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Polymer 42 (2001) 7107–7115

polymer

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Morphological, thermal and mechanical properties of rubber and polysulfone blends

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Received 24 July 2000; received in revised form 5 February 2001; accepted 12 February 2001

Abstract

The study of nine blends between a polysulfone and a thermoplastic elastomer is presented here. These blends are implemented using an extrusion process without addition of compatibilisant. The main properties required are flexibility and thermal resistance of material. We choose a polysulfone for its properties of thermal behaviour, and interpenetrating network as minority flexible phase. The blends carried out contain 5, 10, 15, 20, 25, 40, 50, 60% of rubber flexible phase. We follow the evolution of the mechanical properties by the study of the storage modulus of blends. The thermal properties come from the change of glass transition temperature of each component in the blend. The stability of the properties of the blends can be connected to their internal morphologies. All these properties can be studied with the traditional techniques of characterisation techniques: dynamic mechanical analysis, thermogravimetric analysis, scanning electron microscopy. Results tend to show the immiscibility of phases in these blends. However, in spite of the presence of two different phases, the blends present interesting mechanical and thermal properties thus a uniform morphology.

Keywords: Polymer blends; Morphology; Thermomechanical property

1. Introduction

The blend of several polymers has become one of the most interesting means to obtain new materials with specific properties rather than synthesis of new polymers [1,2]. Several properties can be combined by blending several polymers. Some of them can be thus improved in comparison with initial products. For questions of thermodynamic data the majority of the polymer pairs are immiscible. Two or several phases may always remain present, but a semi-compatibility can exist between them and thus create interactions between the various domains coexisting in the blends. The incompatible blends have bad mechanical properties and a coarse morphology. Interactions, which can exist will exploit this morphology making it thinner and will thus improve the properties of the blend. The method of implementation of the blend is a very significant factor, which will determine the homogeneity of the final product [3–6]. The kind of morphology and its phases dimensions determine blend properties. In immiscible blends we can find co-continuous morphology or fibres of polymer A in a matrix of polymer B. In some cases, fibres may break up into droplets. A compatibilisant agent can be added to stabilise the blend morphology, particularly in the case of droplets in the matrix. In this study the blends are implemented by using the extrusion process, which presents the disadvantage of requiring great quantities of matter for each component. This study could not be carried out with equipment of implementation of laboratory apparatus like an extruder or mixer usually used for other studies [7,8,9]. The characterisation of the blends allows us a correlation between structure and properties. In this study the final material must have properties of flexibility and good thermal behaviour for wires insulation applications. These properties are given by industrial technical requirements. Our choice for initial polymers was made on products having one of these properties. An aromatic backbone with a rigidity allows high temperature resistance of material, interesting for many engineering material applications. The flexibility of elastomer structures or polyolefins will give us access to required mechanical property. We will choose a polysulfone which will constitute the rigid and thermal resistant part; its structure is represented Fig. 1.

The flexibility will be brought in the blend by an interpenetrated network of rubber acrylate, polystyrene and polyacrylonitrile, also interesting for its qualities of thermal resistance improved, compared to other similar structures. After the development of the blends we will be able to study the evolution of the properties of each initial material in the

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PII: S0032-3861(01)00130-6

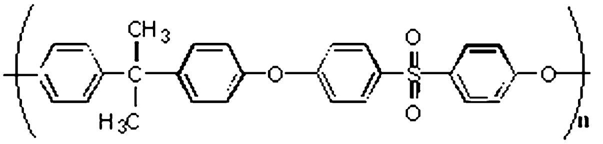

Fig. 1. Polysulfone chemical structure.

final product, the morphology of the dispersed phase in the matrix. The expected performances of the final blend are a good thermal behaviour of material between −40 and 160°C, a storage modulus of approximately 300–400 MPa and a homogeneous and stable morphology with ageing. The observations will enable us to correlate morphology and compatibility of material obtained. We will follow the evolution of thermal properties to check the stability of material in the range of temperature given.

2. Experimental

2.1. Materials

A polymer matrix, a commercial special grade polysulfone sample (Udel P-1700), from Amoco was used. This polymer has a glass transition temperature of about 190°C, and a Flexural modulus about 2.69 GPa at 20°C.

The minor phase was a commercial product of Goodyear (Sunigum) with acrylate rubber for more than 70%, a content of polymers of styrene and acrylonitrile. This polymer is added with 6% of calcium carbonate as a dispersive agent. The glass transition temperature of this polymer is −16°C.

Prior to use, materials were dried at 80°C for 12 h. Blends of polysulfone/rubber polymers were prepared using a Werner and Pfleiderer ZSK 40 twin-screw extruder co-rotating intermeshing. We prepared 95/5, 90/10, 85/15, 80/20, 75/25, 60/40, 50/50 and 40/60 blends in weight ratio without any compatibilizer. Temperatures in the extruder increased from 300 to 360°C with 200 rpm speed. Blends were passed through a water bath, dried in hot air stream and then chopped into pellets.

2.2. Scanning electron microscopy (SEM)

The SEM studies were carried out by a Phillips XL30 microscope with an EDAX X-ray probe. All samples were studied with the secondary electron detector, which gives topographic information. We use an accelerating voltage of 10 kV. The preparation mode of the samples presents difficulties because phases in blends do not show any contrast. Two techniques were tried, the etching way, using a suitable solvent and the fracture way in liquid nitrogen. The first technique did not lead us to find a solvent, which was really selective, all the minority particles of the phase were not etched and a long time of contact solvent/sample led to a damage of the matrix. The second technique seemed more suitable. On samples prepared this way, we will be able to make analyses with X-rays, and to thus follow each component inside the blend.

Samples were fractured after a few minutes immersion in liquid nitrogen. Last of all, the specimen required a conductive coating to be applied for imaging. We chose a gold layer.

Diameters of the dispersed phase D_i were calculated by $D_i = 2(a_i/\Pi)^{1/2}$ assuming the shape of particles to be circular and a_i the particle area.

2.3. Thermogravimetric analysis

These analysis were monitored by an ATD-ATG 92-1750 SETARAM apparatus. Samples were introduced in platinum crucibles and heated from 25 to 500°C with 10°C/mn speed in order to study degradation of blends. Thanks to results, we are able to calculate real percentages of rubber phase in blends.

2.4. Dynamic mechanical thermal analysis

The dynamic mechanical response of the samples was monitored using the RSA II Rheometrics apparatus in dual cantilever mode. Rectangular samples measuring 55 mm × 4 mm × 2 mm were studied isochronally between −60 and 210°C with a 3°K/mn heating rate, and with a deformation of 0.1%. Analysis may enable to see the glass transition temperatures of each component in the blend, and other relaxations, which may belong to interactions between the two phases [17]. For each blend we can represent a curve with loss modulus E'', storage modulus E' and tan δ. Only the two last data were used for this study.

3. Results and discussion

3.1. Scanning electron microscopy

Some studies show blends morphology during compounding [10] and the evolution of the two phases in the different zones of the extruder. In this paper, we will show morphology out of extruder. The micrographs of the blends 10, 20, 40 and 60% obtained in secondary electrons with a magnification of 1600 are presented in Fig. 2.

Fig. 2 shows that the blends have biphasic morphology, with spherical particles up to 25% of acrylate rubber. Polysulfone phase and rubber phase are clearly segregated. This morphology may be representative of immiscibility of the two phases [11,12]. The distribution of these noduli is homogeneous. The polysulfone matrix contains spherical hollows, which can be associated with the flexible phase. All the surface of samples shows the same morphology; there is no zone in which the proportion holes/matrix is unbalanced. No particles remain in the hollows, since they seem to be all pulled out at the time of freeze fracture. We think that the nodules of flexible phase crossing their glass

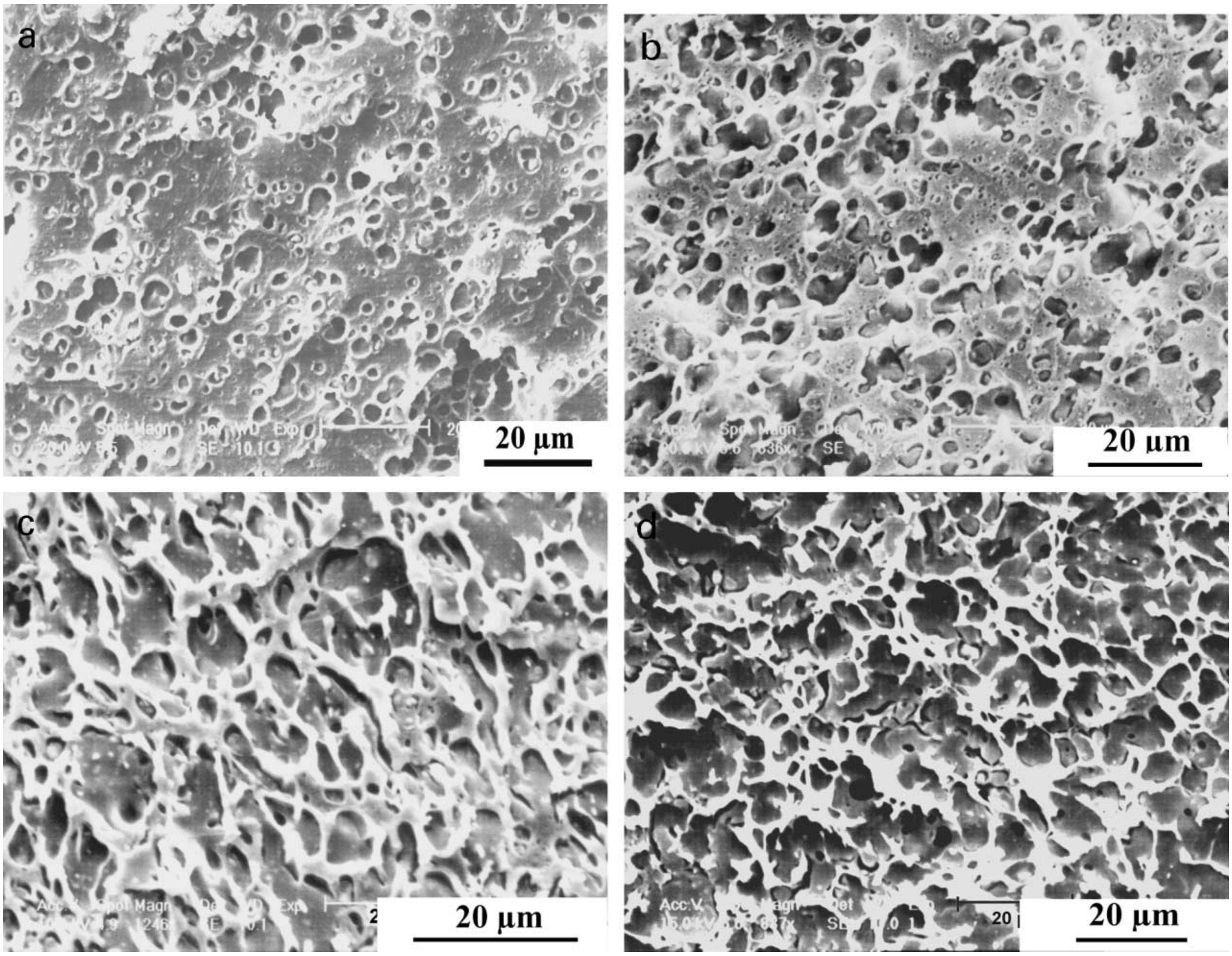

Fig. 2. Micrographs polysulfone/interpenetrating network blends obtained by freeze fracture in liquid nitrogen: (a) 90/10, (b) 75/25, (c) 60/40, and (d) 40/60 weight ratio.

transition in liquid nitrogen retracted in their holes, and during the fracture all these nodules were pulled out. This result can be explained by difference of dilatation coefficient between the acrylate rubber particles and polysulfone. An X-ray analysis enables us to follow the presence of sulphur from the rigid phase on all the sample surfaces. The sulphur element distinguishes polysulfone from the flexible phase. The interpenetrated polymer network is made up only of abundant elements like carbon, oxygen and hydrogen. But it contains calcium carbonate, which will be followed with an X-ray probe. It will not inform us about the particles dispersion, but at least about the presence of the flexible phase.

The presence of rubber phase could not be proved. An analysis was carried out on fragments recovered at the time of freeze fracture. The studied particles do not contain sulphur: that shows there is no polysulfone particle, but that it contains mainly calcium, which can be associated with the flexible phase. This nodular morphology is found until the 40% blend. From there, the flexible phase appears most of the time. From 40 to 60% of the flexible phase, particles change to turn to rubber domains, which remain included, but the polysulfone phase acts as a weaving between the flexible zones. As there is no more nodulus, and that the phase is almost continuous, they can be torn off during the fracture. X-ray analysis shows us the presence of calcium in these continuous zones, and that of sulphur in the intermediate zones. It seems to be close to the limit before phase inversion. A longer residence time of the blends in the extruder, or slightly more significant quantity of flexible phase would be enough to modify morphology.

For the first blends, micrograph analysis on zones from where the particles were torn off will inform us about the evolution of the nodules with increasing the percentage of rubber phase. It will also enable us to deduce percentages of added phase. Table 1 gives us the results of the calculation of the flexible phase percentage from the measurement of surface occupied by the holes compared to the total surface of sample. The calculation of various surfaces is carried out by ANALYSIS software. It is based on a difference in phase contrast. These measurements depend on the errors of detection of phase contrast. Deviation is the difference between these calculated percentages and theorical values (gravimetric feeder of the twin-screw extruder).

Table 1
Evaluation of percentages of rubber phase by micrographs

Theory (%)	Experimental (%)	Deviation (%)
5	4.0	20.0
10	7.0	30.0
15	14.0	6.7
20	18.0	10.0
25	23.0	8.0
40	50.0	20.0
50	40.0	20.0
60	48.0	20.0

Calculated percentages are close to those required. The error made will be more significant than the thermogravimetric one. That can be explained by problems of difference in phase contrast detected by software. There is a bad estimation of hollows surface compared to reality. From 40 to 60% there is a constant deviation of percentages, which can be explained differently. There is probably a slight miscibility of the two phases and especially of rubber phase in the polysulfone matrix. That means there is a part of flexible phase, which disappears from domains. So, until 25% the droplets show the immiscibility of the two phases, and from 40 to 60% blends, areas of rubber phase may be explained by miscibility.

Particle diameters increase with increasing percentage of rubber phase. Mean diameters of blends are presented in Table 2. Particle size, represented by Fig. 3, slightly increases. But diameters remain suitable since values are less than 5 μm. From 40 to 60% blends, the rubber domains size increases but mean diameters stay below 10 μm. It can be noticed that error made on diameter calculation with ANALYSIS software is very important. Dispersion seems to be uniform with mean diameter suitable. Phases seem to be immiscible up to 25%, and then from 40% there's probably a small part of rubber phase which is miscible in polysulfone matrix.

3.2. Thermogravimetric analysis

Thermogravimetric analysis enables us to study the various losses of mass caused by a rise in temperature of the samples. Degradation occurs and the mass remaining decreases as the temperature increases. The flexible phase is degraded first about 200–250°C and until approximately 400°C, the rigid phase remains stable. Just before the beginning of rigid phase degradation, mass losses of blends only result of flexible phase degradation and especially polystyrene and polyacrylonitrile [13,14,16]. With mass losses in the values of blends and pure rubber phase ones, we will be able to compute real percentages of flexible phase in blends and thus to check the validity of our blends. We will have an error on each blend carried out. Thermograms obtained are presented in Fig. 4.

Table 2
Particles mean diameters in five polysulfone/acrylate rubber blends

AR (%)	Mean diameter (μm)	Standard deviation (μm)
5	2.9	1.1
10	3.1	1.1
15	3.7	1.6
20	3.6	1.5
25	3.9	1.6

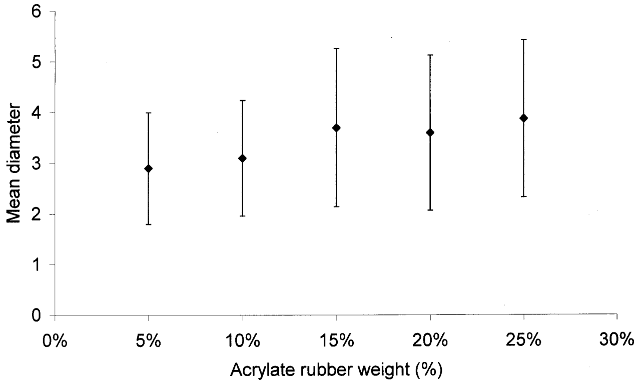

Fig. 3. Mean diameters evolution with acrylate rubber weight in 5, 10, 15, 20, 25% blends. The vertical lines are standard deviations.

Mass losses seem to be proportional to the quantity of flexible phase present in the blend. Calculations will enable us to correlate experimental and theoretical percentages, as shown in Table 3. Deviation column corresponds to the percentage shift between experimental and theoretical values.

It is noted that error made on percentages decreases logically for the highest values. The validity of these blends is shown here. The implementation of these blends by extrusion way under industrial conditions enables us to obtain reliable percentages of flexible phase in rigid phase.

A kinetic study of flexible phase degradation in blends is made by taking into account the interval of temperature corresponding only to the degradation of rubber acrylate. The maximum of the losses of the flexible phase measured about 430°C is taken to 100%. The data, which will be represented, are obtained starting from the following equation:

$$\text{Weight loss of flexible phase (\%)} = (\text{weight loss of blends} \times 100)/\text{max. weight loss in blends}$$

Table 3
Experimental percentages estimated after thermogravimetric analysis

Theory (%)	Experimental (%)	Deviation (%)
5	5.8	16.0
10	9.3	7.0
15	16.5	10.0
20	19.9	0.5
25	25.4	1.6
40	37.7	5.8
50	50.9	0.9
60	59.4	1.0

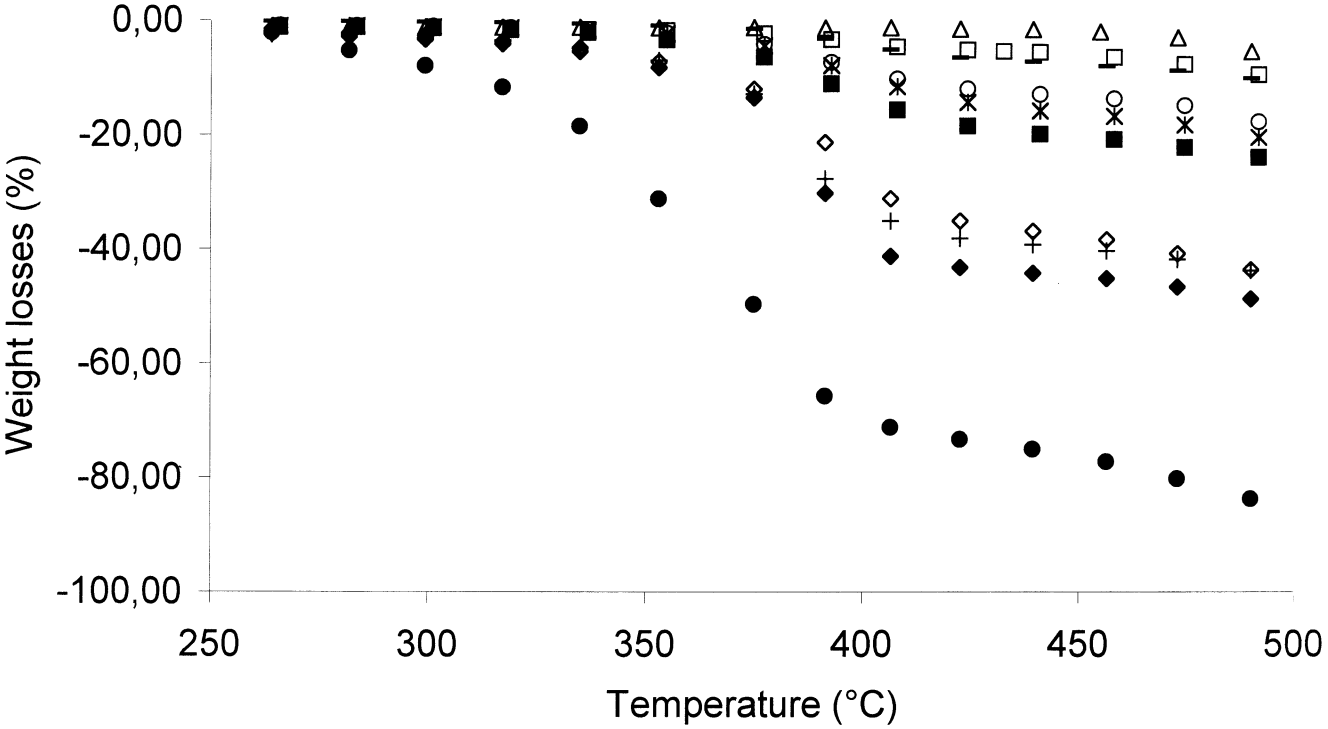

Fig. 4. Thermograms of pure products and eight blends PSU/AR (△, pure PSU; □, 5% AR; –, 10% AR; ○, 15% AR; $*$, 20% AR; ■, 25% AR; ◇, 40%AR; +, 50% AR; ◆, 60% AR; ●, pure AR).

Fig. 5 presents the evolution of the weight loss corresponding to the flexible phase according to the temperature. The study of this figure enables us to note that whatever the rubber acrylate percentage in the blend, degradation occurs at the same rate. It can be compared with the rubber pure acrylate one, which is degraded more quickly. We can think that the rigid phase in the blend acts like a kind of protection, but that the degradation of flexible phase does not depend on its weight ratio in blend. We can suppose there are only some poor interactions between phases in blends.

Morphological results are confirmed about the efficiency of blending. Experimental percentages are very close to theoretical ones. This checking carried out, we will go on and study the main properties of blends.

3.3. Dynamic mechanical analysis

3.3.1. Thermal analysis

To evaluate thermal properties, tan δ curve evolution of blends is studied. This evolution is represented in Fig. 6.

The curves corresponding to various blends (PSU/AR: 90/10, 75/25, 50/50, 40/60) and to pure products are gathered. Tan δ peak appearing towards -15°C is representative of α relaxation of flexible phase (i.e. acrylate rubber). The strong increase in tan δ towards 180°C is the beginning of the characteristic peak of α relaxation of polysulfone. This peak is not entirely represented because the material becoming too flexible at these temperatures, and our equipment cannot take measurements any more.

Moreover we can observe a third peak between the two previous ones at about 90°C. Plotting compliance J'' versus temperature and rubber weight ratio (%) shows a better representation of this relaxation. This phenomenon is plotted in Fig. 7.

This peak does not exist on the polysulfone spectrum and increases with increasing rubber phase percentage the blends. In this way, this peak is attributed to the rubber phase and especially to polystyrene [15] or polyacrylonitrile [16]. Moreover, the fact that this relaxation temperature remains nearly constant enables us to conclude that the rubber phase is poorly influenced by the polysulfone matrix.

The evolution of glass transition temperatures of the two phases in blends is thus studied. These temperatures will be taken at the top of the tan δ peak for the flexible phase, and

Table 4
Glass transition temperatures of the two phases in PSU/AR blends

Blends percentages	AR T_g (°C)	PSU T_g (°C)
0	–	184
5	−15	184
10	−16	186
15	−16	184
20	−15	183
25	−14	181
40	−17	181
50	−16	178
60	−15	165
100	−7	–

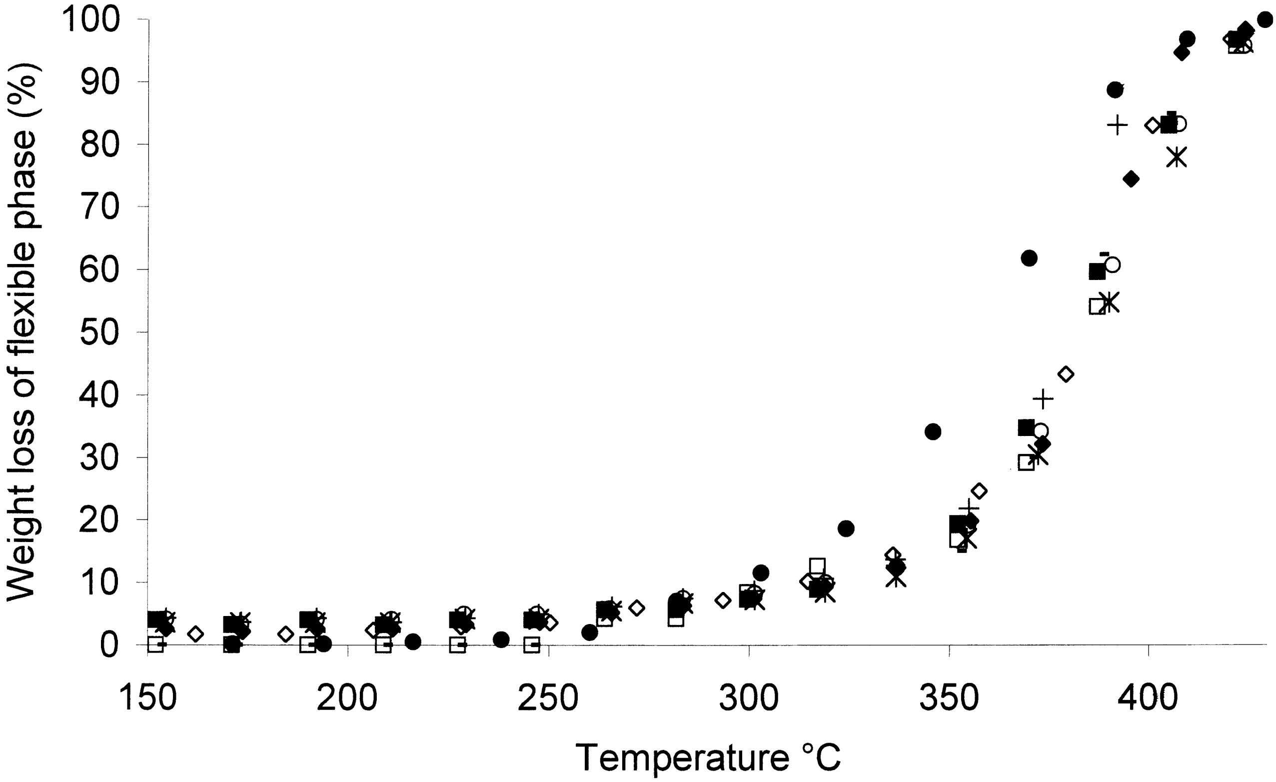

Fig. 5. Weight loss of flexible phase in blends. (□, 5% AR; –, 10% AR; ○, 15% AR; ∗, 20% AR; ■, 25% AR; ◇, 40%AR; +, 50% AR; ◆, 60% AR; ●, pure AR).

determined thanks to the method of the tangents for polysulfone.

The obtained figures of all blends are reported in Table 4.

A systematic evolution is noticed from rubber acrylate as soon as it is blended. This temperature decreases from −7 to −15°C, and then this temperature does not move any more according to the percentage. Values are towards −15°C. The same remark could be made on another blend with the same flexible phase, but a different polymer as rigid phase. We have obtained for an unspecified percentage the

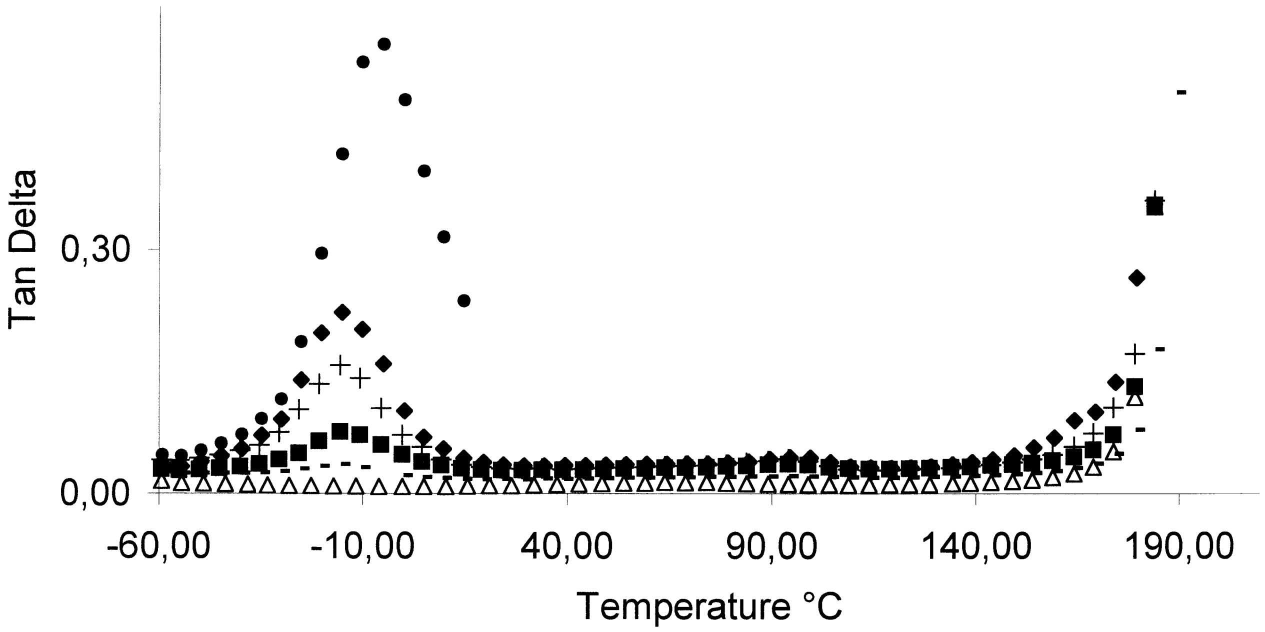

Fig. 6. Tan Delta curves evolution for pure products and different blends of PSU/AR weight ratio. (△ pure PSU; – 10% AR; ■ 25% AR; + 50% AR; ◆ 60% AR; ● pure AR).

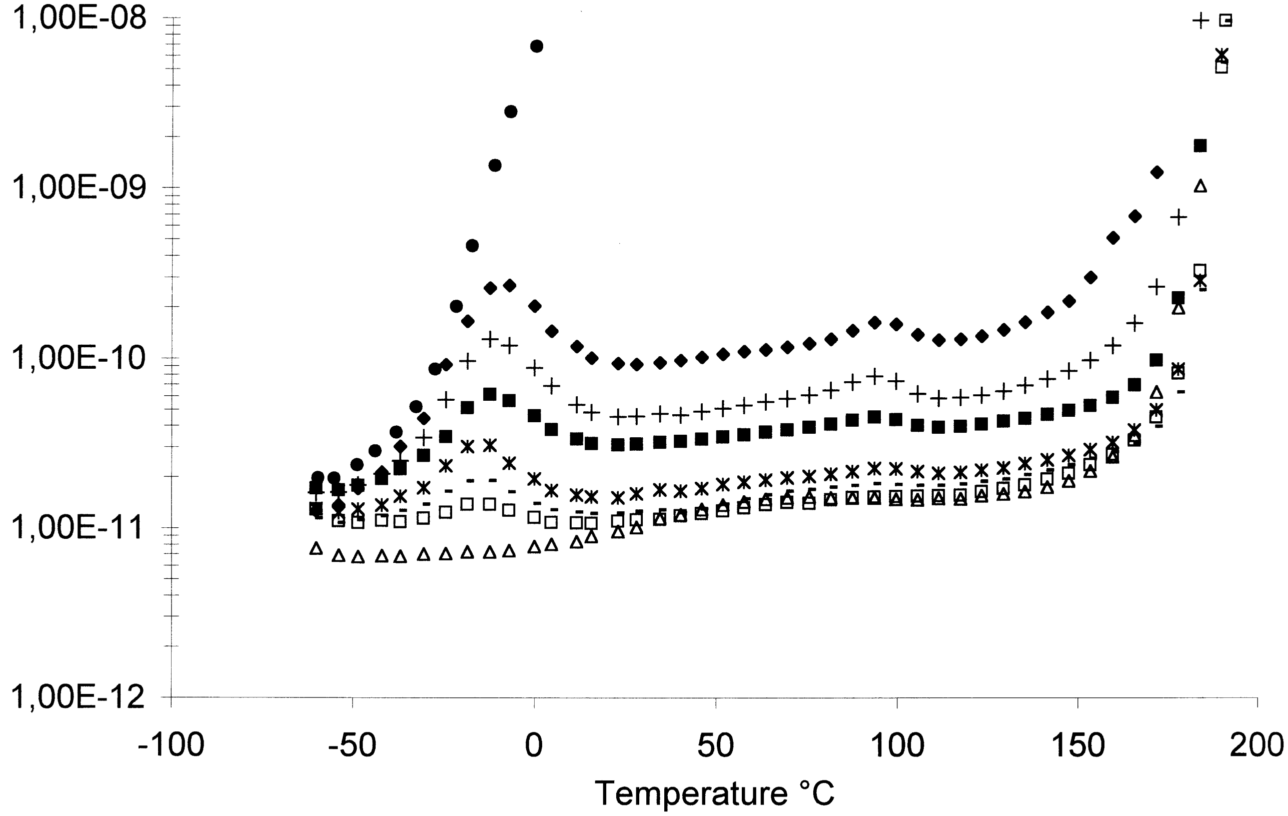

Fig. 7. J'' compliance curves evolution versus temperature for blends of PSU/AR ratio. (△, pure PSU; □, 5% AR; –, 10% AR; ∗, 20% AR; ■, 25% AR; +, 50% AR; ◆, 60% AR; ●, pure AR).

same temperature about −15°C. It seems that this evolution of the temperature is independent of the nature of the second phase, but occurs inside the rubber phase during extrusion. For the glass transition temperature of polysulfone in blends, it does not undergo evolution during blending, but it tends to decrease for high rubber percentages. Its value starts to fall clearly from 40%. We could think there would be a certain miscibility of rubber in the polysulfone, which could explain this deterioration of the thermal properties of rigid phase. Other studies show a similar behaviour, in case of polysulfone/poly(ether ether ketone) systems [11,15]. We still cannot determine which part of the flexible phase is likely to be miscible in polysulfone.

The last remark, which can be made, is that the values obtained for the glass transition temperatures are suitable according to the limits imposed by technical requirements, including for high percentages of acrylate rubber.

3.3.2. Mechanical behaviour

Dynamic mechanical analysis enables us to show mechanical properties of blends with storage modulus, but also gives us its thermal characteristics while following the evolution of tan δ curve. All blends are thus analysed in the range of temperature previously mentioned. The normalized storage modulus (E'/E'max) curve according to the temperature is presented on Fig. 8 for all blends. E'max refers to the maximum of E' for each blend. The plot of E'/E'max is chosen in order to compare all E' curves for different blends.

The study of these curves show two decreases of modulus, which corresponds to molecular motions associated with the glass to rubber transition of initial products in the blends. The first decrease, about −15°C is associated with the acrylate rubber phase in the blend, the second one, to polysulfone matrix [16]. There's an intermediate relaxation, which corresponds to acrylate rubber phase as it can be seen on tan δ curves. Polystyrene and polyacrylonitrile are responsible for this decrease of modulus.

It is noted that the increase of the flexible phase percentage results in a decrease of the blend modulus level between acrylate rubber and polysulfone mechanical relaxation (glass to rubber transition) temperatures. Moreover, this decrease seems to be proportional to the rubber percentage. The mechanical behaviour of each blend can be related directly to its percentage in rubber phase. One can check it with a graph of the variation of modulus during relaxation of rubber phase, according to its percentage. This evolution is represented on Fig. 9. For each blend, the decrease of E' modulus is taken in a temperature interval of 30°C around the acrylate rubber relaxation, given by tan δ curve (Fig. 6). Since the evolution is linear, we can suppose there is, thus, a direct relation between E' variation during

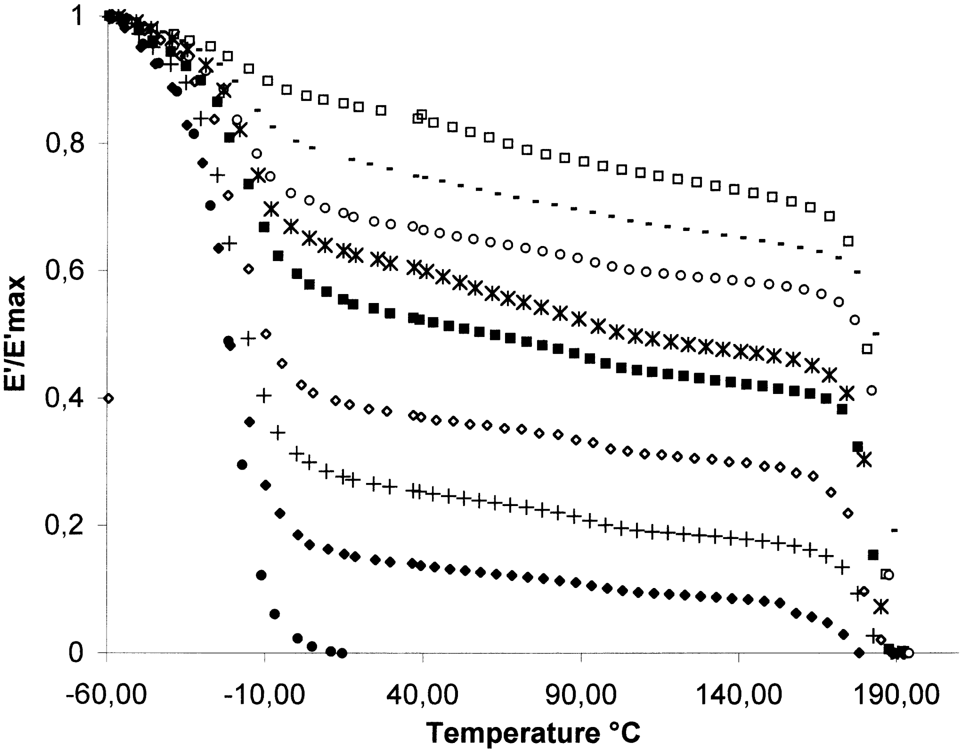

Fig. 8. Normalized storage modulus (E'/E'max) curves of PSU/AR blends. (△, pure PSU; □, 5% AR; –, 10% AR; ○, 15%, AR; *, 20%, AR; ■, 25%, AR; ◇, 40%AR; +, 50% AR; ◆, 60% AR; ●, pure AR).

dynamic mechanical relaxation and blends percentages. The curve exploitation gives us the following equation for the straight line, where $x_{\text{acrylate rubber}}$ is the weigth fraction of acrylate rubber:

$$\Delta E'\ (GPa) = (3.51 \times x_{\text{acrylate rubber}})$$

One can thus calculate for percentages which would not have been implemented, the value of the E' variation during dynamic mechanical relaxation of rubber phase. The same calculations can be made for percentages higher than those implemented during this study. In a way much less rigorous, we can follow the evolution of E' moduli values of blends to ambient temperature. The values according to polysulfone ones at 25°C are gathered in Table 5 and their evolution is represented in Fig. 10.

Blends containing 50 and 60% of rubber acrylate have an E' modulus which is close to the range given by the technical requirements. Morphological characteristics of these two blends have already been studied. There are no really spherical particles, but domains of rubber phase. We can thus think that these morphologies are stable. The same remarks go for Fig. 9; there is a linear relation between the 25°C modulus of blends and rubber phase percentage. In the same way, we can imagine the rubber phase percentage necessary to reach expected E' modulus. Linearity may think of immiscibility of the two phases, but it can be noticed on Fig. 9 that E' modulus for 100% of acrylate rubber would be negative so we can imagine from 60 to

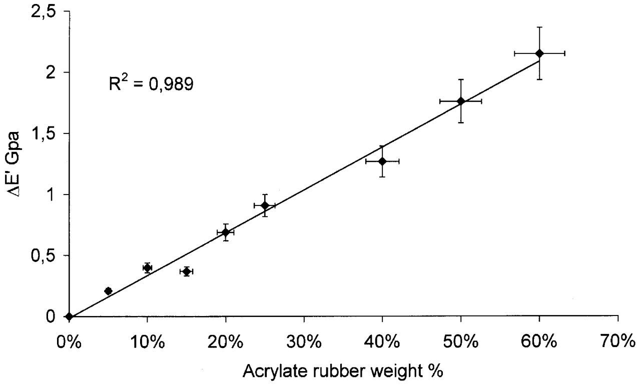

Fig. 9. Evolution of E' modulus variation during dynamic mechanical relaxation of acrylate rubber versus percentage of rubber phase in blends. The horizontal and vertical lines are standard deviations.

Table 5
E' moduli values at 25°C for polysulfone/acrylate rubber blends

Blends percentages	E' modulus (25°C) Gpa
0	2.6
5	1.96
10	1.77
15	1.53
20	1.5
25	1.24
40	0.99
50	0.62
60	0.32

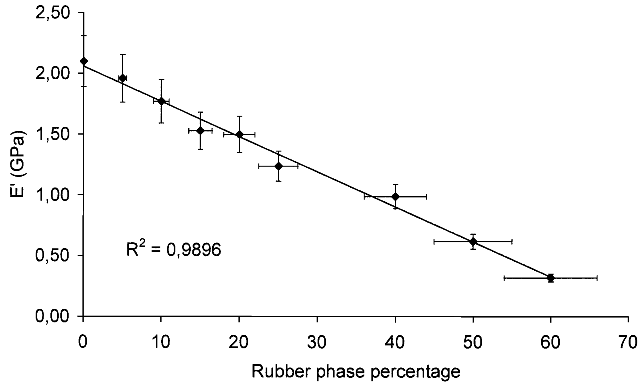

Fig. 10. Evolution of 25°C E' modulus for PSU/Acrylate rubber blends. The horizontal and vertical lines are standard deviations.

100% that E' values tend to that of the pure acrylate rubber. This remark allows us to think of partial miscibility between the two phases with high percentages of acrylate rubber. We miss other percentages between 60 and 100% in order to conclude.

4. Conclusions

Polymer blends have been realised with 5, 10, 15, 20, 25, 40, 50, 60% of acrylate rubber in a polysulfone matrix in a twin-screw extruder. Materials were expected to be flexible, thermal resistant and with a good dispersion. Characterisation enables us to check those different properties.

First thermogravimetric analysis shows us real percentages of rubber phase in the matrix, to compare with percentages theoretically added in the extruder. We can conclude the efficiency of proportioning while extruding.

Morphological analysis shows us a homogeneous dispersion of particles in the matrix. Until 25%, we find spherical particles of acrylate rubber, and then particles change to domains of flexible phase. Freeze fracture way gives a minor phase percentage in the matrix near percentage of acrylate rubber introduced theoretically in the twin-screw extruder. From 40 to 60% it seems to be a part of miscibility between acrylate rubber phase and polysulfone phase.

Mechanical analysis shows evolution of modulus in blends. Acrylate rubber addition as brought flexibility to polysulfone since modulus decreased from 2.6 to 0.32 GPa for 60% blend, which shows that expected modulus is reached. Blends' results could tend towards immiscibility but according to pure initial products results we can think as before of miscibility to high percentages.

The 50 and 60% blends present a good thermal resistance as expected. We are sure that acrylate rubber has undergone degradation in the twin-screw extruder but not enough to reduce its thermal properties out of expected range of temperatures. Glass transition temperatures of polysulfone in blends decrease from 25 to 60%. This evolution may think there is an effect of acrylate rubber on polysulfone, so this induces that there is probably partial miscibility of rubber acrylate or constituents of rubber in polysulfone. We have not yet determined which part of rubber acrylate presents characteristics of miscibility.

Results are very interesting, studying 50 and 60% blends which present good evolution of properties.

To complete these studies, we have to elaborate wires insulation with the more interesting blends and check if properties can be preserved when a product undergoes second extrusion.

Acknowledgements

We thank J. Bonneti from Société MULLER, Amoco and Goodyear for supplying initial products, P. Bouedo from Société Rousset Compounds and B. Triki from CRITT Matériaux de Strasbourg for performing blends with a twin-screw extruder. We thank Conseil Regional Provence Alpes Cote d'Azur for financial support.

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