Polymer Bulletin 40, 623–630 (1998)

Polymer Bulletin
© Springer-Verlag 1998

Multifunctional naphthalene containing epoxy resins and their modification by hydrosilation for electronic application

Chun-Shan Wang*, Ming-Chun Lee

Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan 701, R.O.C.

Received: 19 March 1998/Revised version: 13 April 1998/Accepted: 16 April 1998

Summary

The effect of various functionality (di-, tetra-, pentafunctionality) on mechanical, thermal and moisture absorption properties of naphthalene containing epoxy resins cured with diaminodiphenylmethane (DDS) is investigated. It was found that the glass transition temperature, retention of elastic modulus, thermal stability and moisture absorption increased as the epoxy functionality increased, however, an inverse effect on thermal expansion was observed.

In order to toughen the naphthalene containing epoxy network, the epoxy resin was partially vinylized with 2-allylphenol, followed by hydrosilation using hydride terminated siloxane oligomer. SEM photographs of the modified epoxy networks exhibited a phase separation and the introduction of siloxane into the epoxy backbone has effectively reduced internal stress of the cured products.

Introduction

o-Cresol-formaldehyde novolac epoxy (CNE) is the epoxy resin typically employed to provide a densely crosslinked protective layer for encapsulating microelectronic devices. However, the trend toward miniaturization and thinner electronic equipment and continuing increase in the scale of integrated circuits (IC), many problems have been realized after the high temperature(215-260°C) soldering process, such as package cracking (popcorn phenomenon), delamination and poor performance in humidity testing. Many articles have been reported to improve the solder crack resistance(1-3). In this paper, various multifunctional naphthalene containing epoxy resins were synthesized, partially vinylized with allylphenol, then the allyloxy-ends were modified via hydrosilation using hydride terminated siloxane oligomers to obtain stable silicone rubber dispersion in the epoxy matrix. The effects of epoxy functionality and siloxane modification upon physical properties of cured network were investigated.

* Corresponding author

Experimental

Preparations of Multifunctional Novolacs

{1} 1,1'-Bis(2-hydroxy-1-naphthyl)methane (I-2) was synthesized in accordance with the article reported(3). A pink powdery product in 80 % yield with a melting point of 178°C was obtained. The chemical structure of I-2 was confirmed by mass spectrometry, elemental analysis and ^{1}H-NMR. The synthetic scheme for multifunctional novolacs is shown in Figure 1. MS m/z 300(80; M^+). Anal. Calcd. For $C_{21}H_{16}O_2$: C, 84.00; H, 5.33 Found: C, 84.06; H, 5.39. ^{1}H-NMR (DMSO, d_6): δ 4.70 (s, 2H, C-1), δ 7.06-7.28 (m, 6H, C-2, 3, 4), δ 7.57-7.65(m, 4H, C-5, 6), δ 8.16-8.20(d, 2H, C-7). The assignments of carbon on ^{1}H-NMR of corresponding novolacs were also shown in Figure 1.

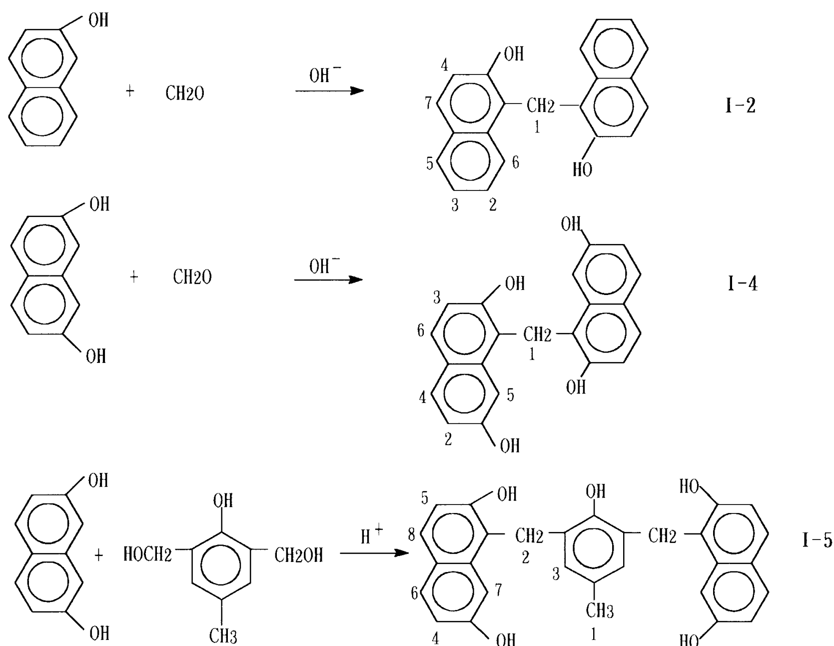

Figure 1. Schematic diagram of the synthesis of multifunctional naphthalene-containing novolacs, and the assignments of carbon on ^{1}H-NMR for novolacs.

{2} 1, 1'-Bis(2,7-dihydroxy-1-naphthyl) methane (I-4) was synthesized by a procedure analogous to the synthesis of I-2 using 2, 7-dihydroxynaphthalene instead of 2-naphthol. Gray powdery product in 96 % yield with a melting point of 253°C was obtained. The chemical structure of I-4 was confirmed as follows: MS m/z 332 (65; M^+). Anal. Calcd. for $C_{21}H_{16}O_4$: C, 75.88; H, 4.85. Found : C, 75.42; H, 4.84. ^{1}H-NMR (DMSO, d_6): δ 4.47(s, 2H, C-1), δ 6 .70-6.75(d, 2H, C-2), δ 6.95-6.99 (d, 2H, C-3), δ 7.37-7.47(m, 6H, C-4, 5, 6). δ 9.15-9.68 (br, -OH).

{3} The preparation of 2, 6 -bis(2, 7-dihydroxy-1-naphthyl-methyl)-4-methyl phenol (I -5) : Into a 500 ml flask was added p-toluenesulfonic acid (PTSA, 0.34 g) and 200 ml MIBK. After purging with nitrogen for 10 min, 2, 7-dihydroxynaphthalene (192.2 g, 1.2 mole) was added to the above solution at room

temperature and mixed well. 2, 6-Dimethylol-4-methyl phenol (mp=124°C, produced in our lab.) (33.64 g, 0.2 mol) was added portionwise over a period of 1 hr. After the completion of addition, it was heated to 65°C and maintained at that temperature for 5hr. Aqueous sodium carbonate was added to the reaction mixture until the solution was neutral. The mixture was rotovapped at 195°C under reduced pressure to remove the unreacted 2, 7-dihydroxynaphthalene and solvent. The crude solid product was washed with water /methanol (68/32, vol ratio) mixture many times to remove the residual 2, 7-dihydroxynaphthalene. A gray product (75g, 83% yield) mp 272-273°C was obtained after vacuum-drying. Elemental analysis (EA) Anal. Calcd. for $C_{29}H_{24}O_5$: C, 76.98; H, 5.35, Found: C, 76.28; H,5.47. ^{1}H-NMR (acetone, δ 1.88 (s, 3H, C-1), δ 4.27(s, 4H, C-2), δ 6.60(s, 2H, C-3), δ 6.88-6.94(d, 2H, C-4), δ 7.05-7.09(d, 2H, C-5), δ 7.30-7.31(d, 2H, C-6), δ 7.59-7.63(d, 2H, C-7), δ 7.65-7.69(d, 2H, C-8).

Preparation of Polyglycidyl Ethers and Siloxane Modified Epoxy Resins

Preparations of polyglycidylether of multifunctional novolacs and their modifications with hydride terminated dimethylsiloxane (mw=17500, purchased from HULS America Inc.) were carried out in accordance with the reported procedures of our previous study (4). The resultant epoxy resins contained ca. 12 wt % dispersed siloxane and had EEWs of 203-285.

Curing Procedure and Specimen Measurements

Each dehydrated epoxy resin was mixed well with a stoichiometric amount of DDS at a moderate temperature to give a pre-cured epoxy powder. The epoxy powder was poured into a aluminum tray (20*14*5mm) and cured in this mold under atmospheric pressure at 150°C for 1hr, 180°C for 2hr and then postcured at 200°C for 4hr to obtain a rectangular specimen for SEM and dynamic viscoelastic analysis. Dynamic viscoelastic properties were performed on a Perkin-Elmer 7 Series with DMA mode between –150 and 300°C, with a heating rate of 10°C/min and a frequency of 1 Hz. The temp/time scan in three-point bending mode was chosen and the dimension of the specimen was 20 x 12.7 x 1 mm according to ASTM D790-95a. The coefficient of thermal expansion (CTE) was measured with TMA mode of Perkin-Elmer 7 series. A specimen ca. 1mm in thickness was tested at the heating rate of 5°C /min. The CTEs were calculated from the slope below Tg. The thermal stability was measured using a Perkin-Elmer Thermogravimetric Analyzer (TGA) with a heating rate of 10°C/min in nitrogen atmosphere. The water pickup was determined by placing preweighted 2.5 thick x 45 mm diameter cured disks in 23°C water for 100 hr. The disks were removed and wiped off with a dry cloth, and weighed to the nearest 0.001g immediately. The density of the cured specimen was determined in a carbon tetrachloride-toluene density gradient column.

Results and Discussion

The synthesis of siloxane modified epoxy resins was proceeded in two steps. The first step involves the vinylization of epoxy resin with 2-allylphenol to form a vinylic macromonomer. The second step is the hydrosilation of the resultant macromonomer with hydride terminated siloxane in the presence of a catalyst (5wt% H_2PtCl_6) to form a stable silicone particles dispersed in the matrix resin which was shown in Figure 2. The completion of hydrosilation was confirmed by the disappearance of the Si-H

absorption at 2126 cm^{-1} and the appearance of a broad Si-O-Si peak at about 1090cm^{-1}.

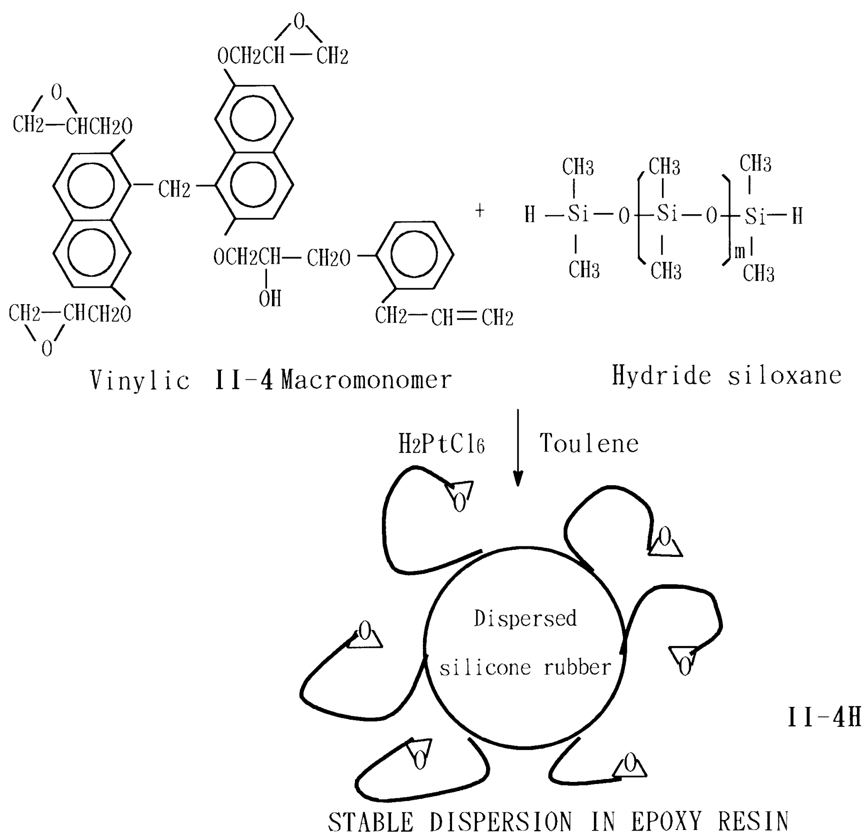

Figure 2 Vinylic II-4 macromonomer and hydride siloxane via "hydrosilation" to form a dispersion. (the hydrosilation of vinylic II-2, II-5 were proceeded in the same manner).

The tan δ curves from dynamic viscoelastic analyses for the cured networks exhibit two major relaxations observed in most epoxy polymers (Figure 3): a high temperature or α transition corresponds to the major Tg of the cured epoxy resin above which significant chain motion takes place; the low temperature or β transition is attributed predominantly to the motion of the CH_2-CH(OH)-CH_2-O(hydroxyether) group of the epoxy resin.

At 180°C(below Tg of III-2), III-2 had 42.7% retention of the original elastic modulus(20°C) while III-4, III-5 had 76% and 82% retention respectively. At 230°C (above Tg of III-2), the retentions were 50% for III-4 and 56% for III-5 which were much greater than 0.65% retention for III-2. Since II-2 had only two oxirane groups, it formed less crosslinked network than II-4 and II-5. When II-2 was modified with hydride terminated siloxane, the number of oxirane group would be further reduced and would result in a much lower crosslinked product, while III-5 exhibited the highest retention of elastic modulus because of its highest crosslink density. The

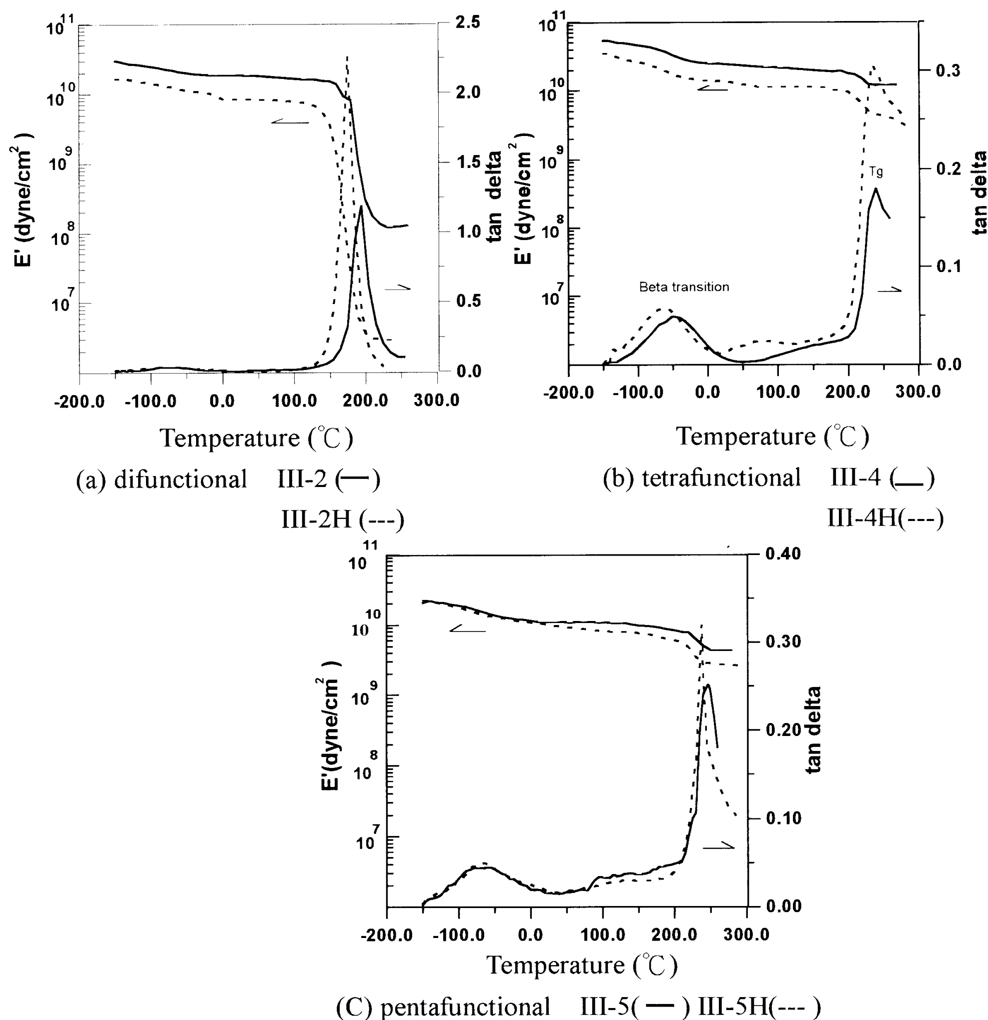

Figure 3 Dynamic viscoelastic analyses of unmodified and modified multifunctional networks

higher the crosslink density, the higher the retention of elastic modulus(5).

Several factors related to chemical structure were known to affect the glass transition temperature (Tg) and the most important factor was chain stiffness or flexibility of the polymer(6). Introduction of rigid and planar naphthalene structure into the epoxy backbone increased the difficulty of chain rotation, so the Tg was increased. In Table 1, III-2 had reached its ultimate Tg because the Tg of 182°C was less than the postcure temperature(200°C). It was attributed to II-2 being two functional and to its low mobility (mp=178°C) in reacting with DDS, and a less crosslinked polymer would be produced in the II-2/DDS system. III-4 had a Tg of 238°C which exceeded the postcure temperature, it might be due to partially cured epoxy still maintained mobility during the post-cured process and cure exotherm. raising T_{cure} above that of the oven temperature. III-5 possessed the highest Tg of 247 °C, the cured system had very high crosslink density which would increase the

difficulty of molecular chain segmental motion. The insertion of siloxane segment into the stacked structure of naphthalene containing epoxy resin would increase the free volume, so the Tg was reduced.

Table 1 The Properties of Cured Naphthalene-containing Epoxys Resins

Properties \ Sample*	III-2	III-2H	III-4	III-4H	III-5	III-5H	CNE
EEW (uncured)	206	285	167	215	161	203	192
Tg (℃)	182	176	238	230	247	238	203
Density (g/cm^3)	1.3061	1.2710	1.3409	1.2584	1.2927	1.2389	1.2602
T_{max} (℃)	398	403	399	411	407	416	380
Water uptake (wt %)	0.35	1.51	1.15	1.79	1.57	1.90	1.60

* number followed by the dash line denotes functionality of epoxy resin, H means the hydride terminated siloxane modification.

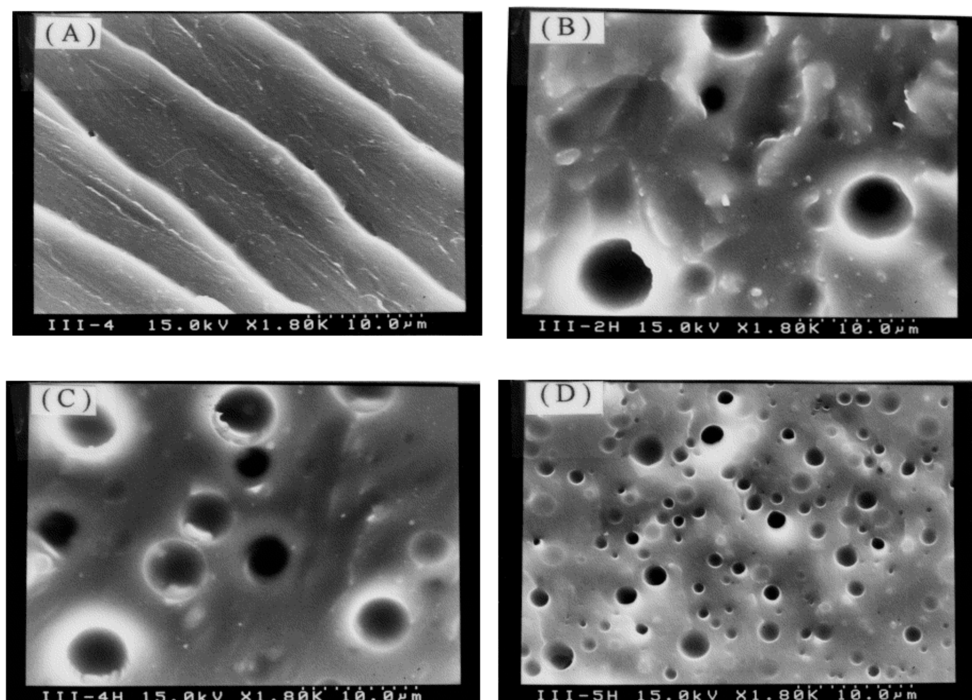

Figure 4 SEM photographs of the cold-snap fracture surfaces of (A) typical neat III-4 and hydride terminated siloxane modified products (B) III-2H (C) III-4H (D) III-5H

SEM photographs shown in Figure 4 revealed that neat epoxy network, bright streamer markings that emanate from the crack tip were the result of the tearing marks of ligament as the crack began to advance (7). For modified epoxy networks, siloxane particles were shown to be embedded in the epoxy matrix and the presence of holes suggested that those particles served as a sort of nucleation site for local shear deformation, in many cases resulting from the particles being pulled out of the matrix. Analyses of experimental results showed that the domain size of dispersed particle decreases as the functionality of epoxy resins increased. This may be attributed to the low compatibility between siloxane and highly crosslinked epoxy networks.

The absorbed moisture in the package was found to cause the package crack during the soldering process (8), lowering Tg of the epoxy networks(9) and has attracted many studies(10-12). Water absorption is based on the following well known mechanism: At the early stage of absorption process, the water molecules occupy free volume entrapped in the crosslinked network(13). At a later stage, more water molecules were attracted by the polar group such as a hydroxyl group which attached to the network, and become hydrogen bonded water. The –OH groups were produced by ring opening during the curing process. As a result, the number of –OH groups in the network increases in proportion to the functionality of epoxy resin. So the amount of water uptake is III-5>III-4>III-2. The introduction of siloxane into the backbone increased the specific volume, and hence more water molecules would invade into the cavity, therefore, the water uptake was increased.

Thermogravimetric analyses were summarized in Table 1. T_{max} was the maximum thermal decomposition temperature taken as the peak of 1st derivative of thermal decomposition curve. T_{max} was found to increase with the functionality. Thermal resistance was also found to increase by the addition of siloxane into the epoxy backbone. EEW, Tg, density, Tmax and the amount of water absorption of the cresol novolac epoxy resin (CNE with a functionality of around 4~5 is the epoxy resin presently being used to encapsulate semiconductor) and naphthalene containing epoxy resins in this study are compared in Table 1. The introduction of naphthalene group into the epoxy backbone has reduced the amount of moisture absorption (CNE compared to III-4 and III-5) and increased the thermal stability (Tg and Tmax) of epoxy resins effectively.

When the specimen was cooled from curing temperature to room temperature, the

Table 2 Viscoelastic Properites and Relative Internal Stress Parameters of Cured Epoxy Resins

Sample	E'(GPa)			α (ppm/℃)	$E'_{ave} * \alpha$ (KPa/℃)
	$E'_{20℃}$	$E'_{180℃}$	$E'_{ave}=(E'_{20℃}+E'_{180℃})/2$		
III-2	1.84	0.79	1.32	51.7	68.2
III-2H	0.83	0.02	0.43	43.6	18.7
III-4	2.42	1.84	2.13	38.1	81.2
III-4H	1.34	1.04	1.19	29.2	34.7
III-5	1.09	0.90	1.00	31.1	31.1
III-5H	1.01	0.66	0.84	27.7	23.3

internal stress would be accumulated in the matrix. Internal stress of modified and unmodified epoxy resins can be approximated by the product of its elastic modulus(E') and the coefficient of thermal expansion(CTE, α) ($E'_{ave} * \alpha$) (14-15).
Table 2 listed the elastic modulus E', CTE α, and $E'_{ave} * \alpha$ of the multifunctional epoxy networks investigated. The dispersed silicone particles effectively reduced elastic modulus and the CTE of the original epoxy resins, therefore, the internal stress of epoxy networks was effectively reduced by the siloxane modification. This could be attributed to the complete separation of the rubber phase from epoxy matrix which acted as a stress reliever.

Conclusion

Multifunctional epoxy resins containing naphthalene ring were produced by epoxidation of corresponding di-, tetra- and pentafunctional novolacs with excess epichlorohydrin. Pentafunctional naphthalene containing epoxy network exhibited highest Tg, highest retention of elastic modulus, highest thermal stability and the lowest CTE. However, the high epoxy functionality resulted in high moisture absorption owing to more –OH groups were produced during the curing process. Epoxy resin with allyloxy end was modified with hydride terminated siloxane which has effectively increased the thermal resistance, reduced the elastic modulus and CTE of the cured epoxy resin. The combination of lower elastic modulus and lower CTE will result in lower thermal stress while the glass transition temperature was only slightly depressed.

Acknowledgement

Financial support of this work by the National Science Council of Republic of China is greatly appreciated (NSC-87-2214-E-151-002).

References

1. Ohta K, Kosaka W, Yanagisawa K(1991)Eur. Pat 0,428,871 A2
2. Lee M.G, Ho T.H and Wang C.S(1996) J. Appl. Polym. Sci. 62:217
3. Oota M (1996) Jpn. Pat 08,176,277
4. Ho T.H, Wang C.S(1997) Polymer, 38:1997
5. Sperling L.H(1993) Introduction to Physical Polymer Science. John Wiley & Sons
6. Sakamoto T, Kyogaku M (1993) Jpn. Pat 05,230,173
7. Clayton A.M (1988)Epoxy Resins. Marcel Dekker, Inc.
8. Kimura H, Ohizumi S, Nishioka T(1992) IEEE 1035
9. Browning C.E(1978) Polym. Eng. Sci. 18(1):16
10. Sabra A, Lam TM, Pascault IP, Grenier-Loustalot MF(1987) Polymer 28:1030
11. Shimazaki A(1968) J Polym Sci. Part C 23:555
12. Uki S, Masanori T(1994) J. Appl. Polym. Sci. 51:1945
13. Min BG, Shin DK, Stachurski ZH(1994) Polym Bull 33:465
14. Gupta V.B, Brahatheeswaran C (1994) J. Appl. Polym. Sci 52:107
15. Ho T.H, Wang C.S,(1994)J.Appl.Polym.Sci. 54:13