

Epoxy resin copolymer with zero shrinkage

Part II *Thermal and mechanical properties*

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Thermal gravimetry, differential scanning calorimetry, stress-strain and dynamic mechanical testing were performed for pure epoxy resin and epoxy copolymers. Shrinkage, equal density or expansion was obtained by copolymerizing epoxy resin with various amounts of the expanding monomer norbornene spiro-orthocarbonate (NSOC). The glass-transition temperature, thermal-degradation temperature and fracture strength decreased with the introduction of NSOC, indicating that the effect of chain structure on the physical properties of epoxy copolymer was more than that of volume expansion arising from the ring-opening polymerization of expanding monomer NSOC.

1. Introduction

It is well known that water expands in volume when cooling down to near 0°C. Ice has good adhesion with almost everything, and can even stick on the surface of Teflon, giving ice specific properties. For the same reason, a resin that cures with zero shrinkage, or even with a slight volume expansion, is highly desirable in various technical applications, such as high-performance adhesives, coatings, precision castings, dental filling resins and binders for solid propellants [1–6]. Unfortunately, almost all commercial resins shrink to some extent due to the molecules of monomer located at van der Waals' distance of 0.3–0.5 nm becoming chemical bonds of about 0.15 nm. This leads to volume contraction and residual stress in the resin.

Bailey and Sun [2] proposed that ring-opening of a bicyclic monomer joined in a chemical bond could give back a van der Waals' distance during the ring opening polymerization. In this way, it is possible to obtain resins with controllable volume change, even zero shrinkage, by copolymerizing epoxy resins with a bicyclic expanding monomer in various proportions.

We have synthesized one type of bicyclic monomer, norbornene spiro-orthocarbonate (NSOC), and copolymerized epoxy resin E51 with various amounts of it. In Part I of this series [7] we reported that the epoxy copolymer underwent no volume change when the epoxy resin E51:NSOC ratio was 5.88:1 in equivalent, and used it as an adhesive to join the optical parts of a large optical telescope.

Thermal and mechanical properties are of vital importance for any new copolymer used as an engineering material. Surprisingly, there have been only few reports in the literature concerning the thermal and mechanical properties of expanding epoxy copolymers [3, 8]. Many factors affect the thermal and mechanical

properties, among which the expansion in volume during cure (polymerization) is only one. Actually, copolymerization introduces another chain segment into the epoxy resin. The change of chain structure will play an important role in determining their properties. Here the thermal and mechanical properties of the epoxy copolymer are reported in order to add data essential to the application of the epoxy copolymer.

2. Experimental procedure

2.1. Materials

The bicyclic monomer 3,9-di(5-norbornene-2,2)-1,5,7,11-tetraoxaspiro(5,5)undecane, referred to as NSOC (norbornene spiro orthocarbonate) was synthesized in our laboratory. The detailed synthesis scheme can be found in [7]. NSOC is a white crystalline solid of m.p. 233°C mol wt. 316 with needle-shaped crystals. It was ground into a powder of below 200 mesh before use.

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

2.2. Samples

The sample names and their compositions of epoxy resin E51, NSOC and boron trifluorideamine, and the related data, are listed in Table I. The results of dilatometry showed that the sample of N₀₀ (pure epoxy resin) and N₁₀ contracted during cure, whereas N₂₅ showed a slight expansion in volume. Sample N₂₁ was the only epoxy copolymer with zero shrinkage [7].

2.3. Thermal analysis measurements

Thermal gravimetry (TG) was performed in the DT-30 Thermal Analyser (Shimadzu, Japan). Differential

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TABLE I Composition of epoxy copolymers and related properties

Sample no.	N ₀₀	N ₁₀	N ₂₁	N ₂₅
NSOC amount (wt %)	0	10	20.8	25
T _g (from DSC)	125.9	116.2	74.1	76.2
(°C) (from tan δ)	198.1	149.5	128.4	129.0
C _p (J kg ⁻¹ K ⁻¹)	427.1	379.7	370.1	350.0
E (MPa)	980.7	1333.7	1186.6	892.4
(1st step)	308–391	215–260	212–314	215–263
T _d (2nd step)	391–420	260–360	314–378	263–372
(°C) (3rd step)	–	360–410	378–425	372–405

scanning calorimetry (DSC) was measured in DSC-2C of Perkin-Elmer, USA.

2.4. Stress-strain testing

Stress-strain tests were carried out in a DCS-5000 testing machine (Shimadzu, Japan). The samples were rectangular with dimensions of 60 × 10 × 1.2 mm cast in a special mould made of Teflon. Testing was at room temperature. The rate of extension was 0.1, 1 and 10 mm min⁻¹, corresponding to the strain rates of 0.005, 0.05 and 0.5 m⁻¹, respectively.

2.5. Dynamic mechanical test

Dynamic mechanical modulus and loss tangent were measured with a Rheograph solid viscoelastometer (Toyo Seike, Japan). The frequency was fixed at 10 Hz and the heating rate was 2 °C min⁻¹ when measuring the temperature spectrum. The temperature was fixed at three temperatures of 30, 50 and 80 °C when measuring the frequency spectrum, with the frequency range of 0.01 to 100 Hz.

3. Results and discussion

3.1. Density-temperature curve

As reported in [7], copolymerizing epoxy resin with expanding monomer NSOC can control the volume change of resulting copolymers effectively. The density-temperature curves of pure epoxy resin and epoxy copolymers before and after polymerization (cure), obtained from the dilatometry measurement, are shown in Fig. 1. Obviously the densities of both pure epoxy resin N₀₀ and epoxy copolymer N₁₀ (with only 10% NSOC) increased after polymerization, but the epoxy copolymer N₂₅ (with up to 25% NSOC) decreased its density after polymerization. Only the epoxy copolymer N₂₁ (with 20.8% expanding monomer NSOC) underwent almost no volume change; its polymerization in the temperature range carried out here was equal-density polymerization.

3.2. Glass transition temperature

The glass transition temperature is one index of thermal resistance of a cured resin and can be obtained from the DSC measurement. Fig. 2 gives the DSC temperature spectrum of the samples of N₀₀, N₁₀, N₂₁ and N₂₅. Their glass transitions (T_g) obtained from the

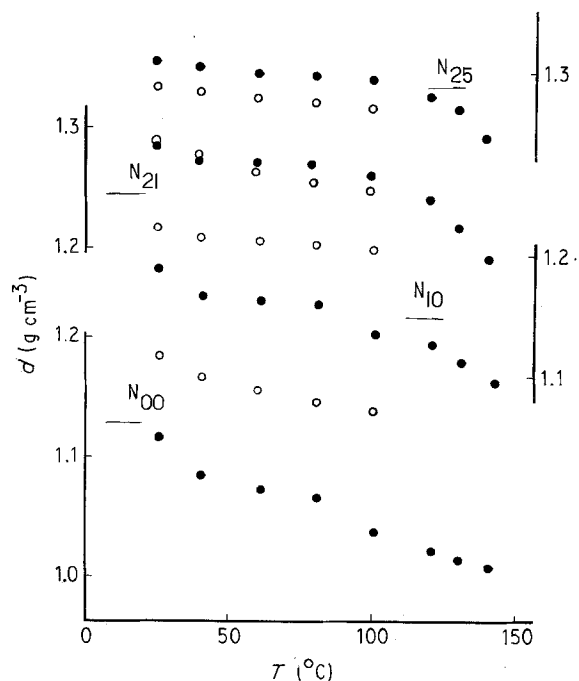


Figure 1 Density-temperature curves of pure epoxy resin and epoxy copolymers (● before and ○ after polymerization).

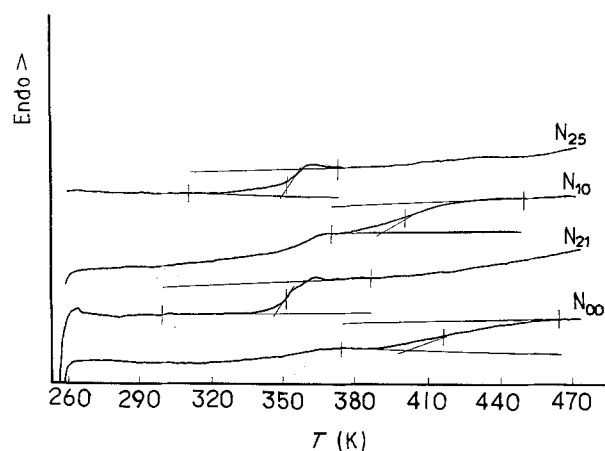
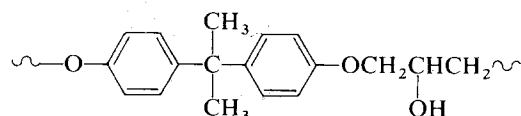


Figure 2 DSC temperature spectrum of the pure epoxy and epoxy copolymers.

DSC measurement are shown in Fig. 3 as a function of NSOC content (see also Table I). It can be seen that the glass transition temperature of the epoxy copolymers decreased with increasing amounts of NSOC, reached its minimum at 20.8% NSOC (sample N₂₁), then increased again. There are many factors which can affect the glass transition. In the present case, the rigidity of macromolecular chain and its free volume are two of the main factors. In the macromolecular chain of pure epoxy resin E51



the internal rotation between the benzene ring is quite difficult, the chain has larger rigidity and consequently

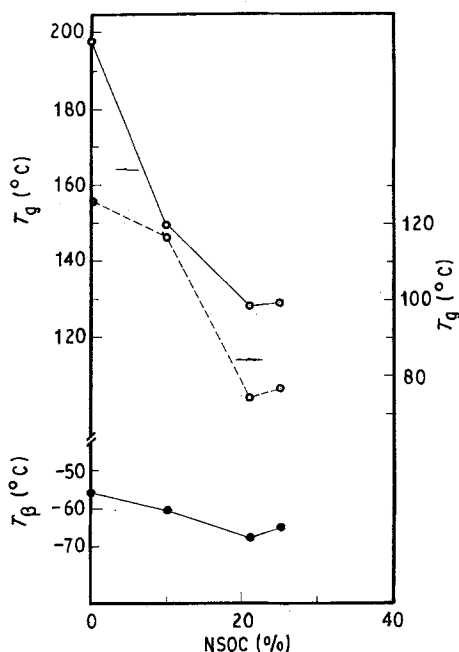
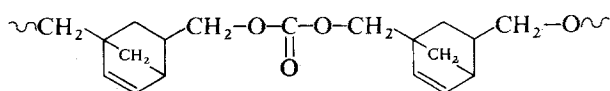


Figure 3 Glass transition temperature T_g of pure epoxy resin and epoxy copolymers as a function of NSOC amounts.

a higher glass transition T_g . By comparison, in the chain of NSOC



there is no bond which has difficulty in internal rotation. Its rigidity is therefore relatively small, and the glass temperature should be lower than that of pure epoxy resin. Hence the introduction of expanding NSOC into pure epoxy resin would be extended to decrease its glass transition. On the other hand, because the NSOC can expand in volume when polymerized, this volume expansion would "occupy" part of the free volume of the resin, so reducing the flow of the resin system. According to the free volume theory of glass transition [9], the temperature of the resin must increase in order to reach the free volume of 0.025 required by the glass transition. The expansion of NSOC in volume arising from the cure (polymerization) could therefore theoretically increase the glass transition of epoxy copolymer. Thus, the copolymer of epoxy with NSOC has two possible completely contrary effects on glass transition of epoxy copolymer. The experimental results here (Fig. 3) suggest that the factor of chain structure in the macromolecules was dominant over the factor of volume expansion. Combining the effect of these two factors implies that the glass transition of epoxy copolymer decreased until the NSOC amount of 25% (sample N_{25}) was reached, at which point the increasing tendency of glass transition appeared, presumably reflecting the volume effect.

Only one glass transition could be observed in the DSC measurement for all of the samples. The situation was the same in the dynamic mechanical test (see Section 3.5). The fact that only one glass transition existed in the samples of N_{10} , N_{21} and N_{25} proved

that the epoxy copolymer was a real and random copolymer.

3.3. Thermal degradation temperature

Selecting $\alpha\text{-Al}_2\text{O}_3$ as a reference substance, samples of 15 mg were measured by thermogravimetric and differential thermal analysis with the heating rate of $10^\circ\text{C min}^{-1}$ at the same time. Fig. 4 shows the thermogravimetric curves of the samples of N_{00} , N_{10} , N_{21} and N_{25} . For pure epoxy resin E51, there were two thermogravimetric steps. However, there were three thermogravimetric steps in the epoxy copolymers. The second thermogravimetric mechanism of pure epoxy resin N_{00} was carbonization; the first thermal degradation of the macromolecular chain of epoxy resin starts from 308°C . The copolymerization of NSOC with epoxy resin introduces NSOC chain segments into the epoxy resin chain and makes a new thermogravimetric step appear in the epoxy copolymer, which started from 215, 212 and 215°C for the samples of N_{10} , N_{21} and N_{25} , respectively. Compared with pure epoxy resin, the first thermogravimetric mechanism of epoxy copolymers was just thermal degradation of NSOC segments in the copolymer and occurred in advance of about 100°C . This indicated that the introduction of NSOC led to a decrease of thermal resistance of the epoxy copolymer. The volume expansion had almost no effect on their thermal stability here.

3.4. Specific heat capacity (C_p)

The specific heat capacity could be obtained from DSC measurements when the accuracy was not required to be too high. Selecting indium ($C_p = 234.5 \text{ J kg}^{-1} \text{ K}^{-1}$, 25°C) as a standard substance, we estimated specific heat capacity for the samples (see Table I).

3.5. Stress-strain curve

The stress-strain curves of the samples of N_{10} , N_{21} and N_{25} in the three chosen strain rates have similar shapes and belong to the hard-brittle type of stress-strain curve, but have obvious differences compared with that of pure epoxy resin N_{00} which had a

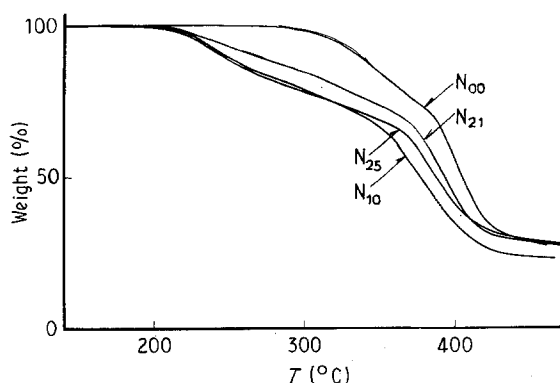


Figure 4 Thermogravimetric curves of pure epoxy resin and epoxy copolymers.

hard-strong type of stress-strain curve. Fig. 5 gives the stress-strain curves at a strain rate of 0.5 mm min^{-1} . It can be seen that the elongation to break was quite small for the samples of N_{10} , N_{21} and N_{25} , all of which copolymerized with NSOC monomer. There was no yield point. The stress-strain curve was almost a straight line. However, for the sample of pure epoxy resin N_{00} , elongation to break was about 10%, and the tensile strength was 3 to 4 times that of copolymer resins. The Young's modulus (E) and tensile strength (σ) of the epoxy copolymers were obtained from their stress-strain curves. Fig. 6 shows the tensile strength of the epoxy copolymers as a function of NSOC concentration.

The rupture of polymeric materials must relate to either the rupture of interaction between macromolecules, or the rupture of chemical bonds in its macromolecular chain. Because the cured epoxy copolymer is a cross-linked polymer, its macroscopic strength is mainly decided by the strength of chemical bond in chain. The copolymerization and cure of NSOC with epoxy resin E51 should decrease the tensile strength of epoxy copolymer, because the chemical bonds in NSOC are weaker than those in epoxy resin E51. With increasing amounts of NSOC, the tensile strength of the epoxy copolymer decreased gradually. On the other hand, it was generally thought that the volume contraction of resin during cure could be released by the flow of resin before the gel point. However, due to the flow of the resin being lost after the gel point, residual stress within the resin arising from the volume contraction might be produced, that is, the resin is acted on by the residual stress without any applied forces. This type of residual stress is directionless and would lead to a decrease in strength of the resin. Thus the resin with zero shrinkage should not produce any residual stress, and should have higher strength than that with shrinkage. This idea is substantiated by the experimental results given here. The anomalous increase of fracture strength of epoxy copolymer with zero shrinkage against the tendency of regular de-

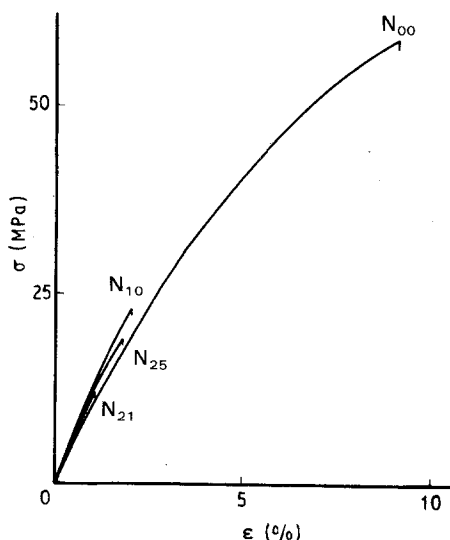


Figure 5 Stress-strain curves of pure epoxy resin and epoxy copolymers at the strain rate of 0.05 min^{-1} .

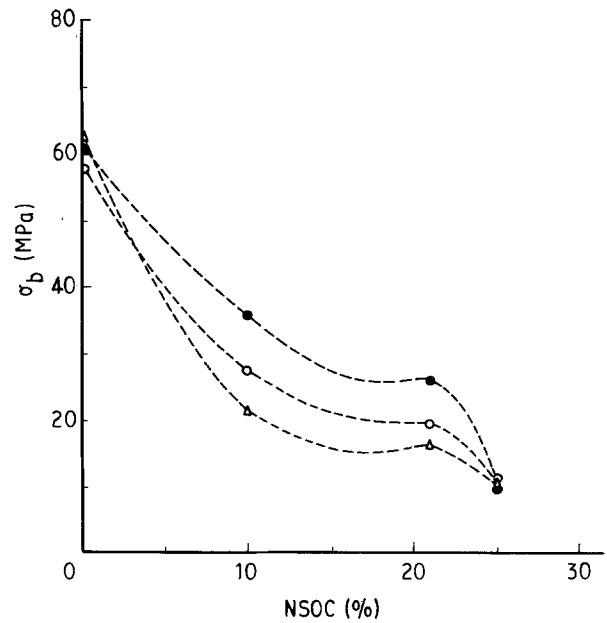


Figure 6 Tensile strengths of epoxy copolymers as function of NSOC amounts. Strain rate: \circ , 0.005 min^{-1} ; \bullet , 0.05 min^{-1} ; \triangle , 0.5 min^{-1} .

crease may be attributed to the zero shrinkage just mentioned.

The experimental results here indicated that the concept of increasing the fracture strength of a resin by releasing the residual stress arising from volume contraction during cure (polymerization) was not conclusive. When certain methods are used to reduce the residual stress, for example, by copolymerization of epoxy resin with expanding monomer NSOC, it is possible that the method simultaneously itself reduces the strength. Hence in order to increase the tensile strength of a resin, it is necessary that the added second component itself, the expanding monomer NSOC in the present case, should have high strength as well as expanding in volume during cure. The monomer NSOC used here does not meet this requirement. However if the epoxy copolymer containing the NSOC is used as a middle layer, and used to treat the surface of glass fibre, then using this glass fibre composite with pure epoxy resin should result in a composite with high strength. Further work is now in progress.

The Young's moduli of the pure epoxy resin N_{00} and the epoxy copolymers N_{10} , N_{21} and N_{25} were 100, 136, 121 and 91 kg mm^{-2} , respectively. It was interesting that the Young's modulus of sample N_{10} had the maximum value. Only the modulus of sample N_{25} was smaller than that of pure epoxy resin N_{00} . For same materials, it was thought that the denseness of the material would increase the Young's modulus, but the effect of chain structure change went beyond that of volume change.

3.6. Dynamic mechanical properties

Fig. 7 shows the dynamic mechanical temperature spectrum for the samples of N_{00} , N_{10} , N_{21} and N_{25} at the frequency 10 Hz and heating rate of $2^\circ \text{C min}^{-1}$ in the temperature range -150 to 240°C . There were

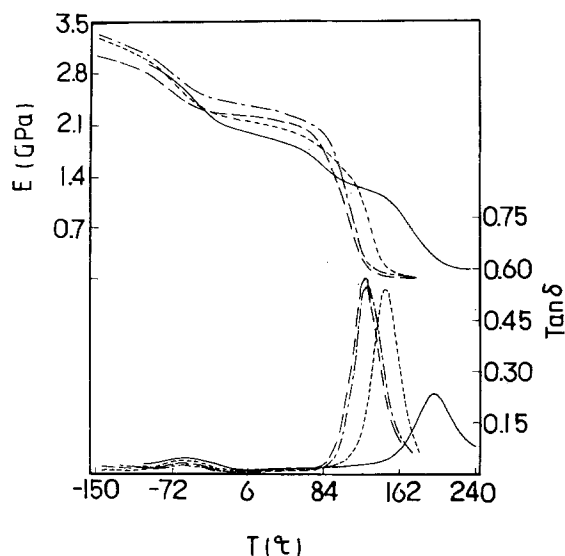


Figure 7 Dynamic mechanical temperature spectrum of pure epoxy resin and epoxy copolymers in the temperature range of -150 to 240 °C at the frequency of 10 Hz and heating rate of 2 °C min^{-1} (—) N_{00} ; (-----) N_{10} ; (- - - -) N_{21} ; (- - - -) N_{25} .

two relaxation peaks in this temperature range for the pure epoxy resin N_{00} : the α -peak of 198 °C (glass transition T_g) and β -peak of -56 °C (T_β). Adding the NSOC into the copolymer would not introduce any new relaxation peak, only lead to some shift of corresponding peak temperatures. The tendency of shift of both T_g and T_β was the same: they shifted to the lower temperature (also see Table I). The glass transition temperatures of the samples obtained from the dynamic mechanical temperature spectrum are also shown in Fig. 3. They had the same regularity as that obtained from the DSC measurement.

We also measured the dynamic mechanical properties of pure epoxy resin and their copolymers with

NSOC in the frequency range of 0.01 to 100 Hz at three temperatures of 30 , 50 and 80 °C. The experimental results showed that neither pure epoxy resin nor their copolymers with NSOC had any relaxation peak in the frequency range of four orders. This suggested that the mechanical properties of the epoxy copolymers were stable when they were used in conditions of lower or middle frequency.

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