Radiopaque Epoxy Resins

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SYNOPSIS

Transparent, X-ray contrast (radiopaque) epoxy resins were obtained by dissolving up to 25 wt % triphenylbismuth in the commercial epoxy resin prepolymers EPON-815, DER-330, DER-383, and DEN-431 which were then hardened with diethylenetriamine. The radiopacities of the mixtures were found to be proportional to the molar concentration of the radiopaque additive. The systems follow the relationship, $R = R_o + (R_a - R_o)\bar{V}_a M_a$ where R, R_o, and R_a are the radiopacities of the mixture, the pure epoxy resin, and triphenylbismuth, respectively (expressed in mm aluminum/mm resin); M_a and $\bar{V}_a$ denote the molar concentration and molar volume of the bismuth compound. R_a for triphenylbismuth was found to be 7.4 ± 0.2 mm Al/mm resin; the average value of R_o for the four epoxies equals 0.16 ± 0.1 mm Al/mm resin. The amount of amine required to harden the radiopaque resins was far less for the epoxy novolac resin DEN-431 than for the three bisphenol-A based epoxies. The concentration of triphenylbismuth required to impart a radiopacity equivalent to that of aluminum measures 14.6 wt % in EPON-815, 14.8 wt % in DER-330, 14.9 wt % in DER-383, and 15.9 wt % in DEN-431. The radiopaque resins remain transparent indefinitely, even when exposed to water. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

X-ray contrast or radiopaque polymeric materials are increasingly in demand in applications where a rapid, nondestructive analysis or detection of the plastic is desirable.[1] These type of systems are frequently used in polymer based medical devices like sutures, catheters, implants, and dental material.[2] The property of radiopacity would also be highly desirable in plastic firearms.[3] Materials can be rendered radiopaque by incorporation of heavy atoms. Most heavy metal salts presently employed for this purpose are incompatible with polymers. This results in heterogeneity that renders the plastic more susceptible to liquid penetration, leaching of additives, and failures at phase boundaries. It can also cause scattering of light and, therefore, loss of transparency. Triphenylbismuth has been used recently as an effective radiopacifying agent that blends homogeneously with a wide range of polymers

including polystyrene, poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), and polypropylene.[4,5] In this study, the radiopacity of different epoxy resins has been measured as a function of the triphenylbismuth concentration. Some preliminary results of this work were reported earlier.[6]

EXPERIMENTAL

Triphenylbismuth was a gift from the Boulder Chemical Company. Epoxy resin EPON-815 was obtained from Shell and DER-330 from Fluka. The resins DER-383 and DEN-431 were procured from Dow Chemical. The hardener, diethylenetriamine, was purchased from Aldrich. To prepare the discs for radiopacity studies, a known amount of triphenylbismuth was added to a known amount of the epoxy resin prepolymer in a testtube. To speed up solubilization, the mixture was stirred for 2 h at 65°C. The clear viscous solution was then cooled to room temperature and after adding diethylenetriamine with stirring, transferred into a plastic vial. The ratio of the hardener to the prepolymer required

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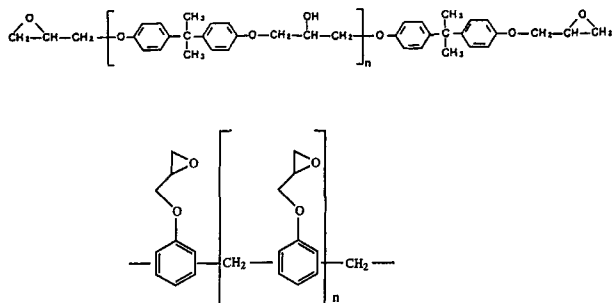
Scheme 1 Chemical composition of the bisphenol-A based epoxy resin prepolymers EPON-815, DER-330, and DER-383 (top) and structure of epoxy novolac resin, DEN-431 (bottom).

for obtaining a hard solid epoxy resin varied with the prepolymer being used and the hardening time (3–8 h at 25°C). The plastic vial was then cut open and the hard, transparent cylindrical stick cut into approximately 2 mm discs. The discs were polished with very fine sandpaper. A hardened epoxy resin without Ph₃Bi was used as a reference. For the 14 wt % Ph₃Bi/EPON-815 sample, discs were cut at 1, 2, 3, and 4 mm in order to determine the relationship between thickness and radiopacity. Radiopacities were measured with a Picker X-ray unit operating at 90 keV and 6 mA. The polymer samples were placed next to an aluminum step wedge on a Kodak ultraspeed double-sided X-ray film no. DF 49. The film was placed 55 cm below the tungsten anode. The developed film was scanned with a Joyce mi-

crodensitometer and the radiopacities of the specimens measured relative to that of the aluminum step wedge.[4]

RESULTS AND DISCUSSION

The commercial epoxy prepolymers EPON-815, DER-330, and DER-383 are structurally based on bisphenol-A and epichlorohydrin. They differ mainly in their viscosities. The compound DEN-431 is an epoxy novolac resin. The structure of these two types of prepolymers are depicted in Scheme 1. The relatively low viscosities of the four resins allow easy laboratory handling.

The hardening time of the resins is a function of the amount of added triamine and the type of resin. For the bisphenol-A prepolymer, hardening at 25°C took about 8 h at a 15 : 1 weight ratio of prepolymer to triamine. The hardening time for the epoxy novolac resin is only 3 hours at a 30 : 1 weight ratio of resin to hardener. Thus, considerably less of the toxic amine is required to harden the novolac resin, probably because of its high epoxy content. This should make this polymer preferred over other epoxy resins for potential biomedical applications.

When triphenylbismuth is blended with the epoxy resins and then hardened, a homogeneous material is obtained up to at least 25 wt % Ph₃Bi. Homogeneity is implied by the transparency of the product. This is depicted in Figure 1 where 2 mm thick Ph₃Bi containing EPON-815 discs were placed on top of
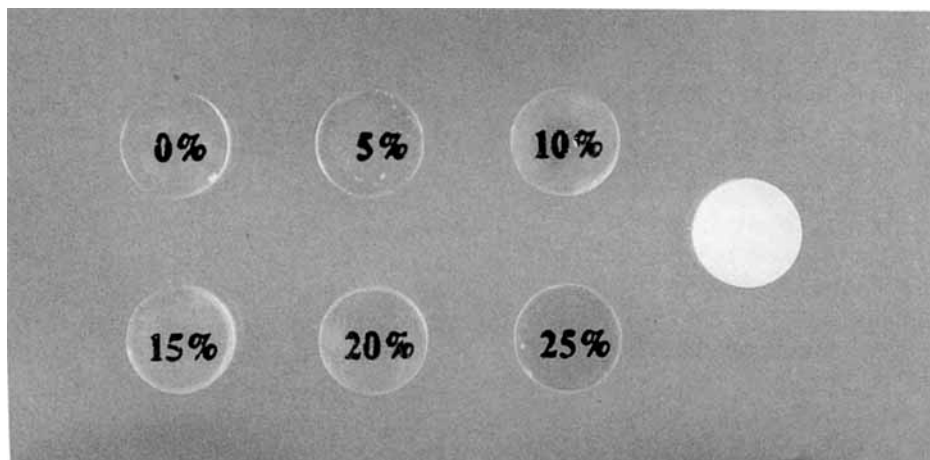

Figure 1 Photograph showing the transparency of epoxy resin discs comprised of a mixture of triphenylbismuth in EPON-815, hardened with diethylenetriamine. The 2 mm thick discs were placed on top of the printed numbers denoting the wt % Ph₃Bi in each sample. An opaque system of 40 wt % triphenylbismuth in EPON-815 is shown for comparison.
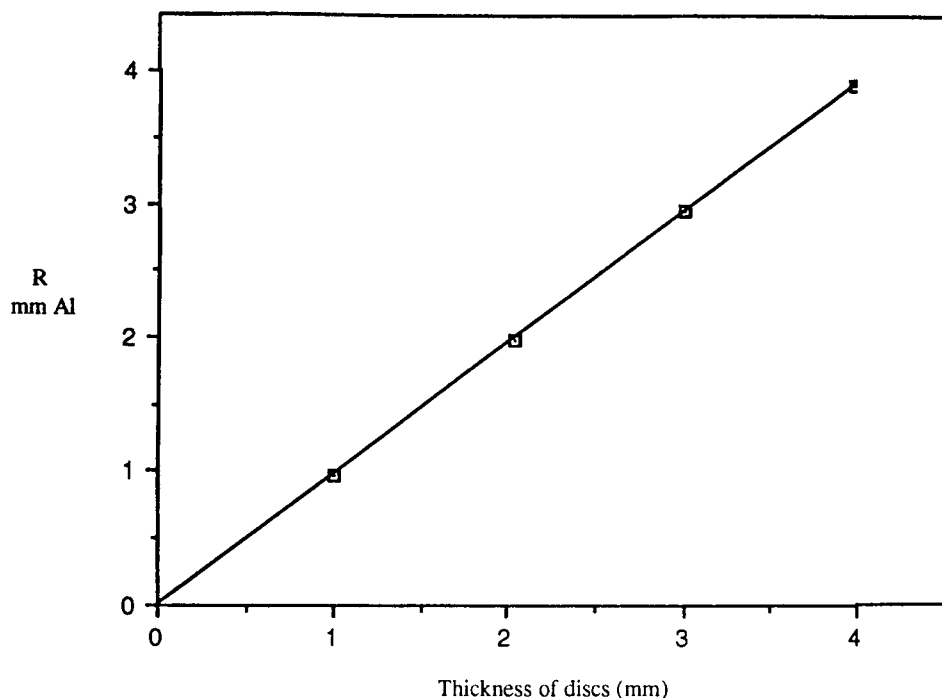
Figure 2 Plot of radiopacity (mm Al) vs. thickness (in mm) of 14 wt % Ph₃Bi containing EPON-815 discs.

printed numbers specifying the wt % of the radiopacifying agent in each sample. The numbers are clearly visible up to 25 wt % Ph₃Bi. However, above 30 wt % Ph₃Bi the hardened resins become opaque indicating the limit of solubility of this bismuth compound. Homogeneity is also indicated by the observed linear relationship between the radiopacity

of the epoxy resins and the thickness of the discs at a fixed triphenylbismuth concentration (Fig. 2).

Positive radiographs of 2 mm discs of radiopaque EPON-815 and DER-330 are shown in Figure 3. They are compared with an aluminum stepwedge. The measured radiopacities (in mm Al/mm resin) are given in Table I as a function of the wt % and
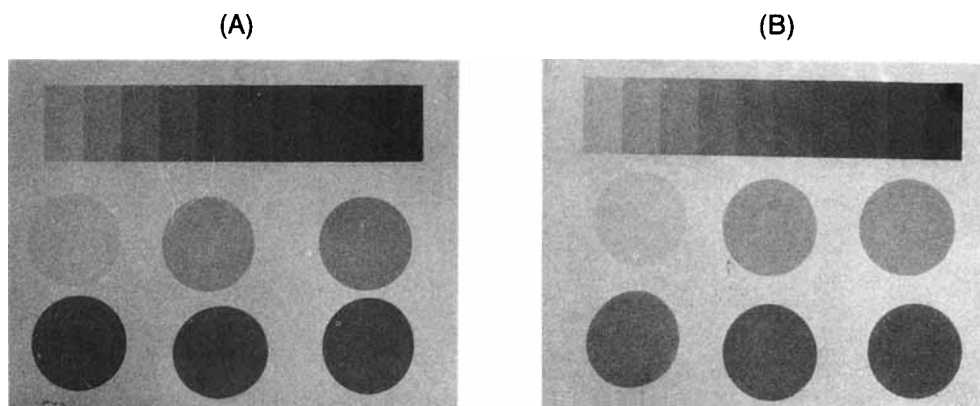

(A)

(B)

Figure 3 Positive radiographs of transparent 2 mm thick discs of: (A) Ph₃Bi/EPON-815 and (B) Ph₃Bi/DER-330. From left to right, top, then bottom: (A) 0, 4, 7.8, 11.3, 14.3, and 17.3 wt % Ph₃Bi; (B) 0, 3.5, 8.7, 12.6, 13.9, and 19.3 wt % Ph₃Bi. Al stepwedge from 0.5 to 5.0 mm in steps of 0.5 mm.

Table I   Correlation Between Radiopacity and Ph₃Bi Concentration

Epoxy Resin	Ph₃Bi (wt %)	Ph₃Bi (mol/L)	R (mm/mm) Al/resin
EPON-815	0.0	0.00	0.17
	4.0	0.11	0.40
	7.8	0.21	0.61
	11.3	0.32	0.80
	14.3	0.40	0.98
	17.3	0.49	1.17
DER-383	0.0	0.00	0.14
	5.1	0.14	0.45
	9.8	0.27	0.73
	14.8	0.42	0.99
	19.8	0.56	1.28
	24.6	0.71	1.59
DER-330	0.0	0.00	0.16
	3.5	0.09	0.36
	8.7	0.23	0.62
	12.6	0.33	0.91
	13.9	0.37	0.94
	19.3	0.52	1.23
DEN-431	0.0	0.00	0.14
	5.0	0.00	0.40
	10.1	0.27	0.77
	14.9	0.40	0.94
	20.0	0.55	1.28
	24.7	0.69	1.57

molar concentration of added Ph₃Bi. It was previously demonstrated[7] that the radiopacity, R, of a polymer blended with a radiopacifying agent can be expressed by Eq. (1).

$$R = R_o + (R_a - R_o)\, \bar{V}_a\, M_a \tag{1}$$

where R, R_o, and R_a are the radiopacities of the system, polymer, and additive, respectively, $\bar{V}_a$ is the molar volume of the additive (0.278 L for triphenylbismuth) and M_a the molar concentration.

Application of Eq. (1) to our X-ray contrast epoxy resins reveals indeed a linear correlation between their radiopacities and the molar concentration of Ph₃Bi. Examples are shown in Figure 4 for the EPON-815/Ph₃Bi system and in Figure 5 for the DEN-431/Ph₃Bi blend. All plots have a correlation factor better than 0.995. Plots of radiopacity vs. the molality of Ph₃Bi in the respective resins are also linear. In calculating the molar content of Ph₃Bi, the volumes of the three components were assumed to be additive. This assumption can of course be avoided when using molality.

The R_o values for the epoxy polymers can be obtained from the intercepts of the respective plots while the radiopacity, R_a, of triphenylbismuth is calculated from the slopes. The data are collected
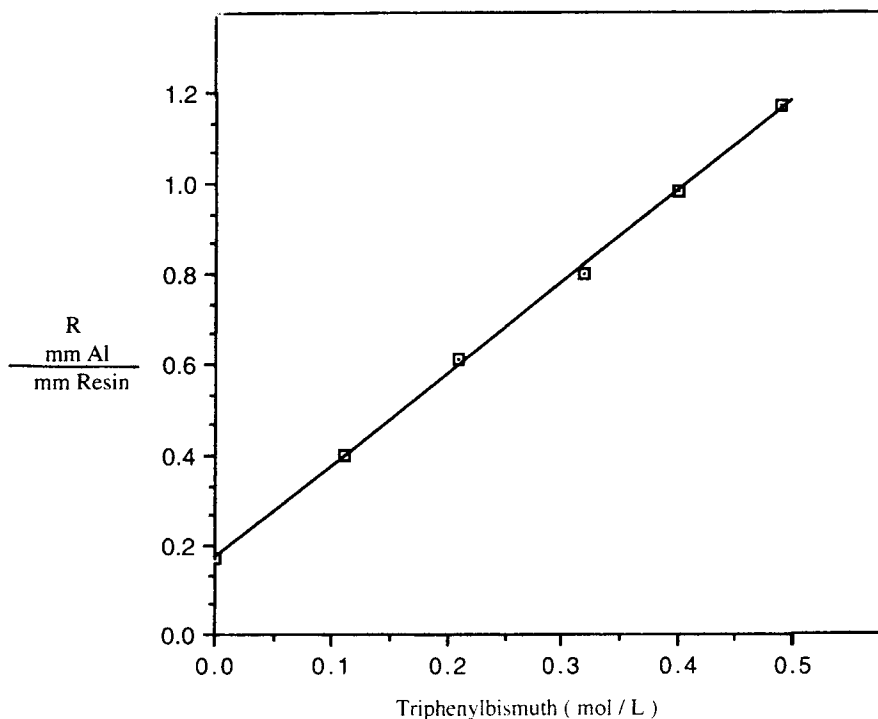
Figure 4   Plot of radiopacity (in mm Al/mm of EPON-815) vs. triphenylbismuth concentration (mol/L).
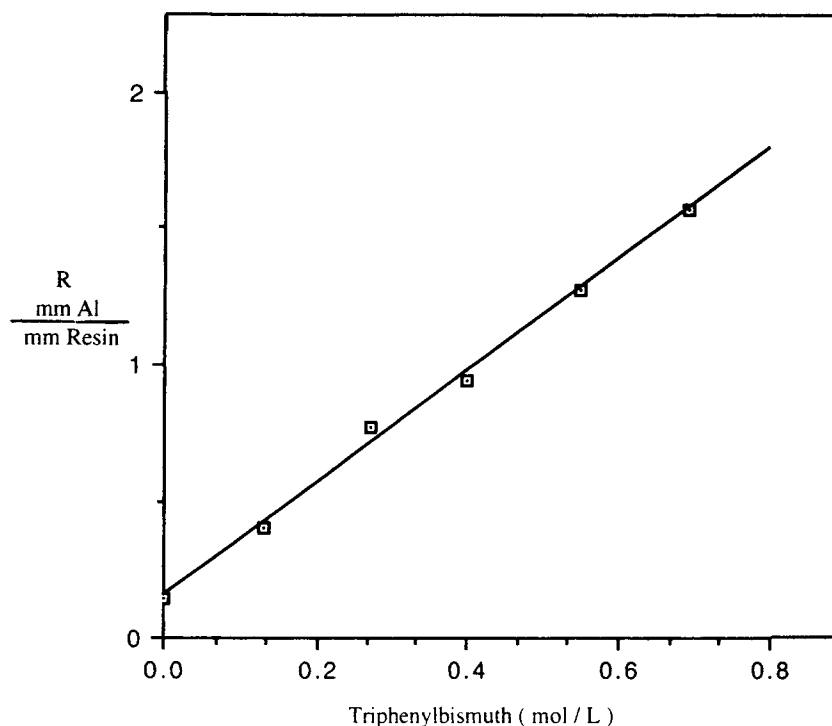
Figure 5 Plot of radiopacity (in mm Al/mm of DEN-431) vs. triphenylbismuth concentration (mol/L).

in Table II. Also listed are values for the parameter E_a that denotes the concentration of radiopacifying agent needed to render the radiopacity of 1 mm material equivalent to that of 1 mm aluminum, a standard adopted by the dental establishment.[8] For

comparison, data reported by us for other polymers and additives ($BiCl_3$ and $BiBr_3$) are also included. The latter data differ slightly from those given in earlier publications[4-6] because the aluminum stepwedge used in previous experiments contained traces

Table II   Radiopacities of Different Polymer-Additive Systems

| | | Al/Polymer | | E_a | |
| | | R_0 (mm/mm) | R_a (mm/mm) | M_a | Wt % |
Polymer	Additive				
PMMA	$BiBr_3$	0.12	32.5	0.31	11.6
PMMA	$BiCl_3$	0.12	22.4	0.53	13.1
PMMA	Ph_3Sb	0.12	2.5	1.52	44.5
PMMA	Ph_3Bi	0.12	7.5	0.44	16.2
PSt	Ph_3Bi	0.09	7.9	0.42	15.8
iPP	Ph_3Bi	0.12	6.9	0.47	22.3
PVC	Ph_3Bi	0.42	7.1	0.36	14.0
EPON-815	Ph_3Bi	0.17	7.4	0.41	14.6
DER-330	Ph_3Bi	0.17	7.7	0.39	14.8
DER-383	Ph_3Bi	0.16	7.4	0.42	14.9
DEN-431	Ph_3Bi	0.15	7.6	0.43	15.9

R_0, the radiopacity of the pure polymer; R_a the radiopacity of the additive. E_a, the concentration of the additive (expressed here in molarity, M_a and in wt % of additive) in the polymer that renders its radiopacity equivalent to that of Aluminum.

of heavy metals. A new stepwedge made of high grade aluminum was employed in our studies with the epoxies. Its radiopacity was found to be 15% less than that of the contaminated stepwedge. Recalculation raised E_a by about 15% while lowering R_o by the same amount.

The radiopacity for the epoxies free of a radiopacifying agent averages 0.16 mm Al, slightly higher than for PMMA, but much less than for PVC which contains an abundance of chlorine atoms. The average value for the radiopacity of Ph_3Bi is 7.4 ± 0.2 mm Al. It is gratifying to find that this value is essentially independent of the polymer used, in spite of the widely different polymer structures. It implies that the method employed in arriving at the R_a value is reliable.

The R_a for Ph_3Bi is considerably below the R_a = 32.5 mm Al of $BiBr_3$ or the R_a = 22 mm Al for $BiCl_3$ (see Table II). It shows the substantial impact of the large halogen atoms on R_a.[4] Close to 15 wt % of Ph_3Bi is needed to render the radiopacity of the epoxy resins equivalent to that of aluminum. However, twice that amount can be incorporated without affecting the transparency of the materials. We also attempted to make transparent radiopaque blends of Ph_3Bi and bisphenol-A based polycarbonates such as lexan, because these polymeric materials have become more popular in dentistry. Unfortunately, the bismuth compound is not miscible with this polycarbonate or with the cyclic oligomers used in their synthesis, presumably because of their rigid backbone.

Although the bismuth halides are less expensive and have higher radiopacities, they are only compatible with carbonyl or phosphonate containing polymers. They are also moisture sensitive, and loss of transparency in bismuth halide containing PMMA samples develops over time when exposed to air. The hydrophobic character of Ph_3Bi makes it miscible in a wide range of polymers and the transparency of the radiopaque materials is not affected by moisture. The compound has a low toxicity index[9] and its insolubility in water prevents leaching into aqueous environments. The properties make Ph_3Bi attractive for use in dental and other biomedical applications. By replacing one of the phenyl groups by a styryl moiety, it can be covalently incorporated into a polymer, preventing its leaching altogether.[10]

Tris(p-tolyl)bismuth was also found to dissolve easily in epoxy resins but on a weight basis it will impart a lower radiopacity to the polymer than Ph_3Bi.

Diphenylbismuth chloride and di(p-tolyl)bismuth chloride, precursors to the styryl-bismuth monomer derivatives[10,11] were found to be soluble in the epoxy resin up to only 5 wt %.

CONCLUSIONS

Triphenylbismuth forms homogeneous, transparent, radiopaque blends with epoxy prepolymer resins hardened with diethylenetriamine. The radiopacities are proportional to the molar concentration of Ph_3Bi and reach values up to 1.5 times that of aluminum. The amount of hardener and the time required to cure the radiopaque epoxy resins is much less for the epoxy resins. The transparency of the systems is not affected by exposure to moisture and remains unchanged over time.

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