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► To cite this version:

T. Okada, S. Nishijima, Y. Honda, Y. Kobayashi. Physical properties of epoxy and free volume evaluated by positron annihilation spectroscopy. *Journal de Physique IV Proceedings*, 1993, 03 (C4), pp.C4-291-C4-294. 10.1051/jp4:1993447 . jpa-00251490

HAL Id: jpa-00251490

<https://hal.science/jpa-00251490>

Submitted on 4 Feb 2008

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Physical properties of epoxy and free volume evaluated by positron annihilation spectroscopy

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Abstract; The macroscopic physical properties of commercially available bisphenol -A epoxy resins cured by acid anhydride in which amount of the plasticizer, polypropyleneglycol was changed systematically have been measured and were compared with the amount of free volume evaluated by the positron annihilation technique. The lifetime and the intensity of ortho-positronium were used to evaluate the amount of the free volume in the epoxy resins. It was found that up to the certain amount of plasticizer, the amount of the free volume did not increase so much and then showed the marked increase. The close correlations were found between the amount of the free volume and the macroscopic physical properties such as hardness and specific volume.

1. Introduction

Positron annihilation spectroscopy (PAS) is thought to be promising method to evaluate the free volume or microvacancies^{1,2} which control the physical characteristics of organic materials. The life time, τ_3 and the intensity, I_3 of the long-lived component in polymers are considered to be the contribution from the ortho-positronium (o-Ps) which has close relationship between size and concentration of free volume.³⁻⁵ PAS could be, therefore, can be applied to the molecular design giving the desirable properties to the glassy polymers. The correlation between the free volume evaluated in terms of PAS method and the macroscopic physical properties should be understood in practical application of PAS to the molecular design of glassy polymers. In this work the epoxy resins were chosen and the evaluated free volume by means of PAS were compared with the physical properties.

2. Experimental

The commercially available epoxy resin bisphenol-A of which molecular weight was approximately 397 was chosen. The acid anhydride as a hardener, tertiary amine as an accelerator and polypropyleneglycol (molecular weight 373) as a plasticizer were used. The amount of plasticizer was changed systematically and was presented in Table 1. The curing condition was 353K for 4 hours and 423K for 5 hours.

The Vickers hardness, Young's modulus and flexural strength were measured as mechanical properties. The Young's modulus and flexural strength were calculated from the results of 3 point bending tests. The bending speed was set at 2mm/min. Vickers hardness was measured at 50gf load. The density was measured in terms of hydrometer. The glass transition temperature and the thermal expansion coefficients were measured by thermal mechanical analysis system at the temperature increasing rate of 5K/min. The positron lifetime measurement was performed by means of fast-fast coincidence system. The resolution time of the system was 400 psec (FWHM). All the measurements were performed at room temperature (approximately 293K).

Table 1 Formulation of blends and their glass transition temperature

Sample No.	1	2	3	4	5
Blend ratio in weight					
Epoxy	100	100	100	100	100
Hardener	100	100	100	100	100
Accelerator	1	1	1	1	1
Plasticizer	0	15	30	45	60
Plasticizer (wt%)	0	7	13	18	23
Glass transition temperature(K)	365.3	341.1	317.7	303.2	291.7

3. Results

In Table 1 the glass transition temperatures of each materials were also shown. The glass transition temperature decreased with increasing the amount of the plasticizer. In Fig.1 the changes of Vickers hardness and Young's modulus were shown. As the amount of plasticizer increased, Vickers hardness and Young's modulus decreased. Especially at more than 13% of plasticizer, the decrement of each properties came to be marked. The flexural strength and density decreased in the same manner.

In Fig.2 the changes of life time of σ -Ps, τ_3 and intensity I_3 with amount of plasticizer were

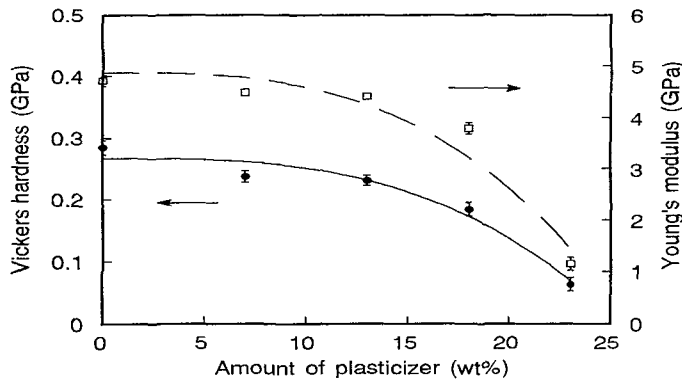


Fig. 1 Amount of plasticizer dependence of Vickers hardness and density.

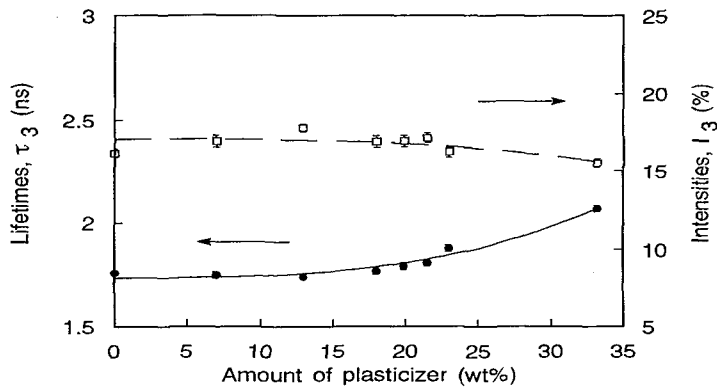


Fig. 2 Amount of plasticizer dependence of τ_3 and I_3 .

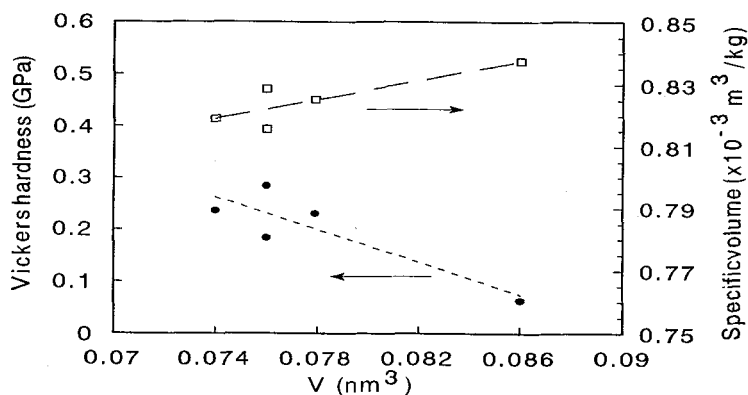


Fig. 3 V dependence of Vickers hardness and specific volume.

presented. The τ_3 increased with the amount of plasticizer. It was reported that as the amount of the acid anhydride of which electron affinity was strong increased, the formation of o-Ps was suppressed due to the chemical quenching results in decrease of I_3 .⁶ In this experiment as the amount of the acid anhydride hardener decreased, that is the amount of plasticizer increased, I_3 decreased and hence the change was not brought by the acid anhydride.

4. Discussion

The long lived life time τ_3 is thought to be related to the size of the free volume.^{7,8} The volume V corresponds to τ_3 was calculated where the free volume was supposed to be sphere. The calculated V and the product V and I_3 were thought to be the representatives of free volume. In Fig.3 the correlation between V and hardness or specific volume were presented and in Fig.4 $V \times I_3$ and hardness or specific volume. It was seen that the strong correlation between the macroscopic properties and V or $V \times I_3$. Both properties are

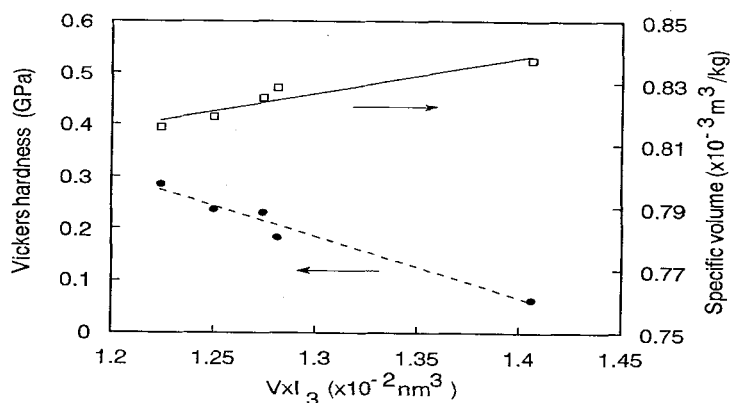


Fig. 4 $V \times I_3$ dependence of Vickers hardness and specific volume.

thought to have closed correlation to the free volume. Hardness should depend on the amount of free volume, because the increase of free volume brings the increase of possible volume for plastic deformation results in the decrease of hardness. The specific volume can be thought to be the sum of free volume and occupied volume by molecules and hence the specific volume decreases with increasing free volume. Within this experiment, the strong correlation was found between them. It means that the free volume control the macroscopic physical properties of glassy polymer. In glassy polymer the amount of free volume is thought to be constant of 2.5%. Though the epoxies in this work were thought to be in the glassy state as shown in Table 1, the total amount of free volume evaluated by PAS method were varied. This is because that the off set of the glass transition might be below 293K or the free volume could change even in glassy state .

The macroscopic physical properties are decreased markedly by the plasticizer higher than 13%. This phenomenon is due to the introduction of free volume by the plasticizer judging from present data. When the plasticizer added excessively, the new phase appears which is mostly plasticizer. The phase contributes to the increase of free volume because of the mobility of the plasticizer should be larger than that of networked epoxy.

5. Conclusion

The macroscopic characteristics of epoxy resins were compared with the V and VxI_3 which are thought to be the representatives of the free volume evaluated by the PAS method changing the amount of plasticizer in the epoxy resins. It was found that the excessive plasticizer came to form the new phase and the plasticizer changed the physical properties of epoxy markedly such as decrease of hardness, Young's modulus, density and strength. The change can be explained by the increase of the free volume due to the plasticizer and the free volume could be evaluated by PAS method.

Acknowledgment

The authors are grateful to Dr. J. Ohkuma in Radiation Laboratory, ISIR Osaka Univ. for his help of handling the radioisotopes. This work is partly supported by the cooperative work "Advanced Materials Creation and Their Limit State Protection for Environmental Preservation" between Institute of Scientific and Industrial Research and Welding Research Institute in Osaka University.

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