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Characterization of the curing behaviour of cyanic ester by a positron-annihilation lifetime technique

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Abstract

The curing process of a dicyanate resin system was investigated by a positron-annihilation lifetime technique (PA). Based on the observation of PA, it was shown that the size of free volumes of cured resins became larger as the curing reaction proceeded. This result was supported by a change in the physical properties related to the size of free volumes, such as a decrease in the specific gravity, a decrease in the dielectric constant and an increase in the water pick-up rate with increasing the decree of the cure. It was therefore found that the curing reaction of dicyanate resin proceeded through a reaction of cyanate groups to form a larger size of free volumes.

Keywords: Cyanate ester; Free volume; Positron-annihilation lifetime technique

1. Introduction

Cyanic ester compounds had previously been considered to be unobtainable. In 1960, however, it was found that cyanic ester could be prepared from sterically hindered phenol by reacting it with cyanogen chloride [1]. Since then many efforts were devoted to revealing the reactivity and properties [2,3]. After dicyanate resins were proved to be useful as starting materials for functional polymers, they have been used as matrix materials for printed-circuit boards in electronic applications because of the properties of a high glass transition temperature (T_g) and low dielectric constants [4–6].

The reaction of cyanides is known to proceed through the reaction of cyanate groups (-OCN) to form a triazine ring, as shown in Scheme 1 [7], and dicyanate resins react with epoxy resins through complicated pathways to form various products [8–12]. Although the reactivity of dicyanate resins was elucidated to some extent, as described before, the cross-linking structure of dicyanate resins, especially the three-dimensional structure, has not yet been clearly clarified. Such properties must be more understood concerning their applications.

A positron-annihilation technique (PA) was proved to be capable of a highly sensitive non-destructive identification and measurement of defects in semiconductor materials [13,14]. PA has also recently been applied to a study of the free volume in polymeric materials [15–18]. The lifetime spectra in polymers have a long-lived component, which is ascribed to ortho-positronium (o-Ps) formed and annihilated in holes created among polymer chains. o-Ps annihilates by a pick-off process in the holes and the lifetime of o-Ps is well known to be a good measure of the size of the holes, in other words ‘free volume’, where it is trapped. Thus, PA was recognized to be a useful technique for investigating the free volumes at the nanometer level. A more detailed characterization of polymeric materials is obtained by combining the results of PA with information obtained by other conventional methods.

In this study, PA was applied to the dicyanate resin system in order to investigate the curing processes and to elucidate the relationships between the free volumes and the physical properties, such as the specific gravity, dielectric constant and water pick-up rate.

2. Experimental

2.1. Materials and sample preparation

The dicyanate resin used was 2,2-bis(4-cyanatephenyl) propane synthesized from 2,2-bis(4-hydroxyphenyl) propane and cyanogen chloride. The cyanate was melted

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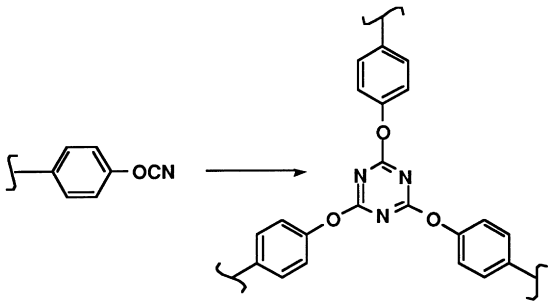

Scheme 1.

and mixed with zinc napthenate as a catalyst (0.2 phr, Kisida chemical Co. Ltd) at 100°C. The resulting mixture was poured into glass plates (15 × 15 × 0.3 cm) and cured at 170°C/2 h. Four samples having different degrees of curing were obtained by carrying out a post cure at different temperatures of 200°C–250°C. The degrees of the cure were estimated by measuring the consumption of the -OCN group, calculated from the i.r. spectra. The cure conditions and the -OCN consumption of four samples are listed in Table 1.

2.2. Apparatus and techniques

The PA experiments were conducted using a conventional fast–fast coincidence system having a time resolution of 270 ps full width at half maximum (FWHM). The details were described elsewhere [15]. The specific gravity of the cured resins was measured by using a specific-gravity meter (Shimadzu Co. Ltd., SGM21OU) at room temperature. The dielectric constants were measured by using an impedance/material analyzer (Hewlett-Packard Co. Ltd., HP4291A). The water pick-up properties for the cured resins were measured as follows: dried and weighed samples of the cured resins were immersed in boiling water. After immersion, the amounts of the absorbed water in the samples were measured by weight.

3. Results and discussion

3.1. Lifetime spectra of cured resins

The lifetime spectra were measured for A–D cured resins having different degrees of -OCN consumption using PA.

Table 1
List of cured resins

Sample	Cure condition	The degree of -OCN consumption (%)
A	170°C/2 h	82
B	170°C/2 h + 200°C/2 h	88
C	170°C/2 h + 230°C/2 h	91
D	170°C/2 h + 250°C/2 h	94

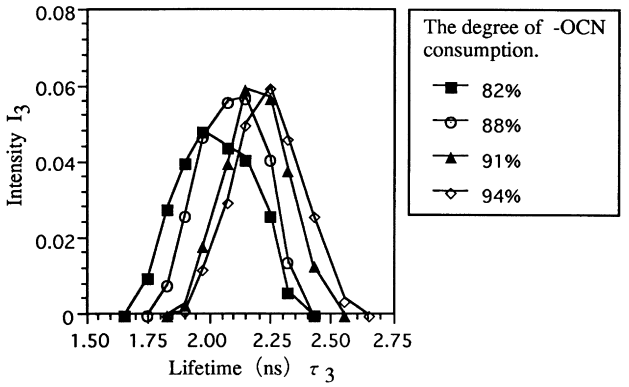

Fig. 1. Distribution of $\tau 3$ in dicyanate resin systems.

The distribution of the long lifetimes (τ_3) of o-Ps is shown in Fig. 1, which indicates that the distribution shifted to a longer lifetime as the curing reaction proceeded. The average diameters of the holes are shown in Fig. 2. They were estimated from the lifetime values by assuming the holes as an infinite spherical potential [19]. These results indicate that the larger sizes of the holes are created in the cured resins with higher -OCN consumption, i.e. the curing process of cyanates proceeds through the reaction of -OCN to form cross-linking structure, resulting in a larger size of the free volumes.

Fig. 1 shows that the full width at half maximum (FWHM) at the curing of 82% and 94% are 0.45 ns (~0.066 nm) and 0.34 ns (~0.029 nm), respectively. These results suggest that cyanates with a lower degree of curing have a wide distribution of hole diameters, and that the hole sizes tend to become equal with an increase in the degree of curing.

3.2. Specific gravity

The specific gravity with the degree of -OCN consumptions observed at room temperature is shown in Fig. 3. Generally, the reaction of thermosetting resins proceeds with cross-linking and curing shrinkage, i.e. the specific gravity

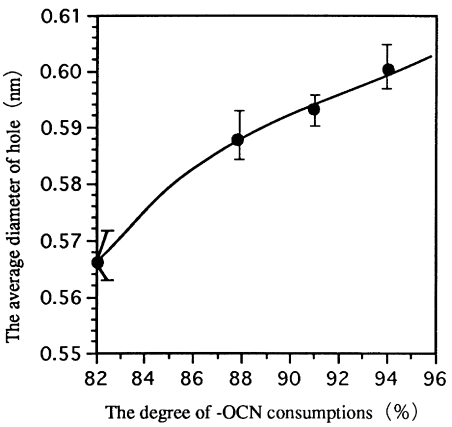

Fig. 2. Relationship between the average diameter of holes and the degree of -OCN consumption.

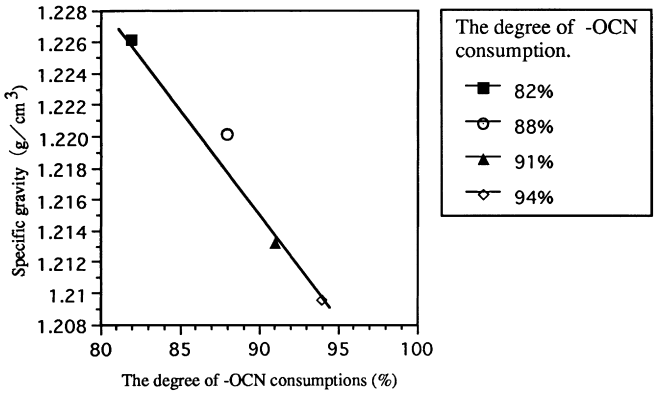

Fig. 3. Changes in the specific gravity of cured resins during a curing reaction in catalytic systems.

increases. However, the specific gravity of cyanates in the catalytic system gradually decreased along with the proceeding of the curing reaction. The variation in the specific gravity during the curing process of cyanate was already reported in a 'non-catalytic system' [5], in which the same tendency as in Fig. 3 was observed. It may thus be concluded that the reactivity and the cross-linking structure of cyanide are not affected by catalysts in the curing process.

The 'anomaly' of a decreasing specific gravity with an increase in the degree of the cure has already been found in other thermosetting resin systems, such as epoxy resins [20–22], and it was mentioned that the size of the free volumes greatly varied according to the degree of the cure. Our study has shown that the same phenomena occurs in cyanate resins.

If the curing systems comprise the same molecular composition, the specific gravity of the cured resin is assumed to be related to the degree of atom packing. Then, in the case of cyanates, the decrease in the specific gravity is considered to be a decrease in the degree of atom packing, i.e., an increase in the specific volumes. The results of PA indicate an increase in the free volumes with curing: the expansion of holes among polymer chains or a decrease in the average number of atoms. Therefore, the result of the specific gravity can be explained without any contradiction to such an assumption as a low packing density of atoms caused by cross-linking and an enlargement of the free volumes.

3.3. Dielectric constant

It was reported that the dielectric constants of cured thermosetting resins and thermoplastics were closely related to the average diameter of holes measured by PA [23] and the cured resins having low dielectric constants tended to have large holes. These results were supported by the fact that the effect of the electronic polarization was decreased by lowering the interaction among the main chains along with increasing the free volumes.

The dielectric constants of cured resins of cyanate having different degrees of cure are shown in Fig. 4: the dielectric constant decreases with curing. In cyanate curing systems, this result might be supported for the following two reasons: (1) a decrease in the effect of the electronic polarization among the main chains, as described before; (2) a decrease in the amount of the electronic polarization of -OCN after forming a triazine ring. It is not clear from the present study which is dominant.

3.4. Water-absorption behaviour

The behaviour of the water pick-up rates of the cured resins are shown in Fig. 5. The cured resins, having higher degrees of -OCN consumption, showed higher rates of water pick-up. In dicyanate resin systems, high-polarized -OCN functional groups changed to low-polarized cyanurate structures during the curing reaction. From the viewpoint of polarity, resins with a higher degree of cure may be thought to have lower rates of water pick-up. However, as shown in Fig. 5, the experimental results were contrary to the expected relation from the polarity. It is concluded therefore that the behaviour of the water pick-up rate in this system is governed by the size of free volumes, rather than the polarity of the cross-linking structure at the early stage of the water-absorption process.

It was reported that the water pick-up rate of epoxy resins cured with phenol novolac were closely related to the size of the free volumes at an early stage of the water-absorption

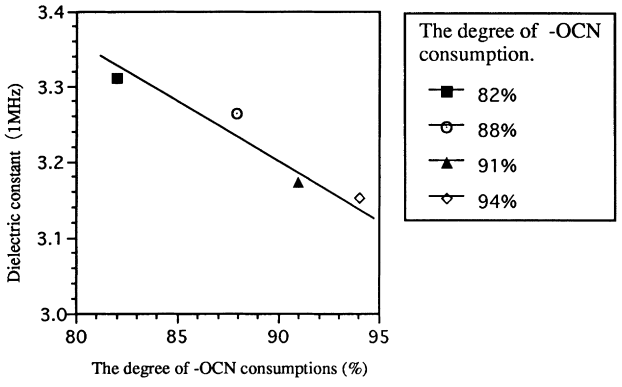

Fig. 4. Dielectric constants of cured resins having different degree of -OCN consumptions.

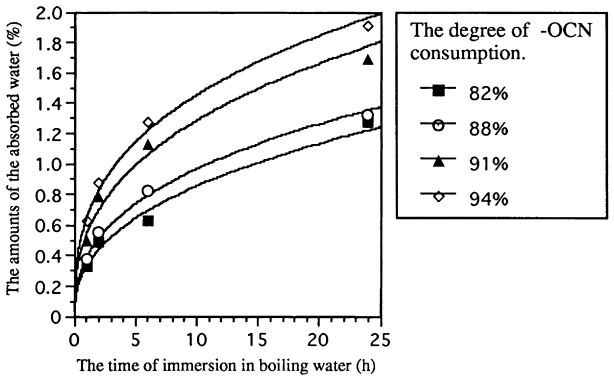

Fig. 5. Behaviour of the water pick-up rate of cured resins.

process [24], and resins with a large size of free volumes had a large water pick-up rate. Fig. 5 indicates that the water pick-up rate of cyanates behaves similarly to the epoxy resins cured with phenol novolac.

3.5. Antiplasticization

In the curing system of cyanates, an unreacted structure with -OCN groups could play the role of antiplasticizers, which occupy free volume in the network [22,25–27]. Proceeding the curing reaction and forming a cross-linking structure, the antiplasticizer is consumed to form the cyanurate structure. Then, the unreacted structures, which occupy the space of the free volumes, undergo restructuring of the polymer network, so as to establish equilibrium at the curing temperature, resulting in an increase in the free volumes. Thus, with increasing the degree of curing, the inner size of the free volume expands. Hence, with increasing the degree of curing, the properties related to the size of the free volumes could be varied, as shown in the last sections.

4. Conclusion

From an investigation of the curing process of cyanate, it has come to be understood that the size of the free volumes of the dicyanate resin increased as a cross-linking structure was constructed through the reaction of -OCN groups to form triazine rings. Hence, the properties of the cyanate resin, especially related to the size of the free volumes, could be varied with the degree of the cure.

In this work, the relation between the size of the free volumes and the properties of cured resins was studied. The curing process of the dicyanate resin system was investigated by a positron-annihilation lifetime technique (PA). Based on the observations of PA, it was proved that the size of the free volumes of cured resins became larger as the curing reaction proceeded. It was clearly shown that an increase in the size of the free volumes is strongly correlated with a change in the physical properties related to the size of the free volumes, such as the decreasing of specific gravity, the lowering of the dielectric constant and the increasing of water pick up rates with an increase in the degree of cure.

It was also found that PA could be a useful tool for evaluating the free volumes.

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