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Studies on thermal and morphological characteristics of E-glass/Kevlar 49 reinforced siliconized epoxy composites

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Abstract

Two different types of siliconized epoxy matrix systems are developed by interpenetrating technique using epoxy resins GY 250 and LY 556 (Ciba-Geigy) and hydroxyl terminated polydimethylsiloxane with γ-aminopropyltriethoxysilane as cross-linker with dibutyltindilaurate catalyst and cured by aliphatic amine (HY 951, Ciba-Geigy), aromatic amine (HT 972, Ciba-Geigy) and polyamidoamine (HY 840, Ciba-Geigy). Electrical resistant glass (E-glass) and Kevlar 49 reinforced composites are fabricated by hand-lay-up technique using siliconized epoxy matrix systems. The effect of curatives and the percentage of siloxanes on the thermal and morphological characteristics of the siliconized epoxy polymer composites are studied. The siloxane incorporation enhances the thermal stability due to the ablative behaviour of siloxane moiety. E-glass fibre reinforcement shows better intermolecular adhesion to epoxy resin than Kevlar-49 reinforcement due to the presence of ionic sites. The siloxane introduction into epoxy resin improves the service temperature of the matrix systems.

Keywords: Siliconized epoxy systems; Interpenetrating network; E-glass/Kevlar 49 composites; Glass transition temperature; Thermal stability; Morphology

1. Introduction

Epoxy resins have widely been used as structural adhesives because of their excellent bonding, thermal and mechanical characteristics [1]. Epoxy resin based composites are used as laminates for printed circuit boards, aerospace, ballistic and engineering hardware components, pollution control equipments, automotive parts, electrical components, and rehabilitation products, etc. However, some of its inferior characteristics viz. impact strength, resistant to weather, thermal stability, restricts the use in high performance applications [2,3]. The modification of epoxy resin with flexible polymeric segments like carboxyl terminated butadiene acrylonitrile rubber (CTBN) and amine terminated butadiene acrylonitrile rubber (ATBN) paved a way for the development of new types of hybrid materials [4–6]. The introduction of these polymeric materials into epoxy resin improve its impact characteristics, but they failed to enhance service temperature, resistant to weather and moisture absorption characteristics of epoxy resin to an expected level for high performance applications.

An interpenetrating network mechanism provides an effective method of obtaining the matrix materials with single glass transition value when compared with polymer blends, which normally exhibit multiple glass transition values due to thermodynamic incompatibility of the components involved. To overcome the phase separation, interpenetrating network mechanism is favoured and can be achieved with the help of multifunctional cross-linkers [7].

In the present investigation, an attempt has been made to improve the properties of epoxy resin to an appreciable extent by incorporating hydroxyl terminated polydimethylsiloxane as toughening agent. Hydroxyl derivative of polydimethylsiloxane has been preferred as

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the toughening agent for epoxy resins because of its inherent characteristic properties [8–10] viz., constant physical properties over a wide range of temperature, flexible molecular structure, resistance to weather and ozone, good wetting, high thermal stability, good dielectric strength, good hydrophobic and excellent physiological inertness.

2. Experimental

2.1. Materials

A siliconized epoxy interpenetrating network system is developed using epoxy resin GY250 (DGEBA) (Ciba-Geigy) and LY 556 (DGEBA) (Ciba-Geigy), and they are referred to as systems X and Y, respectively. Aliphatic amine (HY 951, Ciba-Geigy), aromatic amine (HT 972, Ciba-Geigy) and polyamidoamine (HY 840, Ciba-Geigy) are referred to as A, B and C, respectively, were used as curing agents for curing the epoxy systems X and Y according to their chemical equivalents under appropriate curing conditions. The siloxane component used in the present work for the development of interpenetrating network system of hybrid siliconized epoxy matrix was derived from octamethylcyclotetrasiloxane (Wacker-Chemie, Germany) through controlled equilibration polymerization reaction. The molecular weight of hydroxyl terminated polydimethylsiloxane used in the present investigation is 2000. A silane derivative namely γ-aminopropyltriethoxysilane (Union Carbide), is used as a cross-linker alongwith dibutyltindilaurate catalyst. The nomenclature of curatives, epoxy resins and the concentration of siloxane present in the hybridized matrix systems are presented in Table 1.

2.2. Preparation of prepolymer mix

The varying calculated percentages (w/w) of hydroxyl terminated polydimethylsiloxane prepolymer is thoroughly mixed with calculated percentages of epoxy resin at 30°C. The prepolymer mix is subjected to vacuum to remove the entrapped air in the prepolymer mix.

2.3. Curing of prepolymer mix

The siliconized epoxy matrix systems X and Y and their varying composition alongwith different curatives A, B and C, cross-linking agent and catalyst are presented in Table 2. The calculated amount of curative, aliphatic amine (A) and polyamidoamine (C) are used separately, silane cross-linker (γ-aminopropyltriethoxysilane) and dibutyltindilaurate catalyst (Table 2) are sequentially added to prepolymer blend (hydroxyl terminated polydimethylsiloxane and epoxy resin (w/w)), and the resulting product is cast in the mould at 30°C. The sample is post-cured at 70°C for 10 h in the case of curatives A and C. For curative B (aromatic amine), it is melted at 90°C and is mixed with a siliconized epoxy prepolymer at 120°C followed by the addition of stoichiometric equivalent of γ-aminopropyltriethoxysilane and dibutyltindilaurate catalyst (Table 2). The resin blend and curing agents are thoroughly mixed and cooled to about 60°C and a vacuum is applied. The mixture is then poured into the preheated (70°C) mould

Table 1
Nomenclature of siliconized epoxy matrix system

Curative	Siliconized epoxy matrix system							
	System X (Ciba-GY 250)				System Y (Ciba-LY 556)			
Siloxane/epoxy (w/w)	0/100	10/90	20/80	30/70	0/100	10/90	20/80	30/70
Aliphatic amine A (HY 951)	AX_0	AX_{10}	AY_{20}	AY_{30}	AY_0	AY_{10}	AY_{20}	AY_{30}
Aromatic amine B (HT 972)	BX_0	BX_{10}	BY_{20}	BY_{30}	BY_0	BY_{10}	BY_{20}	BY_{30}
Polyamido amine C (HY 840)	CX_0	CX_{10}	CY_{20}	CY_{30}	CY_0	CY_{10}	CY_{20}	CY_{30}

Table 2
Amount of curatives, cross-linking agent and catalyst in siliconized epoxy matrix systems X and Y

Ratio of siloxane/epoxy	Amount of curative (g)			Cross-linking agent (g)	Catalyst (g)
	A	B	C		
0/100	10	27	50	–	–
10/90	9	24.3	45	1.473	0.1
20/80	8	21.6	40	2.946	0.1
30/70	7	18.9	35	4.419	0.1

and kept for 3 h and then post-cured at 120°C and 160°C for 2 and 1 h, respectively.

2.4. Siloxane introduction into epoxy system

To obtain reasonable thermomechanical characteristics, the tentative requirement of siloxane component is taken as 10% (w/w). This has been ascertained from the data obtained from mechanical, electrical, thermal and aging characteristics of cured siliconized epoxy matrix having varied percentages of siloxane content (viz., 10%, 20% and 30%).

The cure schedule of siliconized epoxy matrix systems are characterized by a differential scanning calorimeter (DSC). During the chemical reaction between epoxy groups and amino groups of both silane cross-linker (γ-aminopropyltriethoxysilane) and curative B, the heat of reaction (exotherm) rises to 120°C and 175°C, respectively. These values are obtained from DSC under nitrogen atmosphere with the heating rate of 15°C min^{-1}. (Fig. 1). The formation of a network structure proceeds in two steps: In the first step, the reaction occurs between the epoxide ring of the epoxy resin and the amino group of the γ-aminopropyltriethoxysilane, and is confirmed from the disappearance of the epoxy band (913 cm^{-1}) by IR spectra. The absorption peaks appearing 2980 and 2850, 1370 cm^{-1} confirm the presence of $SiOCH_2CH_3$, and $Si(CH_2)_3$, respectively. In the second step, γ-aminopropyltriethoxysilane reacts with hydroxyl groups of hydroxyl terminated polydimethylsiloxane. The single glass transition temperature obtained from DSC studies confirms that the polydimethylsiloxane is in the frame of the epoxy network and not in the separate phase (Fig. 2). These reactions reveal that the hydroxyl terminated polydimethylsiloxane is covalently bonded with the epoxy resin through γ-aminopropyltriethoxysilane. Further, this confirms that the siloxane phase spreads over the whole network specimen.

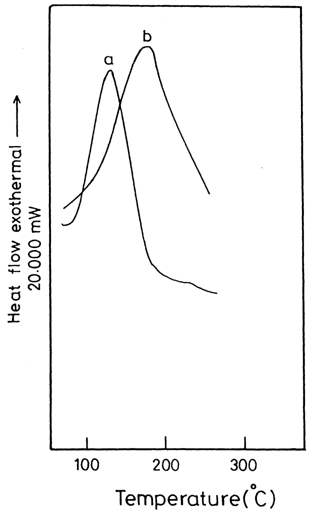

Fig. 1. DSC curves of the reaction exotherms of epoxy resin with (a) α-aminopropyltriethoxysilane and (b) diaminodiphenylmethane.

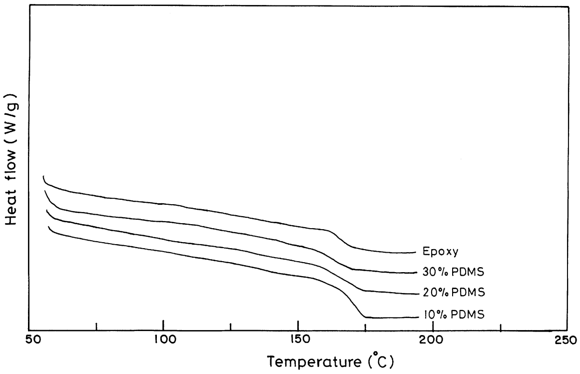

Fig. 2. Glass transition temperature curves (DSC) of siliconized epoxy aromatic amine cured system.

2.5. Fabrication of composites

The composite material is prepared by hand lay-up technique using 10 mil bi-directional woven E-glass fabric. Fabric pieces of size 20 × 12.5 cm weighing 50 g is heated to 150°C in a hot air oven for 2 h to remove moisture and then cooled to 30°C. Preweighed mixture of siliconized epoxy prepolymer resin with a stoichiometric quantity of curing agent (hardener) is applied over a fabric sheet using rubber roller. The fabric pieces coated are kept at 70°C for 3–5 min. The prepreg material is kept one over the other in the releasing agent coated mould and a pneumatic pressure of 2 kg cm^{-2} is applied for a period of 30 min. The mould is taken out and cured at 30°C for 10 h. Then, the composites is removed from the mould and post-cured at 70°C for 10 h. The composite specimens of systems X and Y cured by aliphatic amine and polyamidoamine are prepared by the method described above. For aromatic amine curative, curing is carried out at 70°C for 3 h, and subsequently, step cured at 120°C for 2 h and at 160°C at 1 h, respectively.

The thermal stability of the siliconized epoxy matrix cured with A, B and C was carried out using thermogravimetric analysis in air, and the data on percentage weight loss of the samples are presented in Fig. 3. The glass transition temperature DSC analysis has been carried out in nitrogen atmosphere by using a Du Pont DSC analyzer between 0°C and 350°C at a heating rate of 25°C min^{-1} (Fig. 2).

Heat distortion temperature test, also called deflection temperature under flexural load (DTUL), measures the temperature at which deformation occurs when

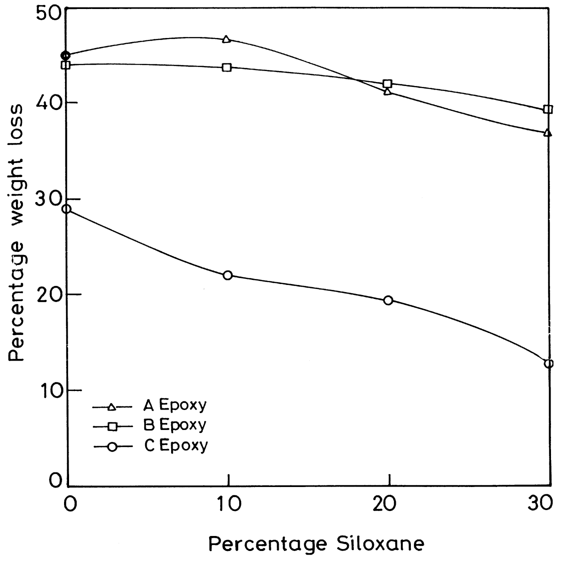

Fig. 3. Plot of percentage siloxane versus percentage weight loss (TGA).

fabricated composite-specimens having dimensions 127 mm in length, 3 mm in thickness and 13 mm in width placed in an oil bath under a load of 1.82 MPa and the temperature is raised at the rate of 2°C min^{-1}. The temperature at which the specimen deflects by 0.25 mm is noted, and the results are presented in Table 3.

Morphological studies of fractured surfaces of composite test specimens used for tensile strength test are carried out by using a scanning electron microscope (Leica Cambridge Stereoscan Model 440).

3. Results and discussion

The DSC thermogram of the samples of unmodified epoxy system and siliconized epoxy systems (10%, 20% and 30%) cured with aromatic amine are presented in Fig. 2. From the thermogram, it is observed that the glass-transition-temperature (*T*g) values of siliconized epoxy systems are enhanced to an extent when compared with that of unmodified epoxy system. This is contrary to the expectation, and this anomalous behaviour may be explained due to the fact that the siloxane component acts as entanglement rather than as a flexibilizer. Flexibilizer introduction into the epoxy system, generally plasticizes the resin system and is expected to increase the free volume and to lower the glass-transition-temperature values of the system. Further, the long siloxane molecule favours chain entanglement and induces the formation of an interpenetrating network structure with an enhanced cross-link density between epoxy matrix and siloxane component through γ-aminopropyltriethoxysilane. In addition, it may also be explained that due to the ablative nature of the siloxane component, which in turn partially dissipates or absorbs the thermal energy supplied to the system.

The plot of degradation temperature against percentage siloxane incorporation is given in Fig. 3. It is observed from Fig. 3 that the degradation temperature increases with the increasing percentage of siloxane, which in turn implies that the siloxane incorporation enhances the thermal stability in addition to the decrease in percentage weight loss.

The delay in degradation of siliconized epoxy resin when compared with unmodified epoxy resin may be explained due to the presence of a siloxane moiety, which in turn stabilizes the matrix system against thermal degradation. However, among the different curative systems studied, the aromatic amine cured system exhibits a higher stability towards the thermal degradation because of its inherent molecular nature. Further, the percentage weight loss of the aromatic amine cured system is considerably lowered when compared with other systems. The increase in thermal stability of siliconized epoxy system over unmodified epoxy system may explained due to the fraction of the heat absorbed or dissipated by the presence of flexible –Si–O–Si– siloxane segment in the siliconized epoxy systems. Further, the siloxane segment is thermally stable at the epoxy degradation temperature; therefore, the thermal energy is dissipated without causing degradation whereas, it is sufficient to degrade the unmodified epoxy matrix system. At the same time, the portion of heat energy is dissipated by the siloxane segment and this may not be sufficient enough for the epoxy segment in the siliconized epoxy system to commence the degradation process. Hence, a delay in degradation was observed for siliconized epoxy systems over the unmodified epoxy system (Fig. 3).

Table 3
Effect of heat distortion temperature on the siloxane introduction

Curatives	Epoxy resin systems								E-glass (60%)		Kevlar 49 (60%)	
	X_0	Y_0	X_{10}	Y_{10}	X_{20}	Y_{20}	X_{30}	Y_{30}	X_{10}	Y_{10}	X_{10}	Y_{10}
A	85	86	88	89	91	92	93	95	164	168	158	163
B	140	143	144	148	148	153	155	158	176	181	162	172
C	74	75	77	78	80	81	83	84	121	132	108	114

The heat distortion temperature of unreinforced matrix systems and matrix systems reinforced with Kevlar 49 and E-glass are presented in Table 3. It is observed that the values of HDT of siliconized epoxy systems are higher than the unmodified epoxy system. The introduction of a siloxane skeleton into the epoxy resin improves the heat distortion value due to the inorganic nature of –Si–O–Si– skeleton and a high value of the silicon–oxygen bond energy. Further, the reinforcement of matrix systems also improves the value of heat distortion by about twofold in all the cases. However, the glass reinforcement imparts a higher value than Kevlar reinforcement due to the inorganic silicate nature. Hence, the siloxane introduction into epoxy resin improves the service temperature of the matrix systems.

The SEM photograph obtained for fracture studies of composites specimens are presented in Fig. 4(a) and (b). From Fig. 4(a), it is observed that the matrix system

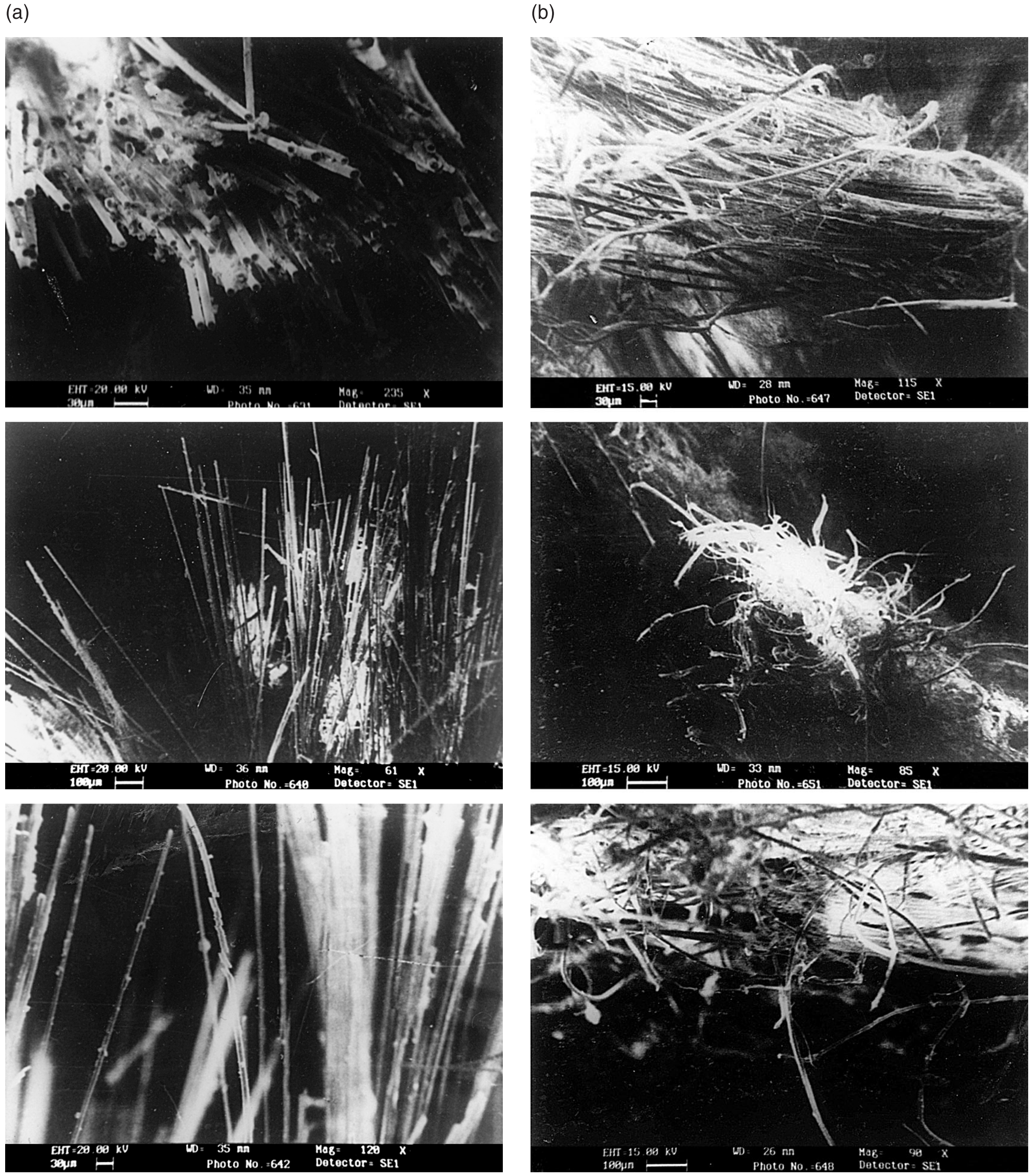

Fig. 4. (a) SEM micrograph of fractured surface of E-glass fibre reinforced siliconized epoxy (10/90) system and (b) SEM micrograph of the fractured surface of Kevlar 49 fibre reinforced siliconized epoxy (10/90) system.

reinforced with E-glass shows that the higher interfacial strength is due to better wetting of E-glass by the matrix resin than that of Kevlar 49 (Fig. 4(b)). From the SEM photograph, it can also seen that the residues of matrix resins are left with fractured glass fibre, whereas no residual resins are attached with the fractured Kevlar fibre. This may be explained due to the strong polar active sites present on the surface of glass fibres imparted by ionic sites of silicon and oxygen atoms and are responsible for the formation of strong intermolecular adhesion between E-glass and matrix resin, which is absent on the surface of Kevlar because of the long organic polymer chain with a smooth crystal structure. The aligned crystalline morphology of Kevlar 49 is responsible for limited adhesion between fibre and matrix (delamination occurs in the case of Kevlar composites under the conditions of fracture test).

However, from the SEM photograph, it can be seen in the case of Kevlar 49 reinforced composites that the individual fibres are pulled out to a fine point before failure and none of the Kevlar fibres shows brittle fracture, whereas glass fibres are sharply broken under the conditions of test. This may further be explained due to polymeric crystalline nature of the former and inorganic amorphous character of the latter. Siloxane introduction into the epoxy skeleton improves wettability of reinforcements including Kevlar, as siloxane possesses low surface tension, better wetting and spreading characteristics even over smooth polished surfaces.

4. Conclusions

Two different types of siliconized epoxy matrix systems are developed by an interpenetrating technique using epoxy resins GY 250 and LY 556 (Ciba-Geigy) and hydroxyl terminated polydimethylsiloxane with γ-aminopropyltriethoxysilane as cross-linker with dibutyltindilaurate catalyst and cured by aliphatic amine (HY 951, Ciba-Geigy), aromatic amine (HT 972, Ciba-Geigy) and polyamidoamine (HY 840, Ciba-Geigy). E-glass and Kevlar 49 reinforced composites are fabricated using the siliconized epoxy matrix materials. Thermal behaviour such as decomposition temperature, glass transition temperature and heat distortion temperature are studied as per the ASTM standards.

The thermal degradation temperature increases with increasing percentage of siloxane incorporation. The aromatic-amine-cured system shows a higher degradation temperature as well as a minimum percentage weight loss. Siloxane introduction into the epoxy resin enhances the values of the glass transition temperature due to chain entanglement and the formation of graft IPN. SEM photographs obtained for fractured surface of Kevlar 49 and E-glass reinforced matrix systems show that the better intermolecular adhesion between matrix and E-glass reinforcement than that of Kevlar 49 reinforcement. It is concluded that the improved wetting and bonding between matrix resin and reinforcements can be achieved by siliconization of epoxy resin. The resulting hybrid matrix materials can be utilized for the fabrication of composites using E-glass and Kevlar 49 reinforcement for high performance aerospace, ballistic and engineering hardware components and for applications in the field of filament wound liquid pressure vessels for a higher service temperature with better performance.

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References

[1] Bucknall CB. Toughened plastics. London: Applied Science Publishers, 1990.
[2] Lin S-T, Huang SK. J Polym Sci Polym Chem Ed 1996; 34:869.
[3] Sung P-H, Lin C-Y. Eur Polym J 1997;33:903.
[4] Bascom WB, Cottington RL, Jones RL, Peyser P. J Appl Polym Sci 1975;19:2425.
[5] Yee AF, Pearson RA. J Mater Sci 1986;21:2475.
[6] Bucknall CB, Partridge IK. Polym Engng Sci 1986;26:54.
[7] Sung P-H, Lin C-Y. Eur Polym J 1997;33:231.
[8] Lin ST, Hung SK. J Polym Sci Polym Chem Ed 1996; 34:864.
[9] Sperling LH. Interpenetrating polymer networks and related materials. New York: Plenum Press, 1981.
[10] Noll W. Chemistry and technology of silicones. New York: Academic Press, 1968.