximum of stress and strain values. Therefore, it can be seen that after Point B both stress and strain decrease. Such a failure representation is applicable to the ultimate properties of unfilled elastomers but also for highly filled rubbers [11, 12]. In Fig. 12, σ_t is plotted against ε_r for different filler volume fractions: the principle of the failure envelope seems to apply to the complex systems of this study. At a constant strain rate and at a temperature superior or equal to 20° C, it appears that only the partial curves beyond the maximum are observed. Therefore, whatever the temperature, both stress and strain are decreased, except for high values of ϕ at high temperatures (80 and 100° C). Such a decrease is only due to the elastomer phase of the blends. In fact, as already shown in Fig. 4, the drop of ε_r rather than that of σ_t must be particularly taken into account to explain the sudden brittleness at temperature. Other failure envelopes are given in Fig. 13 for other systems containing EPDM-2, EPDM-3 or EPR as elastomer phase at a constant filler volume fraction equal to 0.45. In each case both σ_t and ε_r are decreased and the steepest decrease is observed for the EPR-containing blend. As shown in Fig. 13, for each temperature the σ_t values are very slightly affected by the nature of the rubber phase, while on the contrary ε_r values are strongly dependent on the nature of the elastomer. Above 60° C, whatever the nature of the rubber phase, σ_t and ε_r values become

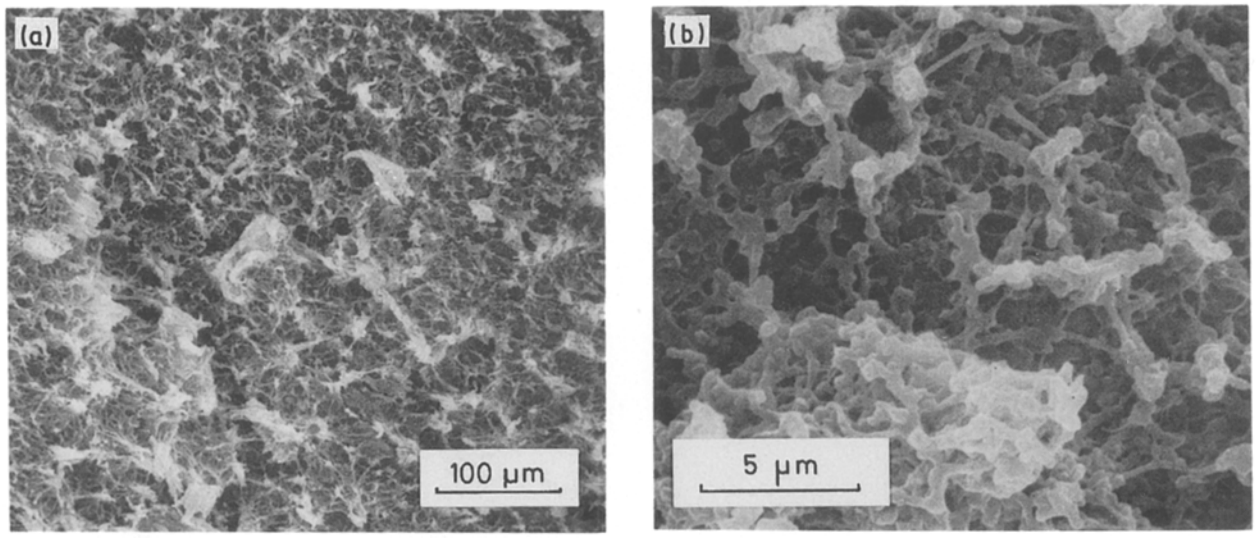


Figure 8 (a, b) SEM micrographs of the fracture surface of filled EPDM-1–PE blend (ϕ = 0.45) at 60° C.

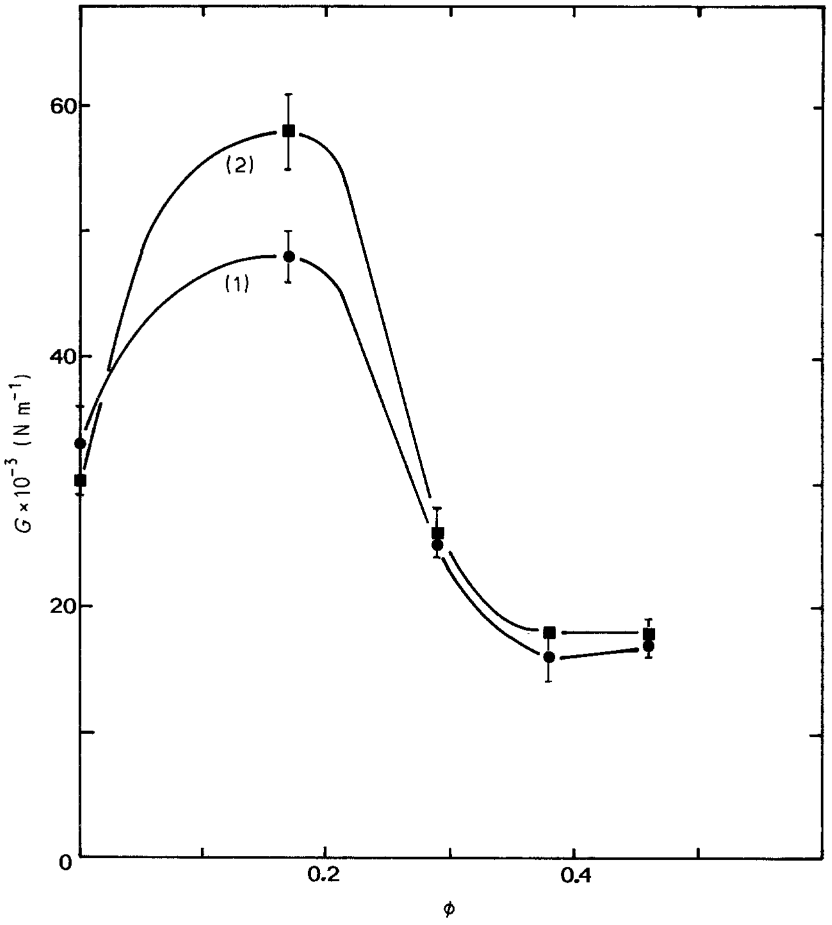


Figure 9 Fracture energy G against filler volume fraction ϕ for (1) EPDM-1-PE and (2) EPDM-1-PE-SMPE blends (θ = 30° C).

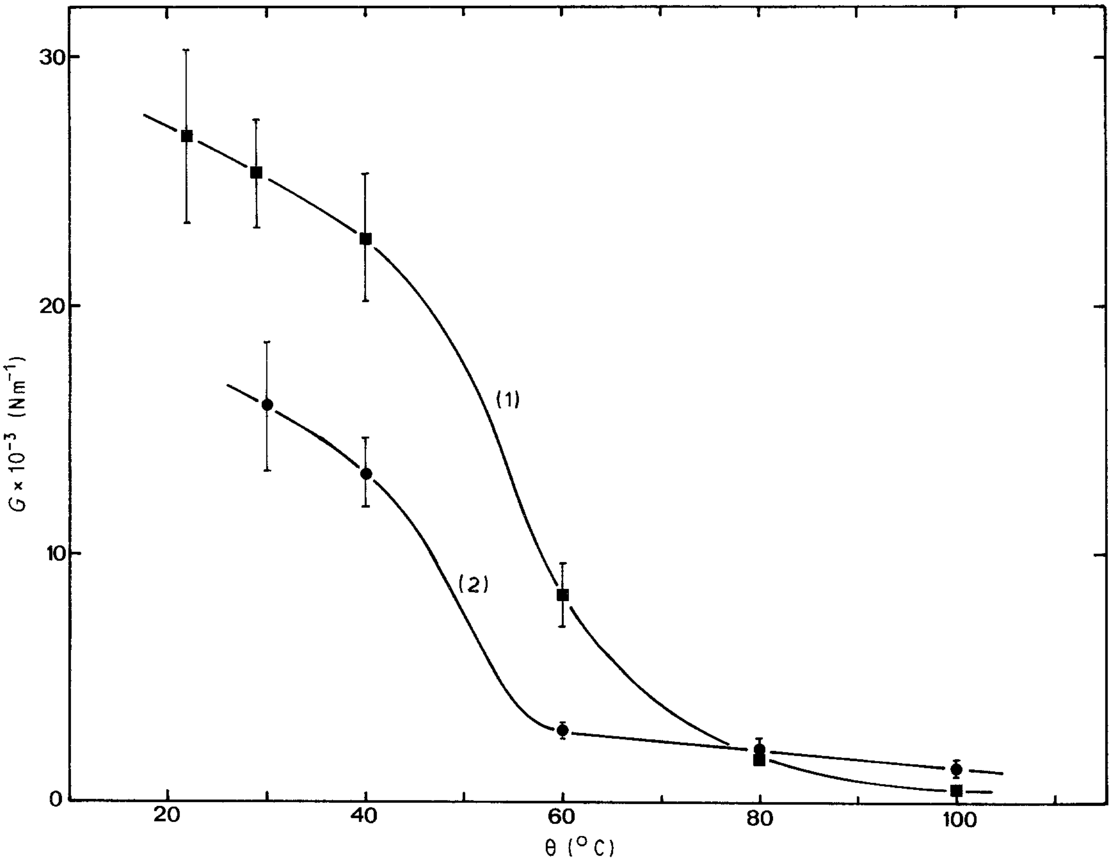


Figure 10 Fracture energy G against temperature θ for EPDM-1-PE blend at (1) ϕ = 0.29 and (2) ϕ = 0.38.

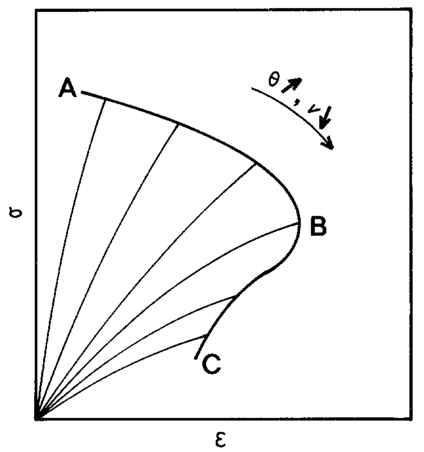


Figure 11 Schematic representation of the dependence of stress–strain curves on strain rate v and temperature θ.

similar since at this temperature the crystalline phase of the rubber has melted (see Table I).

It is also interesting to describe the results given by the simple test developed to determine the critical temperature of brittleness. For this test, folded samples (Fig. 1) are submitted to a constant increase of temperature in an environmental chamber and the temperature for catastrophic failure is recorded. The results are gathered in Table IV. It is seen that, at low filler volume fraction, the samples never fail between room temperature and 120° C, whether or not they contain silane-modified polyethylene. However, we observe that failure occurs for SMPE-containing blends at $\phi > 0.38$, while for the other blends only the most loaded samples fail. In each case, the mean critical temperature values θ_c are included in the range 70 to 80° C.

TABLE IV Critical failure temperature θ_c for different filled blends

Blend	ϕ	Failure	θ_c (°C)
EPDM-1-PE	$\leqslant 0.38$	No	–
	0.45	Yes	70 ± 6
EPDM-1-PE–SMPE	$\leqslant 0.29$	No	–
	0.38	Yes	78 ± 6
	0.45	Yes	71 ± 1

In other terms, considering that the maximum strain $\varepsilon_{\max}$ of the folded samples can be calculated to a first approximation from the classical results concerning the bending of a beam, it is now possible to estimate this critical temperature as follows. If r and e are respectively the curvature radius and the thickness of the sample, the maximum strain in the direction of the axis of the sample, $\varepsilon_{x,\max}$, is given by

$$\varepsilon_{x,\max} = \frac{e}{2r}$$

In the direction perpendicular to this axis the strain ε_z is equal to $-v\varepsilon_x$, where v is Poisson's ratio. Then, since the total strain is equal to $\varepsilon_x + \varepsilon_z$, the maximum strain $\varepsilon_{\max}$ becomes

$$\varepsilon_{\max} \sim (1 - v)\frac{e}{2r}$$

If l is the initial length of the folded part of the sample, then

$$\varepsilon_{\max} \sim (1 - v)\frac{\pi e}{l}$$

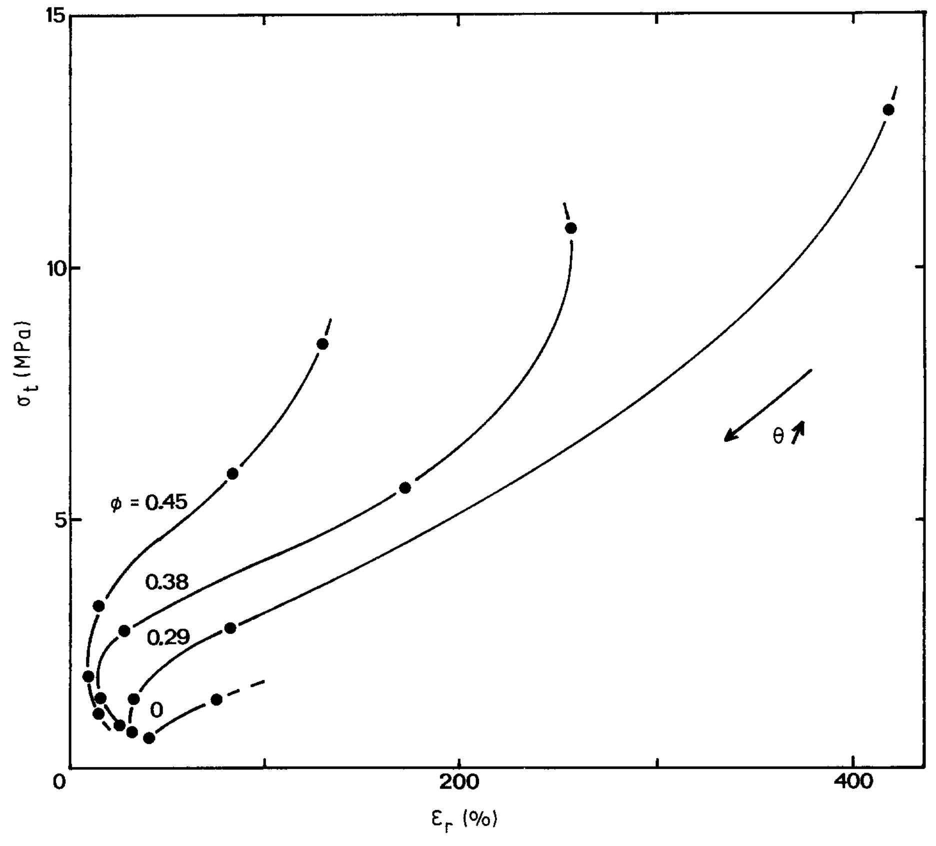


Figure 12 Ultimate tensile properties, tensile strength σ_t against strain at failure ε_r, of EPDM-1-PE–SMPE blend at different filler volume fractions ϕ.

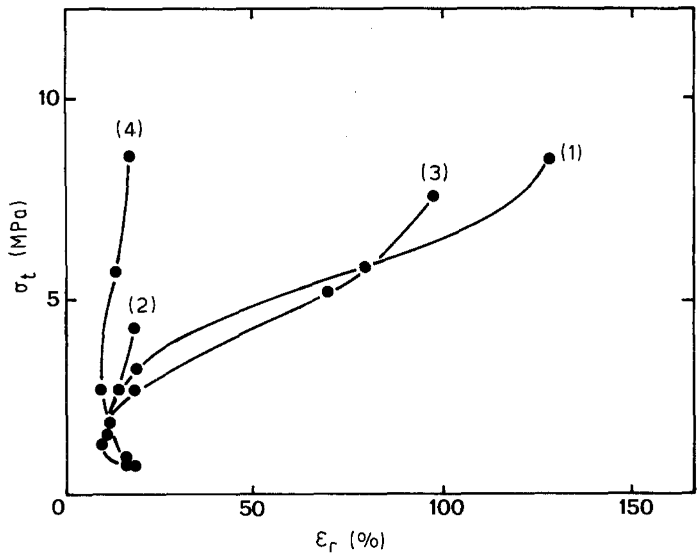


Figure 13 Ultimate tensile properties, σ_t against ε_r, of different filled blends (ϕ = 0.45): (1) EPDM-1-PE-SMPE, (2) EPDM-2-PE-SMPE, (3) EPDM-3-PE-SMPE, (4) EPR-PE-SMPE.

Numerically, taking $e = 2$ mm, $l = 40$ mm and $v = 0.35$, we obtain

$$\varepsilon_{\max} \simeq 10\%$$

It now becomes possible to explain why some samples at low filler volume fraction do not fail, while others do fail at a critical temperature θ_c, by examining in Fig. 4 whether the horizontal line corresponding to $\varepsilon_{\max} \simeq 10\%$ intercepts the curve describing the variations of ε with θ. Consequently, if it exists, such an interception defines the critical temperature θ_c where failure occurs. It can be observed that the results obtained in Fig. 4 are consistent with those given in Table IV. More precisely, from the curves in Fig. 4 we are able to determine the strain at failure for each of the samples at their critical temperature θ_c. The values of $\varepsilon_{\max}$ determined by this method are presented in Table V. These values are in very good agreement with the theoretical one equal to about 10%.

Finally, this simple test allows us to determine very easily whether a filled blend becomes brittle at temperature and to determine at which temperature this brittleness appears.

4. Conclusions

In this second study concerning the characterization of new non-halogen flame-retardant materials, special attention has been devoted to the phenomenon of brittleness which occurs at about 70° C. The tensile mechanical properties of unfilled and filled EPDM-PE blends were first analysed. In particular, it was shown that their strain at failure drastically decreases with temperature, whatever the filler volume fraction. By examining their fracture facies, a ductile-brittle transition at about 70° C has been evinced. Moreover, the fracture energy of these materials suddenly drops from about 50° C corresponding to the melting of the elastomer crystallinity. It was shown that the presence of a rubber phase was solely responsible for this kind of behaviour. Finally, a very simple test on folded samples, allowing the determination of a critical temperature at which the ductile-brittle transition occurs, has been developed. Such a test should be helpful for optimization and manufacturing of these products. Practically, to avoid this brittleness at temperature it is indicated to modify the thermoplastic polymeric phase of the matrix.

TABLE V Strain at failure ε_r for different filled blends at their critical temperature θ_c

Blend	ϕ	θ_c (° C)	ε_r (%)
EPDM-1-PE	0.45	70	10
EPDM-1-PE-SMPE	0.38	78	16
	0.45	71	11

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