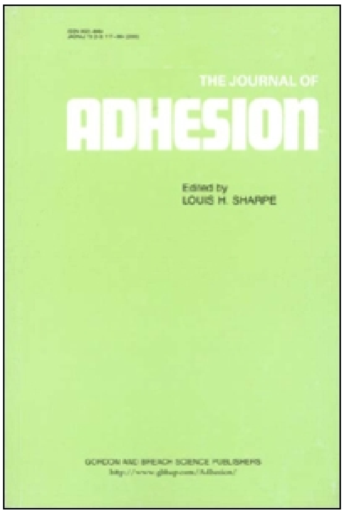

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Epoxy-Polysulfone Networks as Advanced Matrices for Composite Materials

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Epoxy-Polysulfone Networks as Advanced Matrices for Composite Materials*

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Compatibility between polysulfone (PSF) and epoxy oligomers in the melt state as well as the morphology and properties of alloys obtained were studied as a function of composition. The compatibility depends on the length and structure of epoxy molecules, and is best in the case of epoxysulfone oligomers (ESO).

The properties of hybrid matrices are determined by their composition and morphology. The most pronounced effects are observed in the regions of small concentrations of either component. A small quantity of PSF significantly improves thermal stability and heat resistance of the epoxy resin as well as its impact strength. On the other hand, on addition to PSF of small amounts of epoxysulfone oligomers, the processability of the matrix can be substantially improved. In particular, the melt viscosity decreases, and wetting and impregnation of fibrous reinforcement is facilitated. Besides, the matrix adhesion to fibers is increased.

Powdered PSF/ESO/curing agent mixtures are good for application in solvent-free technological processes of fibrous composites production, *e.g.* in electrostatic deposition of matrix particles onto a reinforcing fabric. Plastics based on hybrid matrices are distinguished by improved strength.

Keywords: Polymer blends; epoxy networks; polysulfone; morphology; fiber-reinforced plastics

1. INTRODUCTION

Polymer blends and alloys play an important role as matrix resins in modern composite materials production. By combining polymers of

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*One of a Collection of papers honoring Yuri S. Lipatov on the occasion of his 70th birthday, 10 July 1997.

different natures it is possible to tailor properties of matrices over a wide range [1–4]. Compounds based on thermostable thermoplastics and thermosetting polymers having complementary properties are of particular interest. For instance, engineering thermoplastic polymers, such as poly(ether ether ketone), polysulfone, polyetherimide, etc., have many desirable features including high thermal stability and heat resistance, high impact strength, and good deformability. As their disadvantages, poor adhesion should be mentioned as well as difficulties with their processing caused by high temperature of softening and high melt viscosity. At the same time, thermosetting polymers are, as a rule, easily processable and adhere well to various fillers, but they are often brittle and sometimes lack thermostability and heat-resistance. The combination of these polymers can give a required balance between adhesive, viscoelastic, and processing characteristics of the matrix.

Recent investigations have demonstrated that one of the promising ways to new advanced composite materials is blending polysulfone (PSF) with epoxy oligomers. Addition of small amounts of epoxy resins to PSF was reported to lower significantly the resins' melt viscosity at the stage of impregnation of the fibrous reinforcement, as well as to improve impact resistance, toughness, and water resistance of plastics reinforced by carbon and glass fibers [5–10]. On the other hand, small amounts of PSF (or oligosulfone) added to epoxy resins significantly improved their impact strength and thermal stability [5, 11–13].

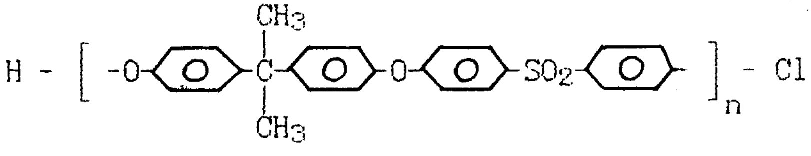
The main problem in production of epoxy/polysulfone hybrid matrices is the poor mutual compatibility of their melts, resulting from a large difference in the melting points and thermal stabilities of the components, along with poor mutual solubility. A number of papers [13–15] have been concerned with the investigation of structure and properties of epoxy/polysulfone interpenetrating networks obtained by dissolution of the components in a common solvent and subsequent moulding accompanied by solvent extraction. However, solvent-free technologies, in particular electrostatic deposition of powdered polymers onto woven and tow reinforcement, are preferred in modern processes for production of fiber-reinforced composites [16–18]. The application of solvents is especially undesirable in the case of thermostable thermoplastics, many of which form highly viscous solutions even at low concentrations. Moreover, the solvent is difficult to evacuate after the reinforcement impregnation; as a result, the prepregs and plastics which are obtained are often porous and have deficient mechanical properties.

Polyarylenesulfones exhibit high melt viscosity (*e.g.*, 10^4 Pa·s for Udel^{TM} polysulfone at 300°C). Also, PSF melts wet all types of fibers poorly [19], and even heating to 400°C does not improve wetting. As a result, PSF-based fiber-reinforced composites show low strength in interlaminar shear which can be increased only marginally by raising processing pressure and temperature [20]. Taking into account the practical importance of developing high-strength PSF-based plastics, the study of compatibility of PSF melt with modifying additives, as well as the investigation of the interaction between the matrix compound and the reinforcement surface seems to be highly necessary. The aim of this paper is to investigate the compatibility between the PSF melts and epoxy resins, and to determine how the properties of the alloys formed depend on their composition and morphology.

2. EXPERIMENTAL

2.1. Materials

Polysulfone PSK-1 of Russian production,



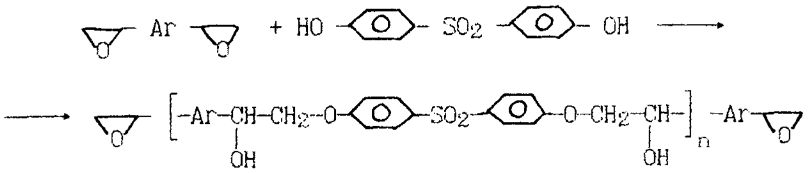
SCHEME

with molecular weight (M_w) of $3.7 \cdot 10^4$ in the form of polydispersed powder (with the particle size 63 to 315 μm) was used. As modifying additives, DGEBA-based epoxy resins of Russian production were chosen: a low molecular weight resin (ED-22; $M_w = 410$) and a high molecular weight resin (ED-8; $M_w = 2000$). The curing agent was 4,4′-dihydroxydiphenylsulfone (DHDPS).

As reinforcing elements in the prepregs and plastics obtained, UTS-76/82 glass fabric and ELUR-0.08 carbon tape (Russia) were used.

2.2. Synthesis of Epoxysulfone Oligomers

Epoxysulfone oligomers (ESO) were synthesized from the low molecular weight epoxide ED-22 and DHDPS, as illustrated by the following scheme: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The reaction was conducted by stirring the stoichiometric mixture of components at 130°C for 3 hours. The ESO obtained had the following characteristics: $n = 3$; $M_w = 2100$; epoxy content 0.98 mEq/g.

2.3. Synthesis of Hybrid Matrices

Particulate PSF was poured into the epoxy monomer or oligomer melt at 150°C. Then the mixture was stirred until a transparent liquid was obtained, and a stoichiometric quantity of the curing agent was added. The composition was stirred again and thermally treated until the completion of curing (2 h at 120°C, then 6 h at 140°C, and finally 10 h at 160°C). In several instances, the alloys were prepared by thermal treatment of the particulate mixture (PSF/epoxy/curing agent), *i.e.* heating up to melting and subsequent curing under the same conditions as mentioned above.

2.4. Preparation and Testing of Prepregs and Plastics

Continuous prepregs were prepared by depositing charged particles of the source mixture onto the glass fabric from a fluidized bed in an electric field [17, 18]. Then, the fabric with the deposited layer was pulled through an infrared heating chamber (~ 10 s at 250°C) to adhere the matrix particles to the fibers. Four-layer microplastic samples were fabricated and tested in shear as described in Ref. [21].

Plastics of 25 prepreg layers were produced by compression moulding at $T = 210\text{–}280^\circ\text{C}$ (see Tab. III) and $P = 10$ MPa for 1.5 h. Their testing for strength in shear and three-point bending was carried out according to standard techniques [22].

2.5. Methods of Investigation of Hybrid Matrices

Morphology of the hybrid polymers obtained was studied by examination of fracture surfaces with an optical microscope (NU-2), Carl Zeiss, Germany). The relaxation properties were measured using the III2-5 dielectric spectrometer (Russia) at a heating rate of 2°C/min and a frequency of 1 MHz. The differential thermal analysis and thermogravimetric analysis were conducted with a thermoanalyser (Mettler TA-3000) at a heating rate 5°C/min. Infrared spectra of polymer films were recorded with the UR-20 spectrometer.

To determine the content of soluble substances within the cured products, the hybrid polymers were milled and exposed to chloroform extraction in a Soxhlet for 24 hours. The starting temperature of film formation for powdered matrices was measured using a home-made heated gradient plate [23].

The wetting of fibrous reinforcement by polymer melt was characterized by the wetting angle θ. The powdered composition was pressed at room temperature into pellets (2 mm diameter and 2 mm height); then pellets were placed onto carbon tape and thermally treated for 30 min at a preset temperature. The image of a droplet formed was projected on a screen, and the wetting angle, θ, was measured [21].

3. RESULTS AND DISCUSSION

The PSF compatibility in the melt with the low molecular weight epoxy oligomer is limited; no more than 20% w/w PSF can be dissolved in the liquid ED-22 resin. To improve the mutual solubility of components, one may use a low molecular weight linear polymer, *i.e.* oligosulfone [11–14]. Oligosulfone was reported to be easily compatible with various epoxy resins, the hybrid polymer obtained having improved thermal stability, heat resistance and impact strength [11–14]. Another possible way is, to the contrary, to increase the length of the epoxy oligomer molecules and to make its chemical structure similar to that of the thermoplastic polymer [5–7]. These resins are solid at room temperature and, thus, can be used to prepare powdered PSF/epoxy/curing agent compositions for use in electrostatic prepregging as well in other "dry" technologies of plastics production.

In fact, it was revealed that the PSF dissolves better in the melt of the higher molecular weight epoxy resin (ED-8), and we managed to obtain and characterize PSF/ED-8/DHDPS alloys within a wide range of compositions. The examination of fracture surfaces of the alloys fabricated has shown that hybrid matrices with PSF content below 5% were transparent and homogeneous (Fig. 1a). They are characterized by a single glass transition point (Fig. 2), which lies between the glass transition temperatures of the components. This is the evidence for their good compatibility in the melt [3]. At PSF content above 5% the hybrid matrices became microheterogeneous. During the curing process, the thermoplastic polymer segregates in the epoxy resin medium as globules of about 1 μm in diameter (Fig. 1b). However, already at 12% PSF content phase inversion takes place: the linear polymer forms a continuous phase in which regions of cured epoxy resin are distributed (Fig. 1c).

At a PSF content of 8%, the plot of dielectric losses against temperature shows two maxima, *i.e.* two separate phases are present in the system (Fig. 2). When the PSF content is above 12% (*i.e.*, after the phase inversion), the cured matrices exhibit, again, only one transition temperature. Similar features were observed in studies of hybrid matrices (PSF/ED-22) by thermomechanical analysis (Fig. 3).

The comparative study of the blends obtained has demonstrated that adding even small amounts of PSF to an epoxy matrix significantly improves its thermal stability and heat resistance as well as impact resistance (Tab. I). The polymer containing about 10% w/w polysulfone, whose morphological feature is globular inclusions of PSF in the epoxy matrix, exhibits the best properties. Such a polymer alloy can be considered as a self-reinforced network [1, 3]. It should be mentioned that a slight variation in the alloy composition results in

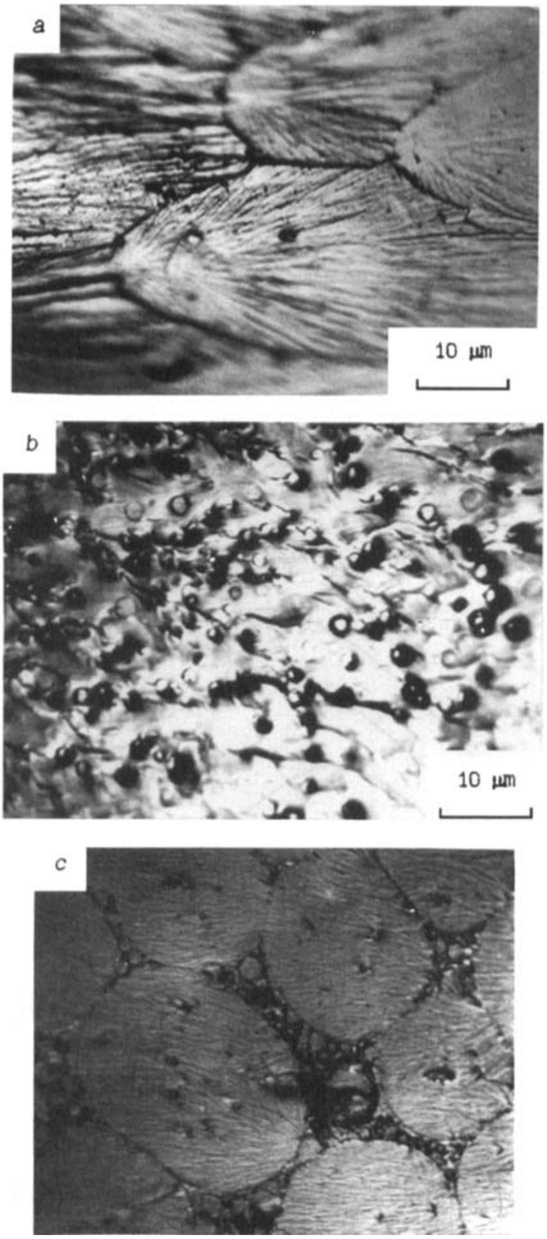

FIGURE 1 Fracture surfaces of PSF/ED-8 hybrid polymers. PSF content, %: 3 (a); 10(b); 20(c).

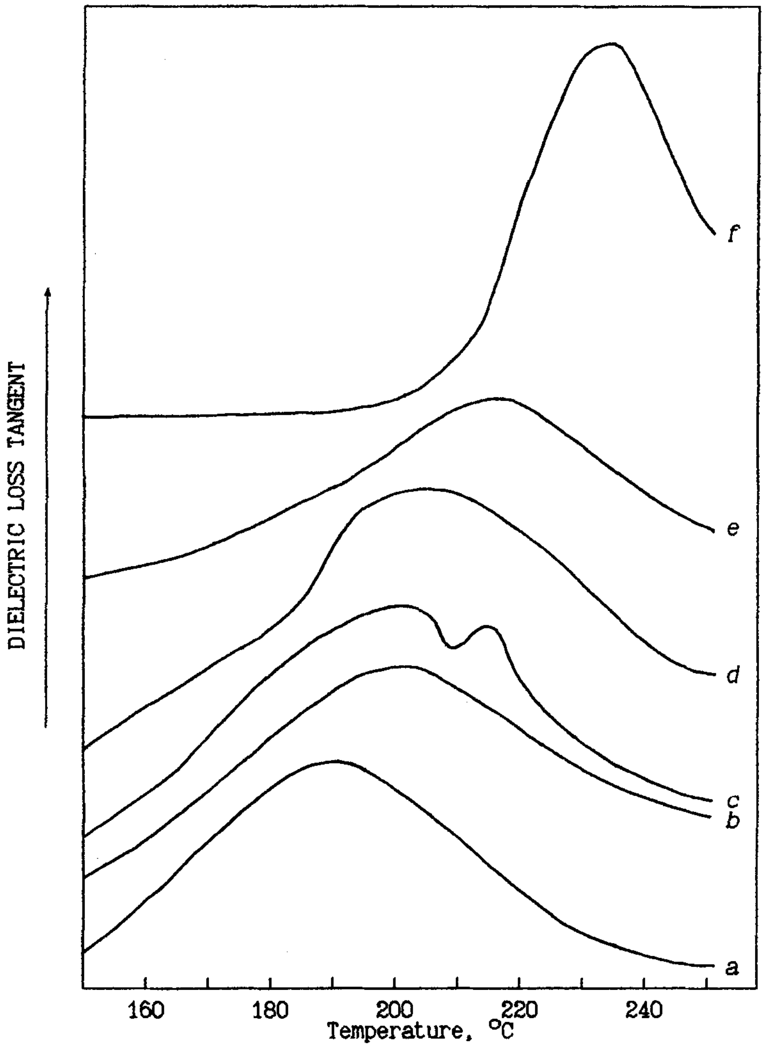

FIGURE 2 Dielectric loss tangent *versus* temperatures for cured PSF/ED-8 blends. PSF content, % 0 (a); 4 (b); 7 (c); 15 (d); 50 (e); 100 (f).

substantial changes in morphology and properties of the hybrid polymer. This fact is well illustrated by Figure 4 where the micro hardness of the obtained hybrid matrices is plotted *versus* the PSF content. One can see that the trend of this curve within the region of low PSF

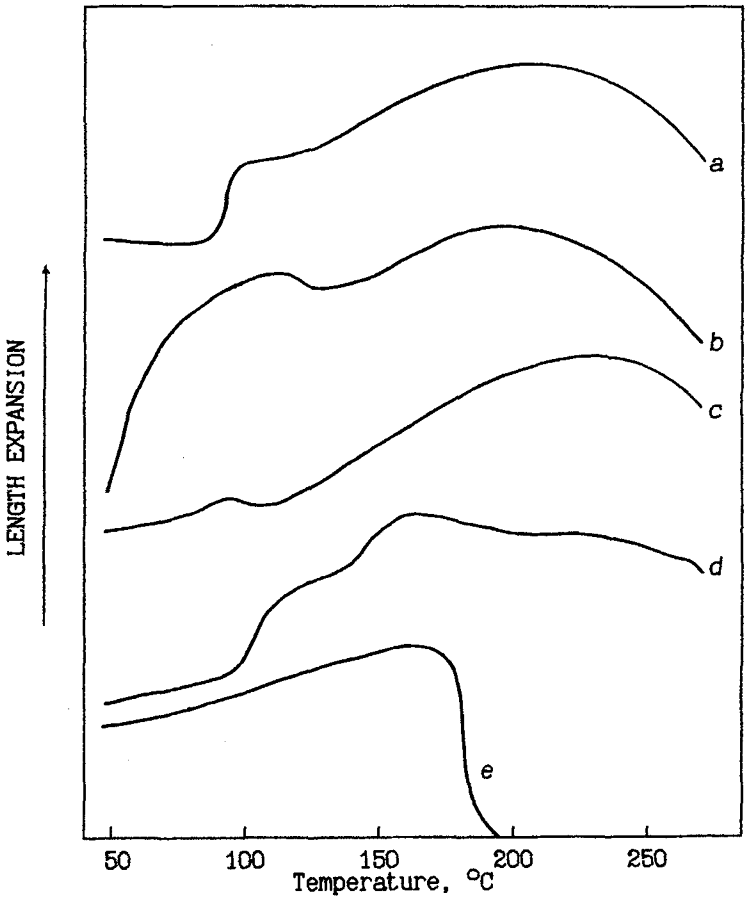

FIGURE 3 TMA curves for cured PSF/ED-22 blends. PSF content, %: 0 (a); 5 (b); 8 (c); 20 (d); 100 (e).

content is the same as that for the glass transition temperature; at first, the micro hardness rises slightly with the polysulfone content up to 4% w/w PSF, then decreases to a minimum corresponding to the highest PSF content in a homogeneous solid solution (5.5%), and increases again as PSF segregates as a separate phase.

Physicochemical properties of reinforced systems are determined, to a great extent, by the structure of interphase layers [2,3]. The microphase separation in common PSF/epoxy oligomer/curing agent melts

TABLE I Properties of ED-8/PSF hybrid polymers

PSF content, %	*Soluble substances content, %*	*Ultimate tensile strength, MPa*	*Elongation to break, %*	*Heat deflection temperature, °C*	*Temperature of 5% mass loss*, °C*	*Impact, Strength kJ/m²*
0	0.9	74	3.4	143	310	7.3
5	0.9	76	5.5	169	339	10.4
8	1.2	87	6.7	165	361	14.7
10	1.9	85	7.5	160	386	15.2
15	8.0	79	7.9	158	377	13.0
20	13.7	76	8.3	156	358	9.9

*At the heating rate of 5°C/min.

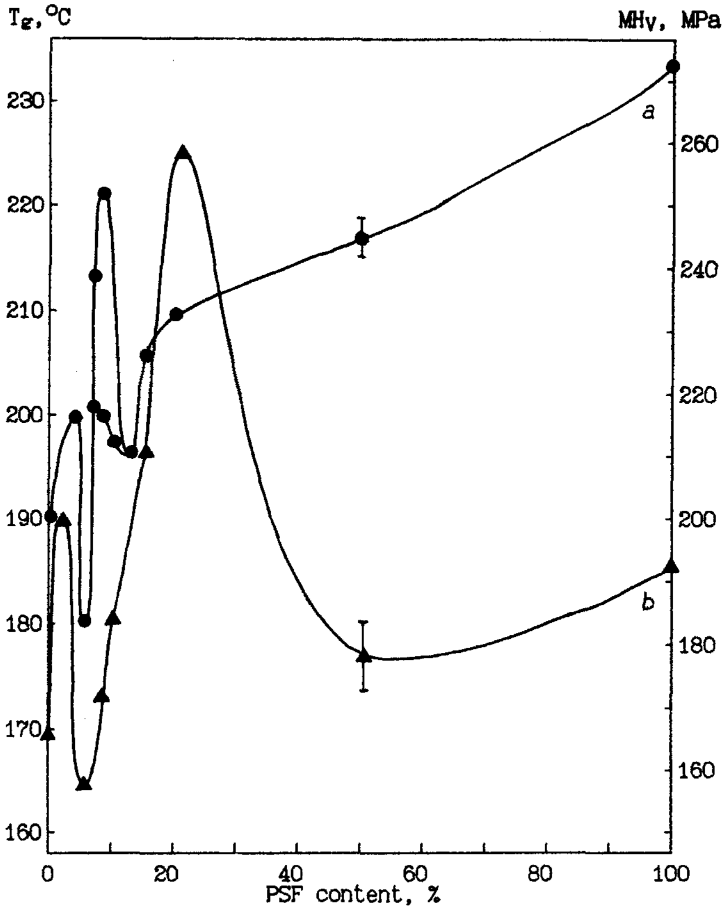

FIGURE 4 Glass transition temperature (a) and micro hardness (b) of PSF/ED-8 hybrid polymers *versus* the PSF content.

during the curing at a PSF content above 5% results in the formation of a highly-dispersed emulsion and retention of this structure in the fully-cured hybrid matrix. Such blends with a developed interphase surface exhibited optimal physicomechanical and thermal properties, thus evidencing a high adhesion between the phases [2, 24]. In all probability, formation of hydrogen and chemical bonds between active molecular groups of PSF and cured epoxy polymer plays an important part. It is known that end hydroxyl groups of PSF are capable of interacting with epoxy rings [6, 11]. As one can see in Table I, the content of soluble substances in the cured compositions is a little lower than the amount of PSF added, *i.e.* some part of the linear PSF molecules is bound to the three-dimensional epoxy network through end groups. In general, however, the chemical structure of PSF does not change during the network formation (as distinct from polycarbonate whose carbonate groups interact chemically with epoxy rings [25]). So, the PSF addition did not influence either the shape of thermograms obtained in the curing process for the epoxy/curing agent mixture or the positions of the maxima (Fig. 5). In the IR spectra of the cured hybrid matrices, all bands attributed to PSF remained without changes, except the band at 1025 cm^{-1} corresponding to C—O—C groups. The marked broadening and splitting of this band and the decrease of its intensity are probably due to

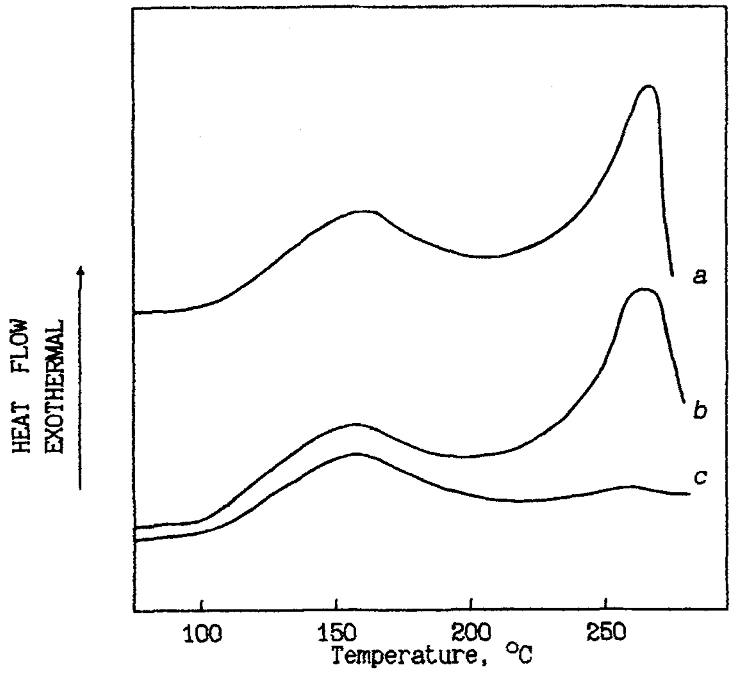

FIGURE 5 Thermograms of powdered PSF/ED-8/DHDPS mixtures. PSF content, %: 0 (a); 10 (b); 20 (c).

hydrogen bonding between ester groups of the PSF and oxy- groups of the cured epoxy resin (Fig. 6). The formation of hydrogen and chemical (through end groups) bonds at the PSF/epoxy interface plays an important part in the stabilization of a highly-dispersed emulsion at the beginning of the crosslinking process as well as in maintaining adherence between phases in the cured hybrid matrix [1–3, 24].

Combining PSF with epoxysulfone oligomers (ESO), distinguished from other epoxy oligomers by their improved thermal stability [26], appeared to be still more effective. The growth of the molecular chains of epoxies during their pre-condensation with DHDPS, and the ap-

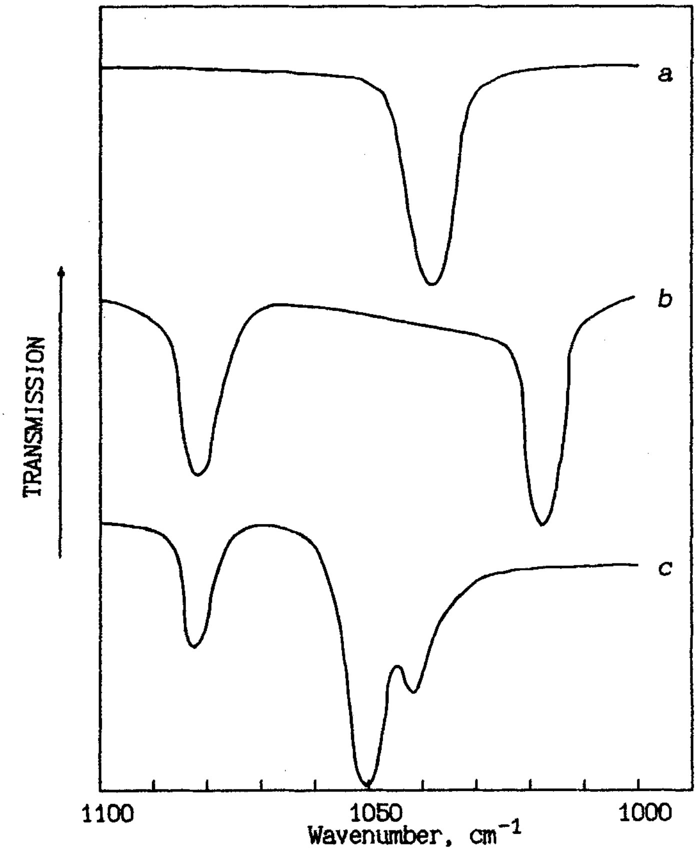

FIGURE 6 Infrared spectra of cured ED-8 epoxy resin (a), polysulfone (b) and hybrid polymer containing 40% PSF (c).

pearance of extra aromatic rings, sulfone and ester groups in the ESO molecules make their structure similar to that of PSF molecules, resulting in close solubility parameters for PSF and ESO [13, 27]. Mixing of the PSF and ESO melts appeared to give hybrid matrices within the whole concentration region (0–100%), Moreover, homogeneous melts are easily obtained under simple thermal treatment of powdery mixtures of PSF/ESO/curing agent, making it possible to use these compositions in electrostatic prepregging and other solution-free technological processes.

Note that the starting temperature of film formation for these blends is much lower than that for a pure PSF (see Tab. II). The addition of even small amounts (10–20%) of ESO to the PSF markedly improves the wetting of woven reinforcement by polymer melt. Thus, ESO can be considered as modifying additives improving technological properties of the polysulfone, in particular the fibrous reinforcement impregnation.

The study of relaxation properties of the ESO/PSF hybrid matrices using TMA and dielectrometry has revealed that they are characterized by only one glass transition point within the whole range of concentrations (Fig. 7). The strength of such matrices is higher than that of PSF (Tab. II). Increasing the ESO content gives rise to a further decrease in the starting temperature of film formation and improvement of the wetting of the reinforcement by the melt; however, hybrid matrices become more and more brittle, and their thermal stability deteriorates. The pattern of TGA curves (Fig. 8) and the data presented in Table II demonstrate hybrid matrices to be intermediate in their thermal stability between PSF and cured ESO, the intensity of decomposition in the temperature region of 350–450°C being significantly higher for alloys with high ($>20\%$) ESO content.

As one can see in Table III, addition of a small amount of ESO to PSF makes it possible to improve substantially the strength of PSF-based plastics. The main reasons for this are evidently the lower melt viscosity, better wetting of the fibrous reinforcement and the larger area of real contact between the fibers and the polymer matrix. In addition, as was shown elsewhere [28, 29], such systems exhibit preferential adsorption of epoxy oligomers on the fiber surface. Under thermal treatment, opening of epoxy rings can be followed by chemical and hydrogen bonding between the matrix and the fiber surface, thus resulting in the reinforcement of the plastic.

TABLE II Properties of PSF/ESO blends

	Properties of powdered mixtures			Properties of hybrid matrices		
ESO content, %	*Starting temperature of of film formation, °C*	*Angle of wetting on carbon tape, deg*		*Ultimate tensile strength, MPa*	*Elongation to, break, %*	*Temperature of 5% mass loss* °C*
		at 250°C	*at 280°C*			
0	280	–	128	68	45	463
10	245	118	104	91	22	391
20	210	102	81	82	14	370
50	195	72	61	84	8	344
80	170	35	18	73	5	335

*At the heating rate of 5°C/min.

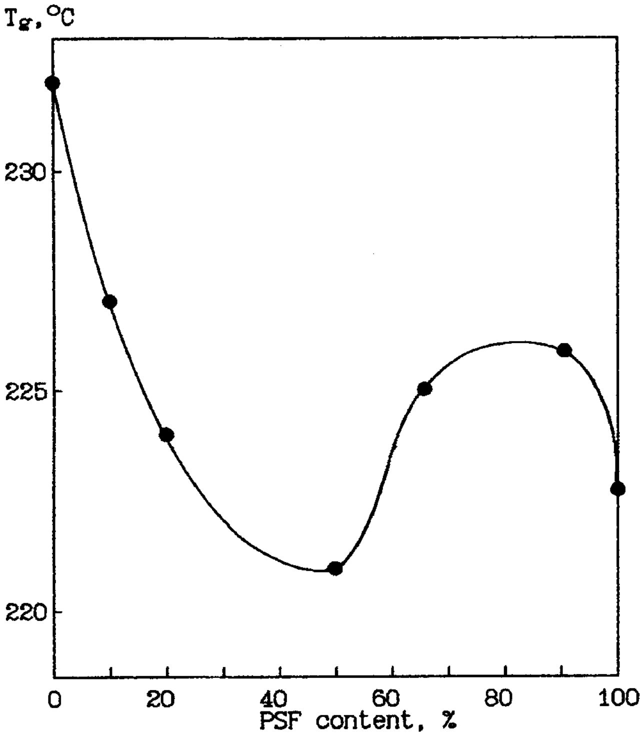

FIGURE 7 Glass transition temperature of PSF/ESO hybrid polymers (from the dielectric loss tangent measurements) *versus* the PSF content.

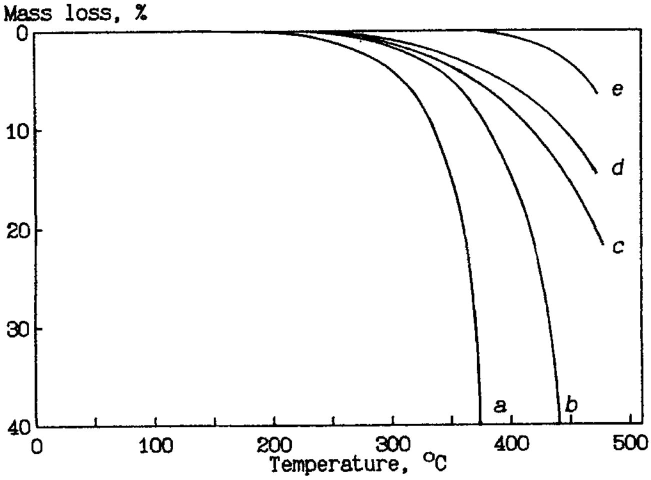

FIGURE 8 TGA curves for PSF/ESO hybrid polymers. PSF content, %:0 (a); 50 (b); 80 (c); 90 (d); 100 (e).

TABLE III Strength of laminates based on PSF/ESO hybrid matrices and glass fabric reinforcement

ESO content, %	*Temperature of formation, °C*	*Shear strength of prepregs, MPa*		*Strength of plastics, MPa*	
		*One-layer prepreg**	*Four-layer micro-plastic* [21]	*Strength to* normal load**	*Interlaminar* shear strength
0	280	10.4	2.6	670	67.4
10	245	20.1	4.8	710	69.5
20	210	29.6	5.5	790	70.1

*Tensile load applied in 10° direction to the main orthotropic axis [22].
**From the three-point bending test [22].

4. CONCLUSION

Blending polymers of different natures – PSF (thermo-plastic) and epoxy resin (thermosetting) – allows one to combine in the hybrid polymer the deformability and thermal stability inherent in thermoplastics with the good processability and adhesion characteristics of thermosetting oligomers.

The PSF-epoxy compatibility in the melt increases with the epoxy oligomer chain length, and is especially good when epoxysulfone oligomers (ESO) are used. The properties of hybrid polymers depend substantially on their morphology and on the alloy composition, especially in the regions of low concentration of either component. For instance, the epoxy matrix containing *ca.* 10% PSF is a self-reinforced network having improved mechanical properties as well as thermal stability and heat resistance. On the other hand, addition of small amounts of epoxy oligomers to polysulfone significantly improves its processability: the melt viscosity is lower, and the fibrous reinforcement wetting and impregnation are better. Powdered PSF/ESO mixtures are convenient for use in "dry" technologies. Plastics based on hybrid matrices are distinguished by high strength.

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