

STUDY ON COPOLYMER EPOXY RESIN MATRIX WITHOUT SHRINKAGE PART I VOLUME CHANGE DURING CURE PROCESSES

HE Pingsheng(何平笙) ZHOU Zhiqiang(周志强) WANG Gengchao(王庚超)
and PAN Caiyuan(潘才元)

*(Department of Applied Chemistry, University of
Science and Technology of China, Hefei)*

WU Renjie(吴人洁)

*(Department of Materials Science and Engineering,
Shanghai Jiaotong University, Shanghai)*

ABSTRACT

The volume change of the copolymer epoxy resins can be controlled by copolymerizing epoxy resin E51 with 3,9-di (5-norbornene-2, 2)-1, 5, 7, 11-tetraoxaspiro [5, 5] undecane (NSOC). During curing, the volume changes of copolymer epoxy resins with various amounts of NSOC were measured with a dilatometer. Cure process does not produce volume change when epoxy resin E51 : NSOC is 5.88 : 1 in equivalent.

The shrinkage would be arisen for all commercial resin matrixes more or less due to the molecules of monomer located at a van der Waals' distance from one another move to within a covalent distance during curing (polymerization)^[1]. The problem has not been solved completely by the various methods available now to improve and compensate the shrinkage. Bailey^[2] reported some bicyclic compounds which expanded on ring-opening polymerization in 1972, and had developed a new method to solve the problem of shrinkage in thermosets on curing. The resin matrixes with different characters during curing could be obtained by copolymerizing epoxy resin with expanding bicyclic compound in various proportions^[3].

The resin that cured with a volume expansion is highly desirable for various practical applications, such as adhesives without shrinkage^[4], strain-free composites, precision castings, dental fillings, potting resins and binders for solid propellants^[5] etc..

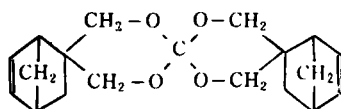
We have synthesized a kind of bicyclic monomer of norbornene spiro orthocarbonate (NSOC)^[3]. This paper describes the volume change during copolymerizing (curing) of epoxy resin E51 with NSOC. It is found that when epoxy resin E51 : NSOC is 5.88 : 1 in equivalent the copolymer resin has no volume change, but shrinks or expands below or above that proportion, thus the volume change can be controlled on curing. It may be used for reducing the residual stress between fibres and resin matrix in composite and increasing the toughness of composite.

EXPERIMENTAL

1. Materials

The bicyclic expanding monomer 3, 9-di(5-norbornene-2, 2)-1, 5, 7, 11-tetraoxaspiro [5, 5]

undecane was synthesized in our laboratory which would be referred as NSOC (norbornene spiro orthocarbonate).



It was white crystal of m.p. 233°C and of m.w. 316 with needle shape and ground into powder of below 200 mesh when using.

The epoxy resin used is bisphenol A E51 made in Wuxi Resin Factory with the epoxy equivalent 196. The hardener was boron trifluorideamine imported from USA.

2. The composition of the copolymer epoxy resin and related data were listed in Table I.

Table 1 Composition of copolymer epoxy resin and their ratio of volume change

Sample No.	Components Amounts W%	E51	E51 : NSOC in			$\Delta V/V$ %*		
			$\text{BF}_3\text{CH}_3\text{CH}_2\text{NH}_2$	NSOC	equivalent	$\Delta V/V$ %*		Calculated from density
						120°C	130°C	
N ₀₀		96.8	3.2	0	1:0	−7.61	−5.43	−5.82
N ₁₀		86.8	3.2	10	13.99:1	−3.14	−3.06	−2.85
N ₂₁		76.0	3.2	20.8	5.88:1	−0.11	+0.05	−0.08
N ₂₅		71.8	3.2	25	4.63:1	+2.09	+1.92	+1.55

* + Expansion, - Contraction

3. Dilatometer

The intra-diameter of capillary of the dilatometer used was 2.822mm. The main part of dilatometer was put in silicone oil medium and kept at constant temperature. The capillary of dilatometer was also put in a glass thermostat with filling water of 50°C to reduce the effect of varying room temperature. The height of silicone oil in the capillary was read by a height finder.

The medium was sensitized directly by the volume change of resins. We selected the methyl phenol silicone oil with stable volume change as the sensitizing medium. The resin sample was filled in a special emulsoid tube which was very thin and transparent to make sure there was no any air bottle in the resin and sensitize the volume change throughout the range of experimental temperature.

4. Experimental procedures

The resins were mixed according to the composition shown in Table 1, and filled in the emulsoid tube under vacuum. The tighted emulsoid tube of height of silicone oil in the capillary was read by a height finder indicating the volume change of resin on curing. The measurement would be stopped in half hour after the medium did not show any height changing.

The volume of dilatometer was calibrated with distilled water at 20°C. The thermal expansion coefficient of medium of methyl phenol silicone oil and the emulsoid tube were measured before experiment and deducted in the calculation.

RESULTS AND DISCUSSION

1. Volume change on curing

Fig. 1 and Fig. 2 show the dependence of height of silicone oil in capillary upon curing time of resins N_{00} , N_{10} , N_{21} and N_{25} . It could be seen that the volumes were contracted throughout the curing for both N_{00} of pure epoxy resin and N_{10} of epoxy resin with 10% NSOC (in weight) at 120°C and 130°C isothermal cure processes, but the magnitude of shrinkage of N_{10} was less than that of N_{00} because of existing 10% NSOC. For the sample N_{25} with 25% NSOC, the volume was not contracted but had some expansion on curing. It suggested that NSOC is the cause of expansion.

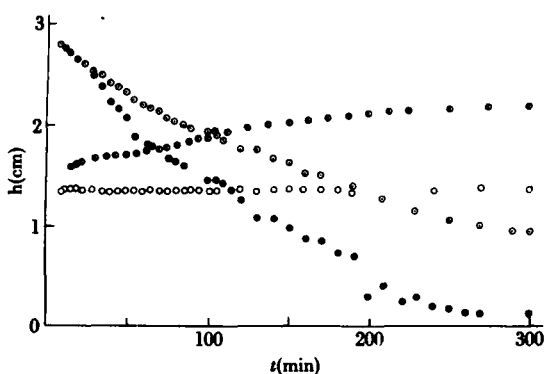


Fig. 1 Dependences of volume change upon cure time of epoxy resins with and without NSOC monomer in isothermal curing at 120°C.

● N_{00} ; ○ N_{21} ;
○ N_{10} ; ○ N_{25}

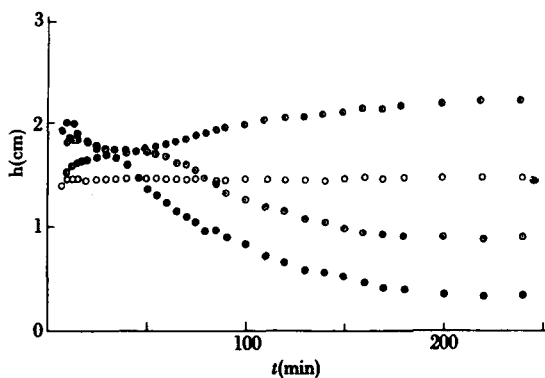


Fig. 2 The same as Fig. 1, but cured isothermally at 130°C.

The original intra-molecular C—O covalent distance (the length of bond is 1.54 Å) in monomer NSOC was broken into a van der Waals' distance (about 3—5 Å), which leads to volume expansion. In other hand, the intermolecular van der Waals' distance in hardener or propagating macroion and NSOC monomer might approach the intra-molecular covalent distance, which would lead to some contraction. These two effects were counterbalanced with each other. Besides, one bond in NSOC went from a C—O bond to a C=O bond after polymerization (cure) and distance between the atoms decreased 0.2—0.3 Å; another C—O bond broke into near intermolecular distance and the distance between atoms increased 1.5—3.5 Å. These two effects were also counterbalanced with each other as shown in Fig. 3. It could be seen from Fig. 3 that two covalent bonds became one double bond and one van der Waals' distance as a result of one monomer taking part in the reaction. But the distance of single bond is only longer than that of double bond by 0.2—0.3 Å, so that the volume was not contracted but expanded during polymerization (cure). Finally, the crystalline NSOC monomer polymerized into an amorphous polymer, which also would lead to volume expansion. the combined results of these three factors produce the volume expansion of NSOC during polymerization (cure).

It could also be seen from Fig. 1 and Fig. 2 that the change of the height of silicone oil medium in capillary with the time was quite stable for both pure epoxy resin and the resins with various amounts of NSOC, which showed that the volume change was homogeneous during polymerization (cure). Although the monomer NSOC was crystal of melting point 233°C, but the ground one mixed with E51 completely would make sure of homogeneity of different components in the resins. No inhomogeneity in the resins could be observed in the scanning electronic microscope figures^[3].

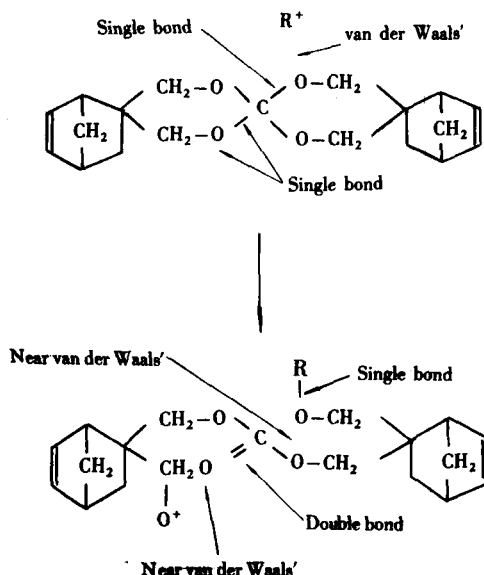


Fig.3 Change of bond distances in NSOC on ring-opening polymerization

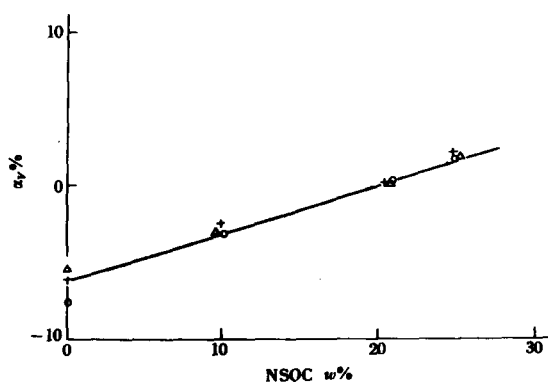


Fig.4 Dependences of ratio of volume change upon the content of NSOC.

○ 120°C; △ 130°C; + calculated from density

The above results showed that the sample N₂₁ of epoxy E51, NSOC being 5.88 : 1 in equivalent, had almost no volume change on curing and was an equal-density cure. In this case it would be possible to reduce completely the residual stress arising from the shrinkage on curing. We had used the epoxy resin copolymerized with NSOC as an adhesive to join the micro-crystal glasses. The internal stress arising from the contraction of volume had been reduced completely when the adhesive had the suitable components. The distort of light circle of light surface of the micro-crystal glass has not even been observed by laser plane interference method. If it was used in composites, there would not exist any shear stress between the resin matrix and reinforcement fibres and it would be hopeful to increase the toughness of glass fibre reinforced composites^[6,7].

The dependence of ratio of volume change of the copolymer epoxy resin upon the various amounts of NSOC was shown in Fig. 4 (also see Table 1). Thus we may vary the contents of NSOC copolymerized with epoxy resin according to the practical application to get the resin matrixes of shrinkage or equal-density or expansion, and control the volume change of resin matrix. It is

convenient to determine the ratio of volume change at a given composition from Fig. 4.

2. Density-temperature curves

From the dependence of density before and after curing upon the cure temperature we can get the volume change of the resin on curing. It would be easy to calculate the ratio of volume change on curing at a given temperature if the densities of the resin before and after curing at various temperature were known. Fig. 5 shows these curves of the samples N_{00} , N_{10} , N_{21} , and N_{25} . Being the same as the results read directly from the height of silicone oil medium in capillary, the samples N_{00} (pure epoxy resin) and N_{10} (epoxy resin with 10% NSOC) were contracted throughout the cure process, and the densities of resin after curing were lower than that before; in contrast to N_{00} and N_{10} , the density of sample N_{25} (which has 25% NSOC) after curing was higher than before. It was only the sample N_{21} which has 20.8% NSOC (in weight) that the density of resin was almost the same before and after curing. It is the equal-density cure. The ratio of volume change of samples N_{00} , N_{10} , N_{21} and N_{25} on curing obtained from the density-temperature curves are also shown in Fig. 4 and in good agreement with that measured directly in isothermal cure.

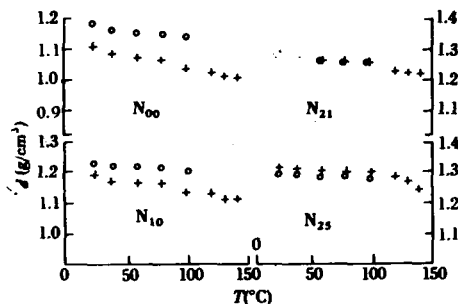


Fig.5 Density-temperature curves of epoxy resins with and without NSOC monomer before and after curing

○ Before curing; + After curing

3. Estimation of volume expanding rate of monomer NSOC

The volume expanding rate of pure monomer NSOC is a useful value. But it is difficult to measure experimentally during cure process because NSOC is a crystal of melting point 233°C . As an approximative calculation, we try to estimate it from the data of copolymer resin. Firstly we estimated the density of NSOC. If the volume would not be any change before and after mixture and could use the principle of linear sum, and the amount of hardener boron trifluoride-amine would be neglected (regard it as the amount of epoxy E51), the density of NSOC calculated from sample N_{10} , N_{21} , and N_{25} were 3.245 , 3.008 and 2.839 g/cm^3 respectively, which suggested that the calculated density of NSOC decreased with increasing amount of NSOC. So the density of pure NSOC monomer could be estimated from the extrapolation to 100% NSOC and was 1.212 g/cm^3 . As an approximative value, it was used in the following calculation of volume expanding rate.

It was supposed that the volume change rate of epoxy resin and NSOC in the copolymer resin were the same as that of their homopolymer at the same temperature, the volume change was only arised from the ring opening in epoxy and NSOC. The effect of hardener was also neglected. The volume expanding rate of NSOC monomer calculated in this way were listed in Table 2. It was obvious that the volume expanding rate of NSOC in the resin with various amounts were different because N_{10} , N_{21} , and N_{25} were the resins of shrinkage, equal-density and expansion respectively. Of course the behaviours of the NSOC in copolymer resin and in homopolymer were different.

Table 2 Volume expanding rate of monomer NSOC

Temperature (°C)	Expanding rate (%)	Sample No			
		N ₁₀	N ₂₁	N ₂₅	Average
120		+ 40.5	+ 30.9	+ 33.7	+ 35.0
130		+ 20.1	+ 22.7	+ 25.8	+ 22.9

Bailey reported that the volume expansion of crystalline monomer 1, 5, 7, 11-tetraoxaspiro [5, 5] undecane on polymerization at 140°C was 17%^[5]. With the same crystalline monomer, the volume expanding rate of 3,9-di (5-norbornene-2, 2)-1, 5, 7, 11-tetraoxaspiro [5, 5] undecane should be larger due to the introducing of two big rings of norbornene. It suggested that the value of the volume expanding rate of monomer NSOC estimated was a recommend datum.

Keywords:

Ring-open polymerization, Copolymer epoxy resin matrix, Volume change, Cure process

Acknowledgement The authors would like to express special thanks to Mrs. Yang Hezheng for supplying the hardener.

REFERENCES

[1] 何平笙、周志强、潘才元, 粘接 (*Technology on Adhesion & Sealing*), 1984, 5(6), 30.
[2] Bailey, W. J. and Sun, R. L., *Amer. Chem. Soc., Div. Polym. Chem. Prepr.*, 1972, 13(1), 400.
[3] 周志强, 中国科学技术大学硕士论文 (Master Thesis, University of Science and Technology of China, 1986.
[4] 潘才元、周志强、何平笙, 粘接 (*Technology on Adhesion & Sealing*), 1986, 7(5), 27.
[5] Bailey, W. J.; Sun, R. L., Katsuti, H.; Endo, T.; Iwama, H.; Tsushima, R.; Saigou, K. and Bitritto, M. M., ACS Symposium Series, 1977 No. 59, p38.
[6] Piggott, M. R., *Proc. ICF5*, 1980, 465.
[7] Piggott, M. R. and Bailey, W. J., *Sampe Quarterly*, July, 1984, p25.