Polymer Vol. 37 No. 14, pp. 3025–3030, 1996

0032-3861/96/$15.00+0.00

Free-volume characteristics and water absorption of novolac epoxy resins investigated by positron annihilation

Takenori Suzuki*, Yuichi Oki, Masaharu Numajiri, Taichi Miura and Kondo Kondo
National Laboratory for High Energy Physics, Radiation Control Center, Oho, Tsukuba, Ibaraki 305, Japan

and Yutaka Shiomi
Fine Chemicals Research Laboratory, Sumitomo Chemical Co. Ltd Kitahara, Tsukuba, Ibaraki 300-32, Japan

and Yasuo Ito
Research Center for Nuclear Science and Technology, The University of Tokyo, Tokai, Ibaraki 319-11, Japan
(Received 9 October 1995; revised 13 November 1995)

A positron-annihilation lifetime technique was applied to four kinds of epoxy resin (cresol novolac, tris-hydroxy-phenyl-methane (THPM), tetra-methyl-biphenol and bis-phenol A) in order to study the relation between the intermolecular-space holes and water absorption. The sizes of the holes were measured, based on the life-time (τ_3) of the *ortho*-positronium. Since THPM has a larger τ_3 value (hence, a larger intermolecular-space hole) and absorption rate than that of the other samples, a correlation between τ_3 and the absorption rate has been shown to be evident. Assuming a very simplified model, the shapes of the holes for the smallest unit cell were calculated using a computer code of molecular dynamics; the shape for THPM was found to be different from those of the other three samples. Copyright © 1996 Elsevier Science Ltd.

(Keywords: positron annihilation; epoxy resins; water absorption)

INTRODUCTION

In order to develop new polymers, it is necessary to test their characteristics. At present there are many standard tests, such as mechanical, electrical, chemical and thermomechanical analyses, which give macroscopic characteristics. For advanced polymers, since these methods are often not sufficient, it is desirable to establish a method to investigate the microscopic structure of the polymers. When measurements of the free volumes of polymers are required, there are few methods to probe directly using a simple apparatus. One is positron annihilation (PA).

During the last decade, PA has been applied to polymers, and has been recognized to be a useful technique for investigation of the free volumes or intermolecular-space holes in the order of nanometres[1–3]. In PA experiments, the radioisotope ^{22}Na is commonly used as a positron source, from which positrons with average energies of 210 keV are emitted. These energetic positrons loose their energy in substances, through inelastic collisions, and finally annihilate with electrons, while emitting 0.511 MeV gamma rays. In polymers, part of the positrons form a positronium (Ps), which is a hydrogen-like bound state consisting of a positron and an electron having two spin states (*ortho*-Ps (*o*-Ps) and *para*-Ps (*p*-Ps)) with lifetimes of 142 and 0.125 ns, respectively, *in vacuo*. *o*-Ps seeks intermolecular-space holes and can remain inside them until it picks up electrons (the so-called pick-off annihilation) from the walls of the holes. From the PA lifetime spectra, three components can be commonly deduced: two short-lifetime components (lifetime τ_1, intensity I_1) and (τ_2, I_2), are normally assigned to self-annihilation of *p*-Ps and free positron annihilation, respectively; a longest lifetime component (τ_3, I_3) is due to the annihilation of *o*-Ps. τ_3 is considered to be related to the size of intermolecular-space holes, and a clear semi-empirical relationship between τ_3 and the size of holes for Ps localized in spherical holes[4] has been used to estimate the volume created among polymer chains. I_3 is often treated as a measure of the number of holes[5]. In this work, τ_3 and I_3 have been employed for discussions.

Novolac epoxy resins have been used in many engineering fields, and even in daily life. One of the extensive uses of novolac epoxy resins can be found in

---

* To whom correspondence should be addressed

integrated circuits (ICs) as encapsulating materials to protect circuits from moisture, dust, shock, and other external obstructions as well as to secure electrical insulation, because they have a large mechanical strength and a high glass transition temperature (T_g). Although novolac epoxy resins have shown these characteristics, the characteristics vary with the combination of resins and their curing agents.

One of the important factors for encapsulation materials is the diffusion coefficient of moisture, which affects the reliability of long term operation. We have shown by PA that this is strongly related to the size and structures of the intermolecular-space holes[2]. Microscopic information concerning PAL was compared with the macroscopic characteristics, such as T_gs, thermal-expansion coefficient, mechanical strength and water-absorption rate, which were obtained by standard methods.

In this work, the intensities (I_3) and lifetimes (τ_3) of the long-lived component of Ps were obtained for samples showing different water absorption. Also, the lifetime distributions were calculated for dry and wet samples, which were kept in a heat bath and a pressure cooker for many months, and compared with the three-dimensional hole structures calculated with a code of molecular dynamics. A correlation between the lifetimes of the long-lived component (i.e. the size of intermolecular-space holes) and the water absorption is discussed from the point of view of the three-dimensional hole structures.

EXPERIMENTAL

The PA experiments were conducted with a conventional fast-fast coincidence system with a time resolution of 0.27 ns full width at half maximum (FWHM). The details concerning PA can be found elsewhere[2,6].

Four kinds of epoxy resins (cresol novolac (CR), tris-hydroxyphenylmethane (THPM), tetra-methylbiphenol (TMB) and bisphenol-A (BA)) were cured with phenol novolac, adding triphenylphosphine. The details concerning sample preparations have already been reported[2]. The molecular structures of the major resins are presented in *Figure 1*.

For measurements of water absorption, three kinds of groups of samples with different water absorption were prepared: (1) First group: for measuring the relations between the absorption and lifetimes and/or intensities of *o*-Ps, the samples were immersed in a water bath, kept at about 100°C under 1 atm. The weights were then measured after a suitable time: every several tens of minutes at the beginning and then every several hours. For these samples, PA measurements were conducted. The results of the weight increase for four kinds of samples are shown in *Figure 2*. The increase is defined by $(M_w - M_0)/M_0$, where M_0 is the original mass and M_w is the mass after water absorption. (2) Second group: for an analysis of the lifetime distribution, the samples were immersed for 5 months in a water bath, kept at nearly 100°C under 1 atm; absorption rates of 2.8, 2.9, 2.7 and

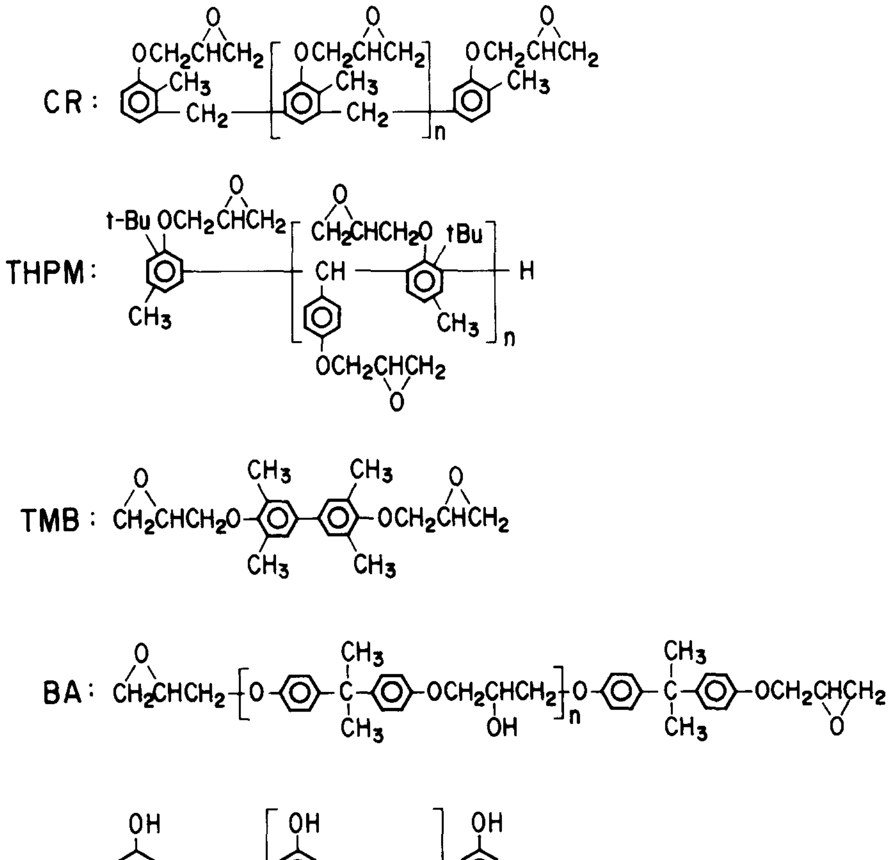

Figure 1 Chemical structures of epoxy resins: CR, cresol novolac; THPM, tris-hydroxyphenylmethane; TMB, tetra-methylbiphenol; BA, bisphenol-A; PH, phenol novolac

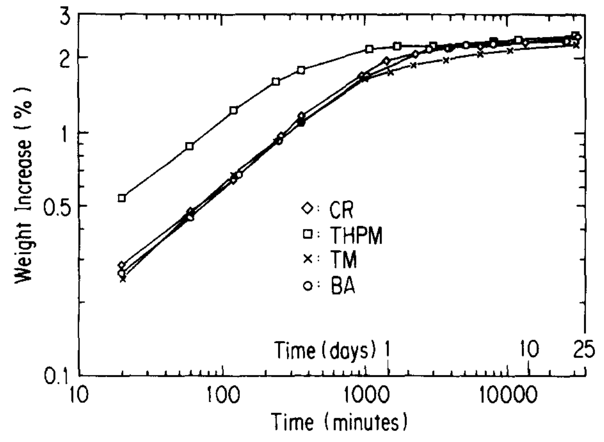

Figure 2 Water absorption *versus* time

2.2% for CR, THPM, TMB, and BA, respectively, were obtained. (3) Third group: in order to force moisture into samples for measuring the lifetime distribution, the different samples were treated in a pressure cooker at 150°C under ca. 3 atm to increase the water absorption; absorption rates of 4.0, 4.4, 3.2 and 2.6% for CR, THPM, TMB, and BA, respectively, were obtained.

PA data for the first group were collected for 1 h to obtain about two million events for analysing the PAL spectra. For the second and the third groups, PA data were collected for 6–7 h to obtain more than ten million events, which was necessary to calculate the lifetime distributions. The PAL spectra were analysed by POSITRONFIT[7], and lifetime distributions were obtained by CONTIN[8].

RESULTS AND DISCUSSION

Water absorption

The water absorption rate is defined by the weight increase *versus* time. The results of the weight increase due to the water absorption after 1 h are as follows (*Figure 2*): 0.47, 0.88, 0.46, and 0.45% for CR, THPM, TMB and BA, respectively. These results indicate that three samples (CR, TMB and BA) show almost similar absorption rates, while THPM absorbs water twice as fast as others.

Figure 2 suggests that the beginning water is absorbed at a rapid rate, and is then absorbed slowly, resulting in a very slow absorption rate after 1 day. It is useful to calculate the diffusion constant (D) for the case of *Figure 2*. The diffusion constants based on the weight increase are calculated from the diffusion equation $dC/dt = D \cdot d^2C/dX^2$, using the simple model with boundary conditions $C_{x=0} = C_{x=L} = C_0$, where L is the thickness of samples and C_0 is the water concentration at both surfaces of the samples[9]:

$$D = (L/\pi)^2 \cdot \{\ln(8/\pi^2) - \ln(1 - Q(t)/Q_0)\}/t$$

where Q_0 is the saturation value of the weight increase and $Q(t)$ is the weight increase at time t. Applying this equation to *Figure 2*, the time dependence of D is shown as *Figure 3*, which implies that, in the short period, D has large values and, after 300 min, D becomes almost constant. This may suggest that at the beginning water is absorbed quickly in the surface region and places where water can easily reach, and then slowly penetrates into difficult places for the access of water molecules.

The water absorption is affected by both the temperature and the pressure of the heat bath. The total water absorption of the first and second groups immersed in the heat bath at nearly 100°C under 1 atm reaches almost the same order after 10 days (*Figure 2*), and even after 5 months. The water absorbed in samples is considered to be attached to hydrophilic radicals. Hence, the result that the water absorption was almost similar at 100°C under 1 atm suggests that the four kinds of epoxy samples used in this experiment have almost the same number of hydrophilic radicals, such as hydroxyl groups, ether, and epoxy groups. However, samples kept in a pressure cooker achieved a larger water absorption for CR and THPM than for TM and BA. This difference may be due to the treatment temperature (150°C). Since T_gs for CR, THPM, TMB, and BA measured by a thermomechanical analysis (t.m.a.) were 192, 204, 139 and 140°C, respectively[2], T_gs for CR and THPM are higher than the treatment temperature, while T_gs for TMB and BA are lower than the treatment temperature.

Water absorption and positron-annihilation results of I_3 and τ_3

The relationship between the weight increase and I_3 (τ_3) is shown in *Figure 4* (*Figure 5*): I_3 and τ_3 were deduced from lifetime spectra using POSITRONFIT, in which three-component fitting was employed. τ_3 obtained in the analysis is considered to be a mean lifetime.

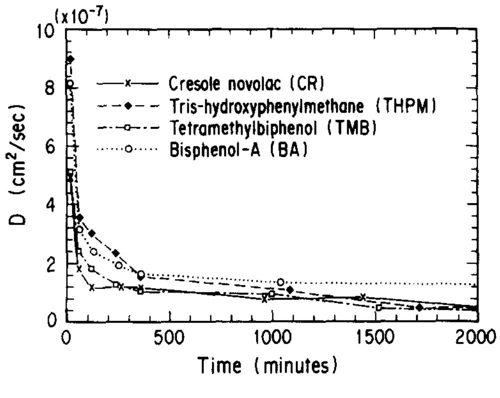

Figure 3 Diffusion constant calculated from *Figure 2 versus* time

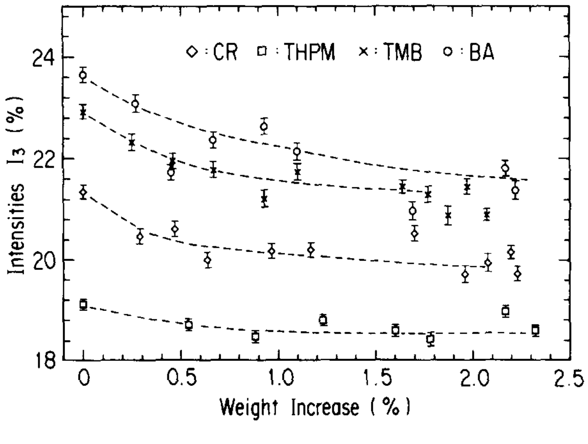

Figure 4 I_3 *versus* water absorption

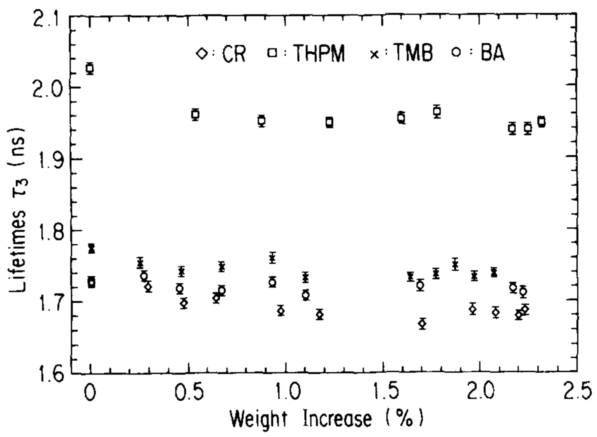

Figure 5 τ_3 *versus* water absorption

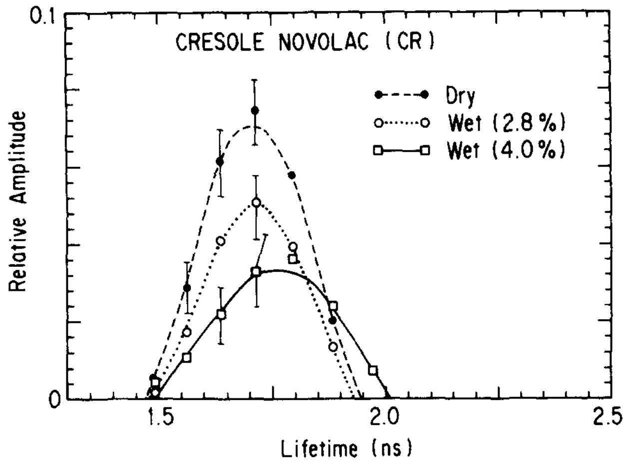

Figure 6 Distribution of τ_3 in CR for dry and wet samples. The wet sample of 2.8% (4.0%) was prepared after immersing it in a water bath (a pressure cooker) for about 4 months

The decrease in I_3 can be seen for all the samples, as shown in *Figure 4*. The decrementation rate of THPM is smaller than of the other three samples. I_3 in dry samples can be presented in the following order: THPM (19.1%) < CR (21.4%) < TMB (22.9%) < BA (23.7%)(*Figure 4*). This order can be explained as follows: THPM and CR have different polymer structures from TMB and BA and the former epoxy group has a higher density of epoxy groups than the latter group, resulting in a higher density of crosslinkings after curing; comparing THPM with CR, THPM is expected to have a higher density of epoxy groups (i.e. higher density of crosslinkings) than that of CR; similarly, TMB has a higher density than does BA; hence, the density of crosslinkings is expected to be in the following order, THPM > CR > TMB > BA. Thus, it can be pointed out that there is a clear relation between the order of I_3 and the crosslinking density: the larger is the density of crosslinkings, the smaller is the I_3 obtained.

Figure 5 shows that THPM has a larger τ_3 value (i.e. larger intermolecular-space holes) than do the other three samples. Hence, it seems that there is a correlation between τ_3 and the absorption rate.

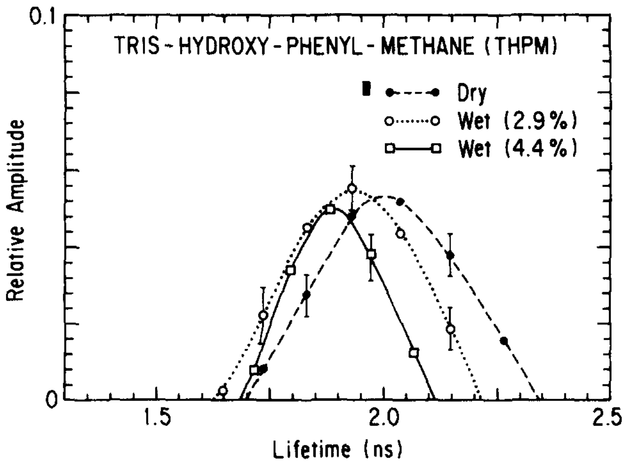

Figure 7 Distribution of τ_3 in THPM for dry and wet samples. The wet sample was prepared in the same way as CR in the caption of *Figure 6*

Lifetime distribution and water absorption

In an analysis of the lifetime spectra using POSITRONFIT, the number of lifetime components must be given as input data. On the other hand, using the computer code CONTIN, the lifetime spectra can be resolved into a smooth solution without knowing the number of lifetime components. The distribution of the lifetimes of the long-lived component is thought to be a hole size distribution, and offers additional useful information concerning intermolecular-space holes in polymers.

CONTIN was applied to the lifetime spectra for four kinds of novolac epoxy resins with and without water absorption. Normally, to obtain the proper lifetime resolution more than 10^7 counts are required; for a spectrum with many components and closely spaced peaks, more than (3–4) × 10^7 counts are required[10]. In our spectra, about 1.5 × 10^7 events were collected.

From an analysis using CONTIN, three distributions were obtained, which correspond to three lifetime components obtained by POSITRONFIT. *Figure 6* shows only the distribution of the long-lifetime component for one dry and two wet samples of CR; the area of the distribution is proportional to I_3 and the distribution shows the spread of τ_3, which is considered to be the distribution of the hole size created inside the samples. The dry sample was prepared in a vacuum oven kept at nearly 100°C for 4 months.

Figure 6 indicates that the shift of the peak position is very small for three samples with different water absorption and that the area of the peaks is reduced with increasing water absorption, i.e. the decrease in τ_3 is very small and I_3 changes with the absorption. Similar results of CONTIN were also obtained for TMB and BA.

CONTIN results for THPM (*Figure 7*) show that the peak positions of the lifetime distribution shifted by about 0.1 ns after water absorption, while the area of a dry sample and a sample with 2.9% water absorption are quite similar. This indicates that, although τ_3 decreases, the change in I_3 is very small, even after water absorption. This result is consistent with the POSITRONFIT results, as shown in *Figure 4*. For samples which experienced enforced water absorption, the area decreased while keeping the peak position.

Simplified model calculation of holes and τ_3

There are two distinct differences between THPM and the other three resins. (1) The result that τ_3 of THPM is larger than that of the other samples (*Figure 5*) indicates that there are large intermolecular-space holes in the polymer structure of THPM. (2) The shift in the lifetime distribution of wet samples towards shorter lifetimes for THPM suggests a decrease in the average hole sizes as a result of the water absorption (*Figure 7*). On the other hand the shifts for CR, TMB and BA were very small, i.e. no change in the average hole size was observed.

Since THPM and CR have similar chemical structure, these differences for THPM and CR are considered to be due to the molecular structure, itself: THPM has a large molecule tertiary butyl (tBu) as its component, and a short distance between aromatic rings, which are considered to hinder the motion of the molecular structures; CR has -CH_2- groups between aromatic rings, which allows rotation of the structures. It currently seems quite impossible to analyse the polymer structures of the three-dimensional networks of epoxy resins in a real system by any calculation methods; hence, the difference in the hole structures between THPM and CR is hard to calculate for a real system. However, assuming the simple unit to constitute one ring under the condition of no effect from the surrounding molecular structures, several computer codes of the molecular-dynamics method are available to calculate the ring structure with minimum energies. Even though the ring structure may be different from the real structures created in epoxy resins, the calculated structures for a simple unit may be helpful in discussions of how the molecular structures affect the hole structure.

In order to investigate the ring structures, a program (CSC-Chem3D)[11] was applied for THPM (*Figure 8*), CR (*Figure 9*) and TMB at 0 K. The results show that the hole is elliptical in shape for THPM and CR, and that THPM has a much longer shape than does CR; the short distance in the holes for the two samples is about 0.6 nm and the long distances for THPM and CR are about 1.8 and 1.0 nm, respectively. This calculation was also applied to TMB; the shape was shown to be much closer to a circle. Since TMB and BA have similar structures concerning epoxy groups, the hole structure of BA is expected to be the same as that of TMB.

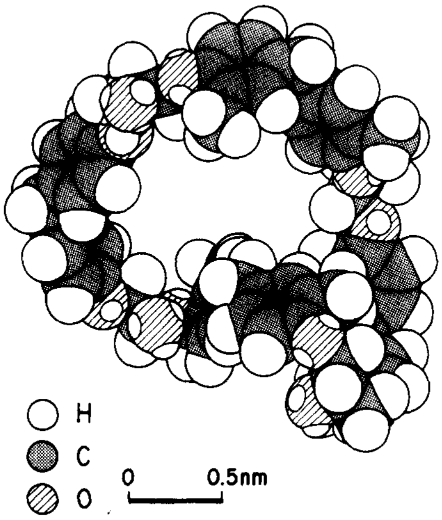

Figure 8 Three-dimensional hole structure for THPM obtained for a unit cell at 0 K

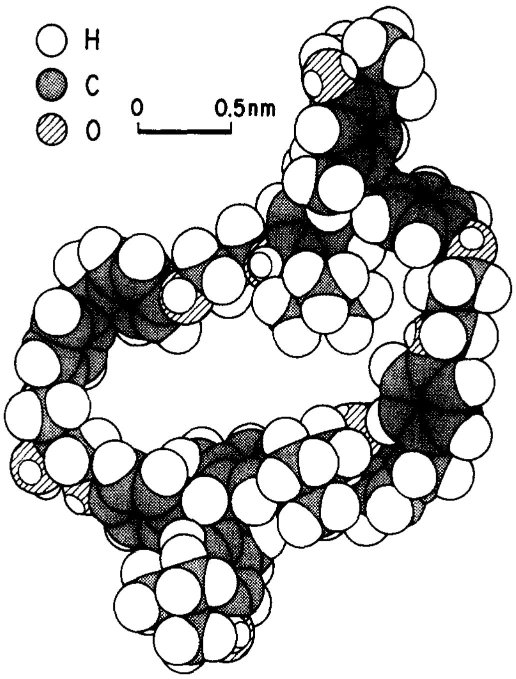

Figure 9 Three-dimensional hole structure for CR obtained for a unit cell at 0 K

τ_3 is related to the volume of the intermolecular-space holes in which Pss are trapped. Assuming that the holes are spheres, the relationship between τ_3 and the radius (R) is described as[4,12,13]

$$\tau_3 = 0.5 \times \{1 - R/R_0 + 1/(2\pi) \times \sin(2\pi \times R/R_0)\}^{-1}$$

where an electron layer has a thickness (ΔR) of 0.166 nm and the radius of the finite spherical potential (R_0) is $R + \Delta R$.

The lifetimes obtained from POSITRONFIT for dry samples of THPM and CR are 2.024 and 1.739 ns, which correspond to 0.58 and 0.52 nm in diameter, respectively. From *Figures 8* and *9*, the short distance in the holes for the two samples is about 0.6 nm and the long distances for THPM and CR are about 1.8 nm and 1.0 nm, respectively. There should be many types of holes created among polymer networks. If Ps is trapped in a hole like the unit structures, it is expected to annihilate within a short distance through pick-off annihilation. It has been shown that the mean hole size obtained by PA is roughly in accordance with the short distance of the calculated hole structure.

The main difference between THPM and CR is in the molecular structures; the other factors, like the chemical elements, are almost the same. Hence, if any difference is observed in PA, the molecular structures are considered to be the cause. The main differences observed in PA between THPM and CR are as follows. (1) A shift in the τ_3 distribution to a shorter lifetime (*Figure 7*) is observed only for THPM after absorbing water. (2) Although I_3 for THPM does not change much, even after absorbing water (*Figure 4*) under 1 atm, it decreases for CR by absorbing water. Hence, it is suggested that THPM has holes with a longer shape and, even after water absorption in one side of the hole, there is still enough space for PS in the other side of the hole.

In the case of THPM, the former result has suggested that the hole size became smaller after water absorption, and the latter that there was no clear reduction in the number of holes. In the case of CR (also TMB and BA), once water molecules were absorbed, the number of holes for Ps decreased, and no change in the hole size was observed. These results may indicate the following: once water molecules occupy the holes of CR (also TMB and BA) there is not enough space for Ps, resulting in a reduction of I_3; for THPM, even water molecules occupy the holes, although there is still enough space left for Ps (which is connected with the small change in I_3), the size becomes smaller (which is reflected in the shift of τ_3).

CONCLUSIONS

A PA lifetime technique has been applied to study water absorption in novolac epoxy resins, and has been proven to be a useful method. It has been shown that intensities (I_3) of the long-lived component of *o*-Ps are related to the density of the crosslinkings of novolac epoxy resins: the larger is the density, the smaller is I_3 obtained. The lifetimes (τ_3), i.e. intermolecular hole size, are related to the absorption rate: the larger is the hole, the larger is the absorption rate obtained.

A shift in the lifetime distribution after water absorption was observed only for THPM. The shift indicates a decrease in the hole size, suggesting that, even when water molecules occupy the holes created in THPM, there is still enough space for Ps, resulting in a reduction of τ_3 and in little change in I_3. On the other hand, for CR, TMB and BA, once water molecules occupy the holes, there is not enough space left for Ps, resulting in a decrease in I_3 and in little change in τ_3. A molecular-dynamics code was applied to the simplified model; the result suggests that THPM may have longer hole structures, due to its molecular structures, than those of CR, TMB and BA.

ACKNOWLEDGEMENT

This work was supported in part by a Grant-in-Aid of the Japanese Ministry of Education, Culture, Sports and Science.

REFERENCES

1 Jean, Y. C. *Microchem. J.* 1990, **42**, 72

2 Suzuki, T., Oki, Y., Numajiri, M., Miura, T., Kondo, K., Ito, Y. and Shiomi, H. *J. Appl. Polym. Sci.* 1993, **49**, 1921

3 Okamoto, K., Tanaka, K., Katsube, M., Kita, H. and Ito, Y. *Bull. Chem. Soc. Jpn.* 1993, **66**, 61

4 Nakanishi, N. and Jean, Y. C. in 'Positron and Positronium Chemistry' (Eds D. M. Schrader and Y. C. Jean), Elsevier, Amsterdam, 1988, p. 159

5 Okamoto, K., Tanaka, K., Katsube, M., Sueoka, O. and Ito, Y. *Radiat. Phys. Chem.* 1993, **41**, 497

6 Suzuki, T., Oki, Y., Numajiri, M., Miura, T., Kondo, K. and Ito, Y. *Radiat. Phys. Chem.* 1995, **45**, 657

7 KirKegaard, P. and Eldrup, M. *Comp. Phys. Commun.* 1974, **7**, 401

8 Gregory, R. B. and Zhu, Y. *Nucl. Instr. Meth. Phys.* 1990, **A290**, 172; Gregory, R. B. 'Proceedings of the International Workshop on Positron and Positronium Chemistry' (Ed. Y. C. Jean), World Scientific, 1990, pp. 138–157; Provencher, S. W. *Comp. Phys. Commun.* 1982, **27**, 213, 229

9 Sugai, S. 'Koubunshi Jikken Kouza 4: Koubunshi no Bussei II (Japanese), Series of Polymer Experimental Techniques, No. 4: Characteristics of Polymers II' (Ed. S. Kanbara) Kyouritu Ltd., Tokyo, 1970

10 Jean, Y. C., Zandiehnadem, F. and Deng, Q. *Mater. Sci. Forum* 1992, **105–110**, 1897

11 This program is written by Cambridge Scientific Computer, Inc. and the basic idea of molecular force is found in the following text books: Burkert, U. and Allinger, N. L. 'Molecular Mechanics', ACS, Washington D.C., 1982; Clark, T. 'Computational Chemistry', Wiley, New York, 1985

12 Eldrup, M., Lightbody, D. and Sherwood, J. N. *Chem. Phys.* 1981, **63**, 51

13 Mogensen, O. E. 'Positron Annihilation in Chemistry', Springer-Verlag, Heidelberg, 1995