JOURNAL OF MATERIALS SCIENCE **24** (1989) 1528–1532

An epoxy resin copolymer with zero shrinkage

Part 1 *Volume change on cure*

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Epoxy resin copolymer with zero shrinkage can be obtained by copolymerizing epoxy resin E51 with the expanding monomer of 3,9-di(5-norbornene-2,2)-1,5,7,11-tetraoxaspiro[5,5]-undecane (NSOC). The volume changes of an epoxy resin copolymerized with various amounts of NSOC during cure was measured with a dilatometer. The epoxy copolymer giving zero shrinkage was an epoxy resin with a E51: NSOC ratio equivalent to 5.88:1. This epoxy resin copolymer with zero shrinkage has been used as an adhesive to join the optical parts of a large optical telescope.

1. Introduction

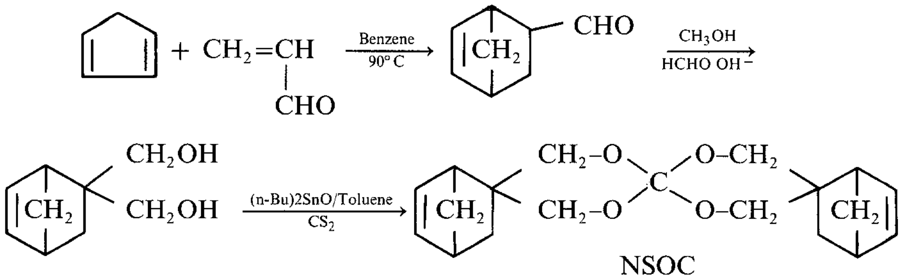
The resins that cure with zero shrinkage or with a volume expansion but no voids are highly desirable for various practical applications, such as high performance adhesives, coatings, precision castings, dental filling resins and binders for solid propellants etc. [1–6]. However the shrinkage from almost all commercial resins is due to the fact that the molecules of monomer located at a van der Waals' distance from one another move to within a covalent distance during the curing process. Presently available non-solvent polymer resins can achieve, with utmost care, volume shrinkage in the range of 2–6%. The problem is not solved completely by the various methods available to improve and compensate for the shrinkage. Bailey and Sun reported in 1972 a series of bicyclic compounds which expanded on ring-opening polymerization [2]. Polymers with different characteristics of volume change during the curing process could be obtained by copolymerizing epoxy resin with an expanding bicyclic compound in various proportions.

We have synthesized a type of bicyclic expanding monomer of norbornene spiro orthocarbonate (NSOC), and copolymerized epoxy resin E51 with various amounts of NSOC [7]. The volume change on cure, thermal and mechanical properties and morphology of the resulting epoxy copolymer have been measured. The application of these materials, particularly as adhesives, was tested. In this part the volume change of the epoxy copolymer on polymerization (cure), measured with a dilatometer, is reported. It was found that the epoxy copolymer underwent no volume change when the epoxy resin E51 : NSOC ratio was 5.88 : 1 in equivalent, but it was found to contract or expand below or above this proportion. The volume expansion rate of pure NSOC was also estimated. The epoxy resin copolymer with zero shrinkage has been used as an adhesive to join the optical parts of a large optical telescope.

2. Experimental details

2.1. Materials

The bicyclic expanding 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 according to the following scheme:



All the reagents used were chemically pure. NSOC is a white crystalline solid of m.p. 233° C and mol wt 316 with needle-shaped crystal. It was ground into a powder of below 200 mesh before use.

The epoxy resin used was bis-phenol A E51 made in

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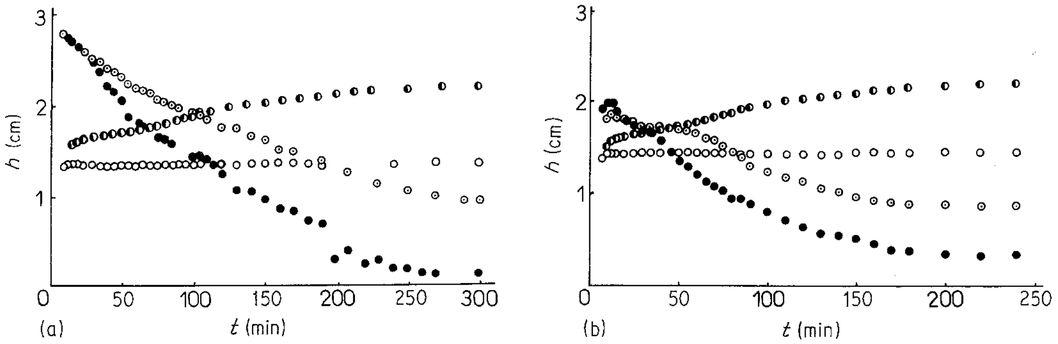

Figure 1 Change of height (h) of the silicone oil in capillary of dilatometer on curing time (t) of epoxy resins with and without NSOC monomer in an isothermal curing process at (a) 120° C and (b) 130° C. (●) N_{00}, (⊙) N_{10}, (○) N_{21}, (◐) N_{25}.

Wuxi Resin Factory (China) with the epoxy equivalent 196. The hardener was boron trifluorideamine imported from the USA.

2.2. Composition

The composition of epoxy resin E51 and boron trifluorideamine and the related volume data of the resulting epoxy copolymers are listed in Table I.

2.3. Dilatometry

The volume change of the mixture of epoxy resin E51 and boron trifluorideamine cured with various amounts of NSOC was measured by a dilatometer. The dilatometer bulb was put in silicone oil medium and kept at constant temperature. The internal diameter of the capillary of the dilatometer was 2.822 mm and the whole capillary was put into a glass thermostat containing water at 50° C in order to reduce the effect of a varying room temperature. The height of silicone oil in the capillary was read using a cathetometer.

The dilatometer liquid was affected directly by the volume change of the resin mixture during the curing; the methyl phenyl silicone oil was used as the liquid because of its stable expansion behaviour. The resin sample was prepared in a special emulsoid rubber tube which was very thin and transparent so that the resin mixture could be observed for the presence of air bubbles which would affect the volume change.

2.4. Experimental procedure

The resin was mixed with hardener according to the composition shown in Table I, and the emulsoid rubber tube was filled under vacuum. The emulsoid rubber tube was then closed with a fine metal wire, and it was put into the dilatometer and cured isothermally. The change of height of silicone oil in the capillary was read using the cathetometer, so indicating the volume change of the resin mixture during the curing process. Measurements were stopped after 0.5 h after the height of the capillary liquid was constant.

The volume of the dilatometer was calibrated with distilled water at 25° C. The thermal expansion coefficient of methyl phenyl silicone oil, the emulsoid rubber tube and the metal wire were measured initially and deducted in the subsequent calculations.

3. Results and discussion

3.1. Volume change on cure

Fig. 1 shows the dependence of height of the silicone oil in the capillary on the curing time of resin samples N_{00}, N_{10}, N_{21} and N_{25}. Because the height change of the dilatometer liquid is proportional to the volume change of resin during cure, it can be seen from Fig. 1 that the volume contracted throughout the curing process for both N_{00} (pure epoxy resin) and N_{10} (epoxy resin with 10% NSOC by weight) at both 120 and 130° C, respectively. The magnitude of shrinkage of N_{10} was less than that of N_{00} because it contained 10% bicyclic compound NSOC. For resin sample N_{25} containing 25% NSOC, the volume did not contract, but had some expansion during the cure. It is suggested that the norbornene spiro orthocarbonate could give rise to volume expansion during the curing process.

The reason for the volume expansion of NSOC is obvious. In the present case, the original intramolecular C–O covalent bond (the length of this bond is

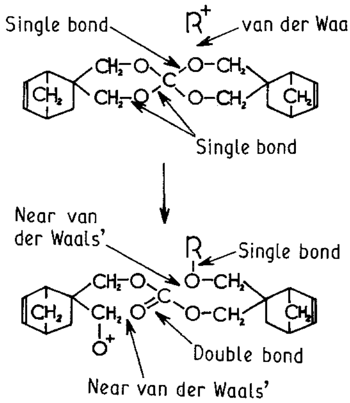

Figure 2 Change of bond distances in NSOC on ring-opening polymerization.

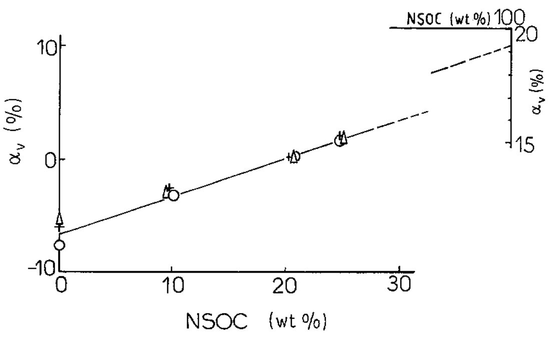

Figure 3 Dependence of the ratio of volume change (α_v) upon the content of NSOC in the epoxy copolymers. (○) 120° C, (△) 130° C, (+) calculated from the density.

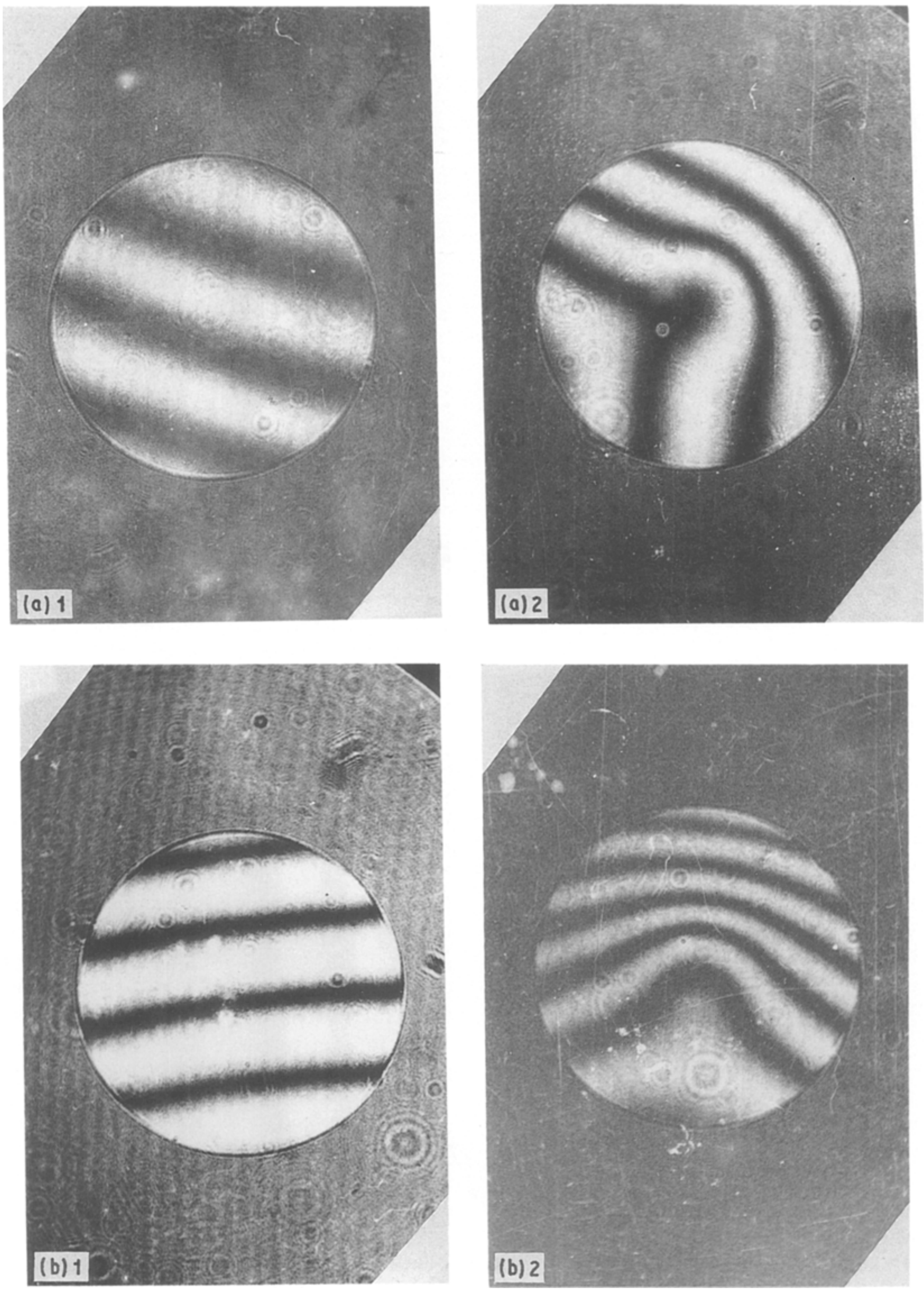

Figure 4 Change in the distortion of the light circle of the optical surface of the microcrystalline glasses joined with epoxy copolymers (a) N_{00}, (b) N_{10}, (c) N_{21} and (d) N_{25} before (1) and after (2) curing. λ = 632.8 nm.

TABLE I Composition of copolymer epoxy resins and their ratio of volume change

Sample No.	Composition (wt %)			E51 : NSOC in equivalents	Volume change (%)*		
	Epoxy E51	$BF_3CH_3CH_2NH_3$	NSOC		At 120° C	At 130° C	Calculated from density
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

*Volume change: (+) expansion, (−) contraction.

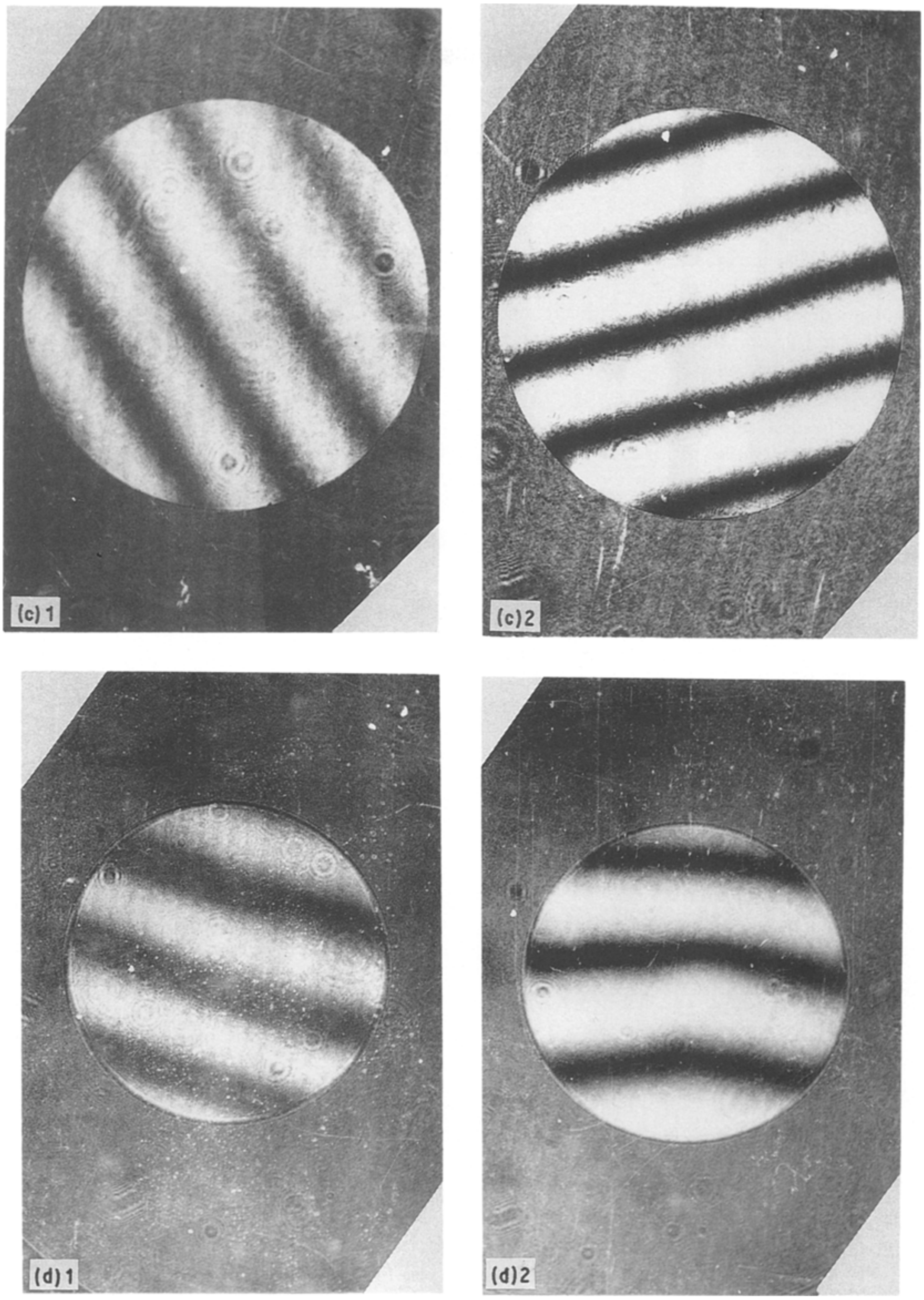

Figure 4 Continued

0.154 nm) in monomer NSOC is broken into a van der Waals' distance (of about 0.3–0.5 nm), which would lead to some volume expansion. On other hand, the intermolecular van der Waals' distance in the hardener or propagating macro-ion and NSOC monomer might approach the intra-molecular covalent distance, which would lead to some contraction. These two effects counterbalance each other. Also, one bond in NSOC changes from a C–O to a C=O bond after polymerization and the distance between the atoms decreases by 0.02–0.03 nm. These two effects counterbalance each other as shown in Fig. 2. It could be seen from Fig. 2 that two covalent bonds changed to one double bond and one van der Waals' distance as a result of one monomer taking part in the reaction. However the length of a single bond is only longer than the double bond by 0.02–0.03 nm, so that there is expansion rather than contraction during polymerization. Finally, the crystalline NSOC monomer polymerized into an amorphous polymer, which would also lead to a volume expansion. The combined result of these three factors produce the observed volume expansion of NSOC during polymerization.

The most meaningful result from Fig. 1 is that the plot of volume change against curing time for the resin sample N_{21} with 20.8% NSOC (by weight) is a line almost parallel to the time axis. This means the resin sample comprising E51 : NSOC at a ratio of 5.88 : 1 in equivalent has almost no volume change during the isothermal cure at both 120 and 130° C. The contraction of the epoxy resin and the expansion of NSOC just counterbalance each other in this resin, giving the observed zero shrinkage.

It can also be seen from Fig. 1 that the expansion–time curves are quite smooth for both pure epoxy resin and its copolymer with various amounts of NSOC, indicating that the volume change of the samples was homogeneous during polymerization. Although the monomer NSOC is a crystal of melting point 233° C, grinding ensures homogeneity for different compositions in the resin mixtures. No inhomogeneity in the final epoxy copolymer could be observed in the scanning electron micrograph.

The dependence of the volume change of the epoxy copolymer calculated from the data in Fig. 1 upon the various amounts of NSOC is shown in Fig. 3. (also see Table I). Therefore by varying the NSOC content of the copolymers, various degrees of contraction or expansion can be obtained, depending on the application requirements. From the degree of volume change at a given composition from Fig. 3 it is also possible to control the volume change of the resin.

3.2. Volume expansion rate of NSOC

The volume expansion of pure monomer NSOC is a useful property, but it is difficult to measure experimentally during the curing process because it is a crystal of melting point 233° C. However it can be estimated from the data on the copolymers.

Fig. 3 shows the dependence of the volume change of the copolymer resin upon the amount of monomer NSOC content, so that the volume expansion of pure monomer NSOC can be estimated from extrapolation to 100%. This gives a value of 19.2% (Fig. 3).

Bailey *et al.* [1] reported that the volume expansion of the crystalline monomer 1,5,7,11-tetraoxaspiro-(5,5)undecane during polymerization at 140° C was 17%. The volume expansion of 3,9-di(5-norbornene-2,2)-1,5,7,11-tetraoxaspiro(5,5)undecane should be larger due to the introduction of two big norbornene rings. It is therefore suggested that the value obtained here for the monomer NSOC is a reasonable value.

3.3. Optical observation of the volume change of the epoxy resin adhesive

Adhesion of optical glasses should not result in optical distortion due to internal stresses arising from the volume change of adhesive during the curing process. The ideal adhesive would not have any volume change during the cure. Adhesion of the optical parts in telescopes is one of the practical applications needing adhesives with zero shrinkage. In order to observe directly whether optical glasses joined by the adhesive with zero shrinkage have any change of optical properties, an attempt was made to adhere microcrystalline glass to indium – still using the epoxy resin copolymer. The optical distortion was measured in the microcrystalline glass by means of a laser plane interference method. Fig. 4 shows the changes of distortion of an illuminated circle of optical surface of the microcrystalline glasses joined by resins N_{00}, N_{10}, N_{21} and N_{25} before and after cure. Both the resins N_{00}, N_{10} with a contraction in volume, and N_{25} with an expansion in volume, produced changes in the interference lines in the optical surface of the microcrystalline glasses after the cure (Fig. 4a, b and d). It is therefore obvious that these resins are not suitable for use as an adhesive for optical purposes. There is no distortion of the optical surfaces of the microcrystalline glasses after cure for the resin N_{21} with zero shrinkage (Fig. 4c). It should therefore be an ideal adhesive in optical applications. The adhesive based on the epoxy copolymer N_{21} has already been used to adhere the secondary lens in a large optical reflecting telescope.

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Received 13 January
and accepted 9 September 1988