X-Ray contrast miscible blends of polyacrylates and bismuth trihalides: glass transition temperatures and radiopacities

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Bismuth tribromide and bismuth trichloride were dissolved in poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) to yield transparent materials with radiopacities exceeding that of aluminium by at least a factor two. The radiopacities of the mixtures were found to be proportional to the molar concentration of the X-ray contrast additive and obey the relationship $R = R_0 + (R_a - R_0)\bar{V}_a M_a$, where R, R_0 and R_a are the radiopacities (expressed in mm aluminium per mm material) for the mixture, the pure polymer and the bismuth compound, respectively, while M_a and $\bar{V}_a$ denote the molar concentration and molar volume of the additive. For $BiBr_3$, R_a was found to be 31.4 and the value for $BiCl_3$ is 22.4, while R_0 for PMMA is 0.125. The bismuth compounds lower the T_g of the two polymers by 0.3 ± 0.03°C per wt% of the halide. The transparent, radiopaque materials are moisture sensitive and slowly turn hazy due to the formation of bismuth oxyhalides.

(Keywords: radiopacity; X-ray contrast polymers; polyacrylates; bismuth trihalides; glass transition temperature)

INTRODUCTION

X-ray contrast radiopaque polymeric materials are increasingly in demand in applications where rapid, non-invasive analysis or detection of the plastic is desirable or required. This is frequently the case for polymer-based medical devices (sutures, catheters, implants) and dental materials and would certainly be desirable for plastic firearms[1,2]. Materials can be rendered radiopaque by incorporation of heavy atoms. This can be accomplished by adding glasses or heavy metal salts such as barium sulphate or bismuth oxycarbonate[3,4] or by using halogenated monomers[5]. Most heavy metal salts employed for this purpose are incompatible with polymers. The heterogeneity renders the plastics more susceptible to liquid penetration, to leaching of additives, and to failures at the phase boundaries. It also causes scattering of light, and therefore, loss of transparency.

Our search for radiopacifying agents has focused on heavy metal containing compounds compatible with polymers. In this respect, triphenylbismuth is a particularly effective X-ray contrast additive[6,7]. It forms miscible blends with a variety of polymers including polystyrene, polyalkenes, poly(vinyl chloride) and polyacrylates. Radiopacities can easily reach values twice that of aluminium. Earlier we reported that bismuth tribromide and bismuth trichloride are miscible with carbonyl and phosphonate containing monomers and polymers up to 70 wt% (ref. 8). Unlike triphenylbismuth, their high solubility in these materials derives from the interaction between bismuth and the carbonyl or phosphonate moiety as evidenced by infrared and ^{13}C n.m.r. shifts[9]. Salts such as uranyl nitrate hexahydrate[10] or barium bromide dihydrate[11] also form miscible blends with poly(methyl methacrylate). In these systems, the water molecules apparently play an important role in solubilizing the salts.

In this paper radiopacity studies on mixtures of bismuth trihalides with poly(methyl methacrylate) and poly(ethyl methacrylate) are reported as well as the effect of these additives on the glass transition temperatures of these polymers.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and ethyl methacrylate (EMA) were distilled at reduced pressure from CaH_2. Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were recrystallized from methanol. Tetraethyleneglycoldimethacrylate (TEGDMA) (Polysciences) and organic solvents were used without further purification. Anhydrous $BiBr_3$ and $BiCl_3$ (Alfa) had sharp melting points at 218 and 231°C, respectively.

Polymer–bismuth trihalide mixtures

Two methods were used, namely, bulk polymerization of a monomer-salt mixture, and solvent casting films from polymer–salt solutions. In the first procedure, known amounts of $BiBr_3$ or $BiCl_3$ were dissolved in the monomer and the mixtures polymerized under nitrogen for 48 h at 50°C with 0.5 wt% AIBN or BPO as initiator. In some experiments, MMA was directly distilled from CaH_2 into ampoules containing known quantities of $BiBr_3$, and the ampoules sealed off. This avoids any contact with moisture, an important prerequisite for obtaining transparent radiopaque polyacrylates. Solutions with $BiCl_3$ contained some insoluble impurities which could be removed by centrifugation. The impurities were weighed

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in order to calculate the correct $BiCl_3$ concentration. When moisture is excluded, clear, transparent specimens of the polymers with $BiCl_3$ and $BiBr_3$ can be obtained. In some experiments, 2 wt% TEGDMA was added as cross-linker.

In the second method, bismuth trihalide was dissolved in a 10 wt% polymer solution in ethyl acetate, methyl ethyl ketone or ethyl acrylate. The weight percent of bismuth additive was varied from 0 to 45. Films were cast at room temperature from a glass or Teflon dish by slow solvent evaporation under a flow of dry nitrogen. The use of ethyl acrylate as solvent has the advantage that after evaporation traces can easily be detected in the infrared.

Measurements

A Perkin Elmer DSC-4 differential scanning calorimeter (d.s.c.) was used for measuring glass transition temperatures (T_g). The instrument was calibrated with indium and scans were run under dry nitrogen at a heating rate of 20°C/min. Each sample was scanned three times between 30 and 150°C until a reproducible T_g value was obtained. The T_g was taken at the inflection point of the tracings.

Radiographic data were acquired on a Picker condenser discharge X-ray diagnostic unit DGC-1010 operating at 90 kV and 6 mA. One or two mm thick specimens were cut from cylindrical rods of transparent polymer–salt mixtures obtained by carrying out polymerizations in ampoules with a 12 mm inside diameter. The specimens were carefully polished, their volume measured and then placed on a Kodak DF49 ultraspeed double sided dental X-ray film positioned 55 cm below the tungsten anode. An aluminium stepwedge with 1 mm steps placed alongside the specimens to be measured was used for comparison. The developed X-ray films were scanned on a Joyce Lobel double-beam recording microdensitometer. The radiopacities of the specimens, expressed in mm of aluminium, were plotted as a function of the molar concentration of the added bismuth compound. The latter was calculated from the wt% of additive in the polymer and the weight and volume of the specimen.

RESULTS AND DISCUSSION

Poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) containing up to 45 wt% $BiBr_3$ or up to 35 wt% $BiCl_3$ can be obtained as transparent materials as long as during the polymerization of the monomer-salt mixtures or during the solvent casting process, moisture is rigorously excluded. Water turns the mixtures cloudy due to formation of insoluble bismuthoxyhalide. Our earlier reported findings[8] of low $BiCl_3$ solubility in MMA (less than 9 wt%) apparently resulted from the presence of such insoluble impurities. Once they are removed by centrifugation, clear MMA/$BiCl_3$ mixtures with at least 35 wt% $BiCl_3$ can be obtained[12].

Glass transition temperatures

Figure 1 displays d.s.c. scans of transparent PMMA/$BiCl_3$ specimens. Similar scans were obtained for PMMA/$BiBr_3$ and PEMA/$BiBr_3$. The T_g values as a function of salt content (expressed as wt% salt as well as the molar ratio of monomer units to bismuth halide) are collected in *Table 1*. None of the d.s.c. tracings exhibited endotherms at the melting points of $BiBr_3$ (218°C) or $BiCl_3$ (232°C). Hence, no large phase-separated domains of bismuth trihalide are present in the samples.

It is worth mentioning that solid $BiBr_3$ itself, when placed in the aluminium d.s.c. sample pan, does not give an endotherm at its melting point (*Figure 2*). The first scan reveals a large exotherm at 213°C followed by an endotherm at 271°C. On the second heating cycle only the endotherm at 271°C remains (*Figure 2*). This temperature coincides precisely with the melting point of bismuth metal. $BiCl_3$ shows the same behaviour, with an exotherm and endotherm at 227°C and 271°C, respectively, the exotherm being absent in the second heating cycle. Visually the formation of black particles in the aluminium sample pan is noticeable. When heated in a glass tube the two salts register their proper melting points. Black spots were also noted when films of PMMA/$BiCl_3$ or PMMA/$BiBr_3$ were cast in an aluminium pan, but not when cast in a glass or teflon dish. We attribute the behaviour of these salts in the presence of aluminium to the reaction $BiCl_3 + Al \rightarrow AlCl_3 + Bi$, a reaction which apparently is exothermic and produces metallic bismuth.

The results of *Table 1* demonstrate that addition of $BiBr_3$ or $BiCl_3$ lowers the T_g of PMMA and PEMA. This is graphically depicted in *Figure 3* as a plot of T_g *versus* wt% of bismuth salt. The plots are nearly linear below 30 wt% salt. The T_g of salt-free dry PMMA is 117°C, close to the value of 120°C recently reported for the dry polymer[13]. The reported T_g for atactic PMMA is 105°C (ref. 14). This compares with our value of 108°C for PMMA made without taking special precautions. Water in PMMA is known to act as plasticizer and can lower its T_g by as much as 20°C (ref. 13).

The decrease in the T_g of polyacrylates on adding bismuth trihalides is not surprising. The salts, as shown by ^1H and ^{13}C n.m.r. were found to form 1:1 adducts with carbonyl compounds[9], unlike Lewis acids such as $SnCl_4$ which can form 2:1 complexes[15]. Complexation to more than one binding site usually increases the T_g of polymers due to cross-linking (intermolecular interactions) or chain stiffening (intrachain adduct formation). For example, the T_g increases in a system such as $ZnCl_2$/poly(oxypropylene)[16] or in solvent free polymer electrolytes made from alkali salts and comb polymers with oligo-oxyethylene side chains[17]. In both cases metal

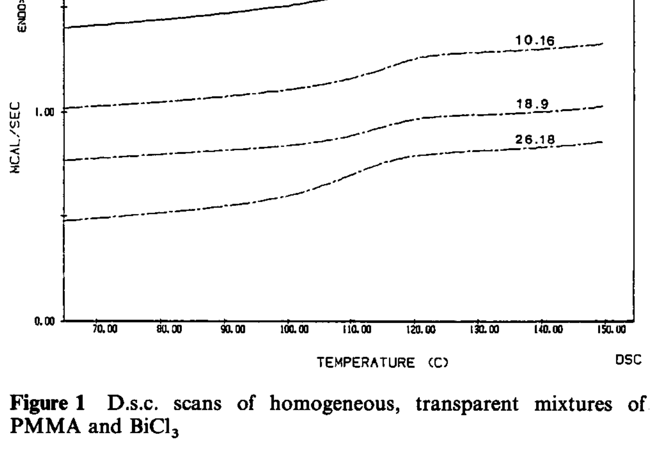

Figure 1 D.s.c. scans of homogeneous, transparent mixtures of PMMA and $BiCl_3$

Table 1 Glass transition temperature, T_g, of poly(methyl methacrylate) and poly(ethyl methacrylate) containing bismuth trihalides

Polymer	BiX_3 wt%	[Monomer]/[BiX_3]	TEGDMA[a] wt%	T_g °C
PMMA/$BiBr_3$[b]	0.0	–	–	117
	4.7	91	–	114
	8.5	48	–	113
	21.4	16	–	110
	28.0	11	–	107
PMMA/$BiBr_3$	0.0	–	–	108
	0.0	–	2	112
	2.0	220	2	114
	5.1	83	2	113
	10.0	40	2	112
	25.0	13	2	89
	30.0	10	2	88
PMMA/$BiCl_3$[b]	4.8	62	–	116
	10.1	28	–	115
	18.9	14	–	113
	26.2	9	–	110
PEMA/$BiBr_3$	0.0	–	–	74
	0.0	–	2	76
	2.0	193	2	75
	5.0	75	2	75
	10.0	35	2	74
	20.0	16	2	68
	25.0	12	2	66

[a] Tetraethyleneglycol dimethacrylate cross-linker

[b] These samples were prepared under vacuum, the remaining sets under nitrogen (see Experimental section)

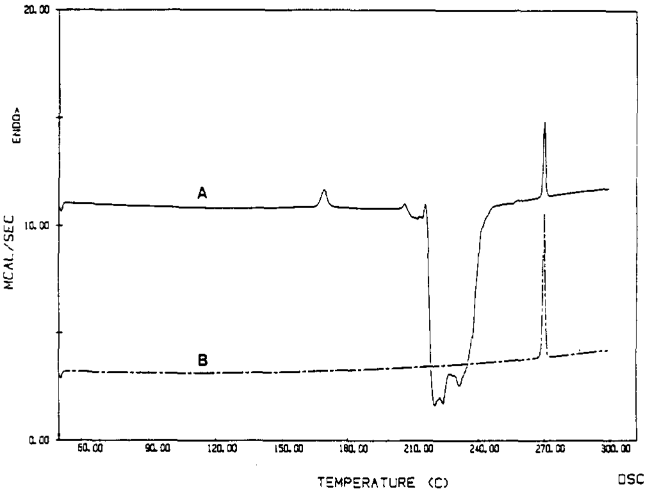

Figure 2 D.s.c. scans of $BiBr_3$. Curve A first scan; curve B second scan

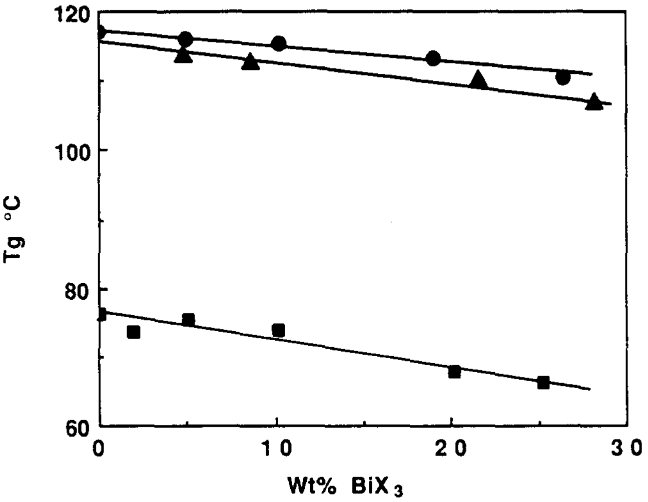

Figure 3 Plots of T_g *versus* wt% of bismuth trihalide for (▲) PMMA/$BiBr_3$; (■) PEMA/$BiBr_3$ and (●) PMMA/$BiCl_3$

ions are bound to more than one oxygen atom. In our system the bismuth salt functions more as a low molecular weight additive and increases the free volume of the polymer. However, the decrease in T_g is attenuated by the interaction of bismuth with a carbonyl moiety which in turn reduces the mobility of chain segments. The decrease in the T_g for PMMA on adding $BiBr_3$ or $BiCl_3$ is approximately 0.3 ± 0.03°C per wt% of bismuth salt, and slightly larger for PEMA. This is substantially less than was found with triphenylbismuth. The latter additive forms miscible blends with PMMA, polystyrene, poly(vinyl chloride), and other polymers, and lowers their T_g by 1.3 ± 0.1°C per wt% of Ph_3Bi. With this compound no adduct formation in PMMA could be detected. It essentially functions as a non-interacting additive.

Radiopacities

As outlined in the Experimental section, radiopacities of polished, transparent, cylindrical PMMA specimens of known thickness and containing known quantities of $BiBr_3$ or $BiCl_3$ were compared with that of an aluminium step wedge. A number of positive radiographs of PMMA/$BiCl_3$ pellets with the step wedge at the top are shown in *Figure 4*. Similar radiographs were obtained for PMMA/$BiBr_3$. The observed contrast is determined by

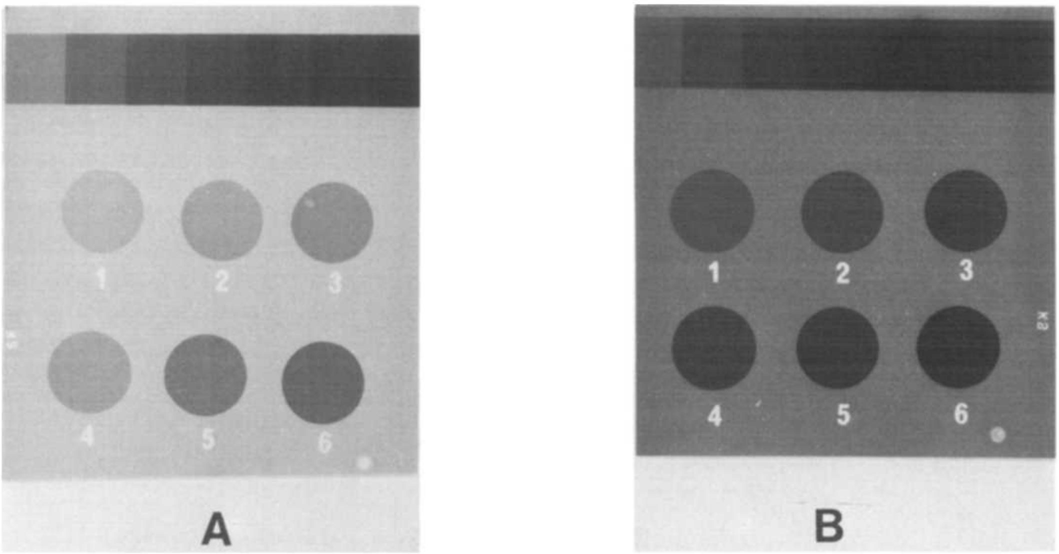

Figure 4 Radiographs of homogeneous, transparent mixtures of PMMA and $BiCl_3$. Wt% $BiCl_3$/thickness in mm, series A: 4.5/1.12 (1); 10.2/1.01 (2); 14.1/1.01 (3); 4.5/1.88 (4); 10.2/1.93 (5); 14.1/1.98 (6). Series B: 18.9/0.94 (1); 26.2/1.0 (2); 33.1/1.22 (3); 18.9/2.0 (4); 26.2/1.62 (5); 33.1/1.88 (6)

Table 2 Radiographic data for transparent specimens of PMMA with $BiBr_3$ and $BiCl_3$

Salt	wt% Salt	[Salt], M[a]	Thickness (mm)[b]	Radiopacity (mm Al/mm resin)
$BiBr_3$	0	0	0.90	0.11
	4.7	0.13	0.95	0.41
	10.0	0.33	0.79	0.77
	22.0	0.63	1.04	1.57
	28.5	0.80	1.12	2.18
	0	0	1.83	0.12
	4.7	0.13	2.00	0.37
	10.0	0.26	2.08	0.81
	22.0	0.64	1.82	1.64
	28.5	0.83	2.22	2.38
$BiCl_3$	4.5	0.16	1.12	0.29
	10.2	0.38	1.01	0.59
	14.1	0.57	1.01	0.87
	18.9	0.77	0.94	1.21
	33.1	1.56	1.22	2.46
	4.5	0.17	1.88	0.38
	10.2	0.41	1.93	0.65
	14.1	0.57	1.98	0.87
	18.9	0.81	2.00	1.31
	26.2	1.17	1.62	1.84
	33.1	1.55	1.88	2.40

[a] The values for the molar concentrations of bismuth salt (calculated from the wt% of salt and the volume and weight of the specimens) sometimes differ for the one and two mm series at the same wt% of salt due to uncertainty in the measurement of the volume of the specimens (from diameter and thickness)

[b] Values represent the measured thickness of the specimens in the direction of the X-ray beam

the thickness of the specimen in the direction of the X-ray beam and by the concentration of the radiopacifying additive.

The radiographic data are collected in *Table 2*. Radiopacities (column 5) are expressed in mm Al per mm resin, and were obtained by dividing the measured values by the thickness of the specimens (column 4 of *Table 2*). This procedure is justified because it was ascertained that a linear correlation exists between the radiopacity of a specimen and its thickness at constant $BiBr_3$ content (*Figure 5*).

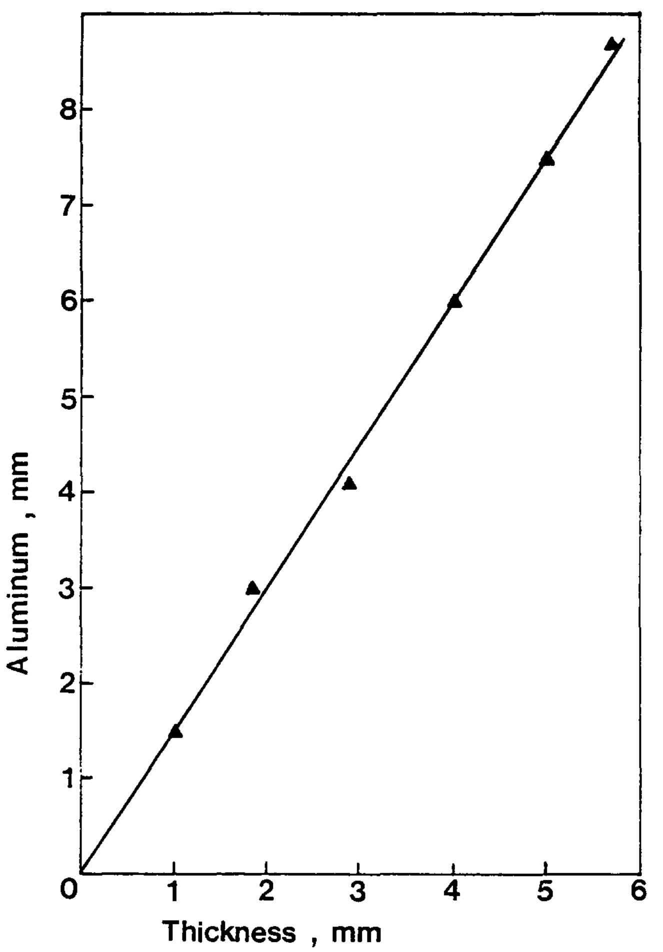

Figure 5 Radiopacities (in mm aluminium) of transparent pellets of 2% cross-linked PMMA containing 20 wt% $BiBr_3$ as a function of the thickness of the pellets

To check the dependence on radiopacifier content we ran two sets of experiments, one with specimens of approximately one mm thickness and a second set with specimens about 2 mm thick. The data obtained for the latter set are considered to be slightly more accurate

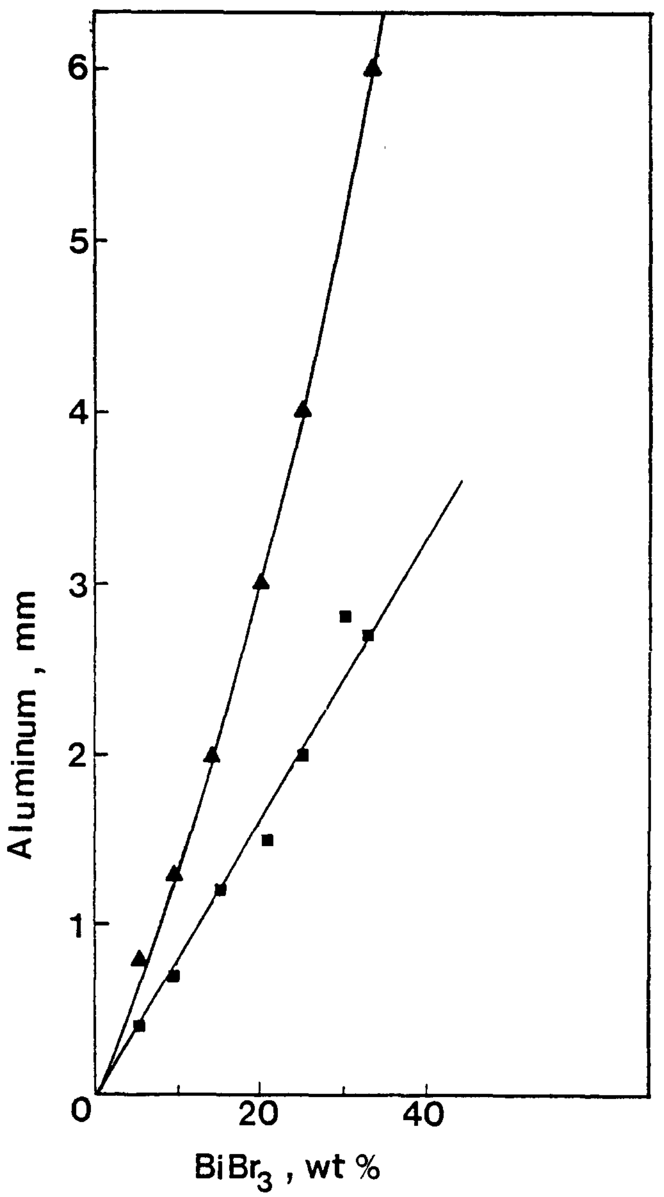

Figure 6 Radiopacities (in mm aluminium) of transparent (■) 1 mm and (▲) 2 mm pellets of 2% cross-linked PMMA/BiBr$_3$ resins as a function of the wt% of BiBr$_3$

because of the error in measuring the thickness. For reporting purposes 2 mm specimens are preferred since the specified standard for the radiopacity of plastics for dental applications are materials of 2 mm thickness[18]. The 2 mm standard is not a critical factor in our system because of the observed proportionality between radiopacity and thickness.

Plots of radiopacity as a function of the weight percent of bismuth salt in PMMA are not linear but curve upward at higher salt content (*Figure 6*). The curvature is caused by the increased density of the specimen as more bismuth salt is added. It means that doubling the weight percent of salt increases the molar concentration by more than a factor two. For a series of commercial radiopaque dental formulations filled with barium or strontium glass a linear relationship was reported[19] between the radiopacity expressed as equivalent thickness (mm) of aluminium and the weight percentages of the radiopaque component in the glass filler. In this case the density of the four composites that were compared deviated less than 10% from the average density.

It can be shown that a linear correlation exists between the radiopacity of a material and the molar concentration of the radiopacifying agent. Assuming that radiopacities are additive one may write:

$$R = V_o R_o + V_a R_a \qquad (1)$$

or

$$R = R_o + (R_a - R_o) V_a \qquad (2)$$

where R_o, R_a and R are the respective radiopacities of the polymer itself, the additive and the mixture, all in mm aluminium per mm of the material, and V_o and V_a are the volume fractions of polymer and additive, respectively. The volume fraction $V_a = M_a \bar{V}_a$, where M_a is the molar concentration of the additive and $\bar{V}_a$ its molar volume. Substituting this expression in equation (2) gives

$$R = R_o + (R_a - R_o) \bar{V}_a M_a \qquad (3)$$

Hence, a plot of the measured radiopacity of the mixture *versus* the molar concentration of the additive should yield a straight line with slope $= (R_a - R_o)\bar{V}_a$.

Figure 7 shows that a plot of R *versus* the molar concentration of BiBr$_3$ or BiCl$_3$ is indeed linear. The intercept $R_o = 0.12$ is the radiopacity of pure PMMA in mm aluminium per mm PMMA. The respective slopes are 2.55 ± 0.05 for BiBr$_3$ and 1.48 ± 0.02 for BiCl$_3$. From the molecular weights of BiBr$_3$ (MW = 449) and BiCl$_3$ (MW = 315) and from their densities (5.72 and 4.75, respectively (ref. 20)) we calculate a molar volume of 78.5 cm^3/mol for BiBr$_3$ and 66.3 cm^3/mol for BiCl$_3$. Combining the slopes and the $\bar{V}_a$ values yields $R_a = 32.5$ for BiBr$_3$ and $R_a = 22.4$ for BiCl$_3$, both in mm Al per mm of bismuth compound. In principle the R_a values can be used to calculate radiopacities of BiBr$_3$ or BiCl$_3$ mixtures with other polymers or compounds. We are

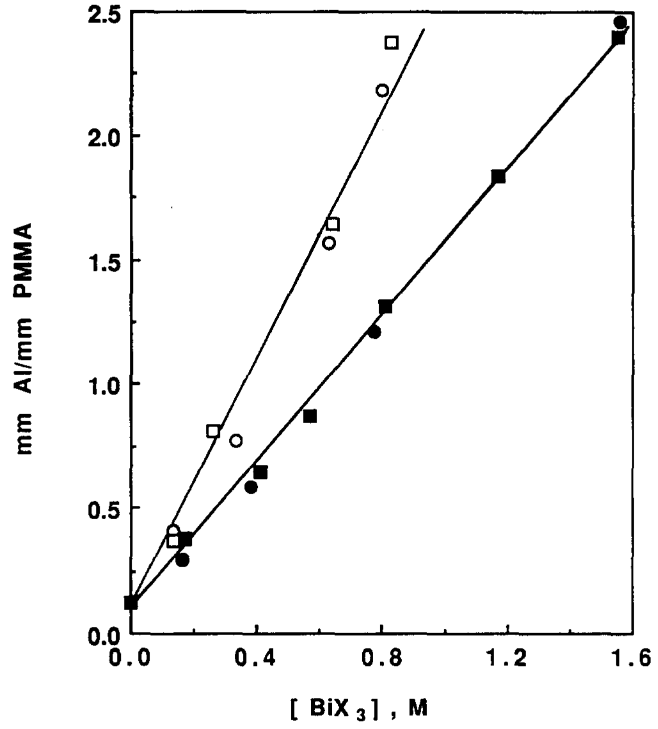

Figure 7 Plot of the radiopacity (in mm of aluminium per mm resin) for transparent mixtures of PMMA/BiBr$_3$ (1 mm (●) and 2 mm (■) series) and BiBr$_3$/BiCl$_3$ (1 mm (○) and 2 mm (□) series) as a function of the molar concentration of the bismuth halide

currently checking whether calculated and experimental radiopacity values for such mixtures agree.

From *Figure* 7, or from equation (3) using the appropriate R_a and $\bar{V}_a$ values it can be calculated that $R=1$ when $M_a=0.35$ M $BiBr_3$ or 0.60 M $BiCl_3$. In other words, these are the molar concentrations of $BiBr_3$ and $BiCl_3$ needed to render the radiopacity of PMMA equivalent to aluminium. Expressed in weight percent the values are 13 for $BiBr_3$ and 15.3 for $BiCl_3$. At these concentrations the respective molar ratios of MMA units to bismuth halide in the materials are 28 and 17. The difference between the two salts reflects the larger contribution of the bromine atoms of $BiBr_3$ to the radiopacity relative to that of the chlorine atoms in $BiCl_3$. In fact, the contribution of the chlorine atoms to the radiopacity is small, because aluminium equivalence with Ph_3Bi as radiopacifier is achieved at 0.67 M Ph_3Bi (24 wt%), only slightly higher than for $BiCl_3$.

Heat and moisture sensitivity

No phase separation occurs when samples of PMMA/$BiBr_3$, PMMA/$BiCl_3$ or PEMA/$BiBr_3$ containing 25 wt% of the halide are heated to 140°C. The samples remain transparent and soluble in organic solvents. The latter observation implies that no cross-linking takes place on heating. However, the materials are moisture sensitive as also noted by Combe[12]. As mentioned earlier, exposure of bismuth halide solutions of MMA to moist air develops cloudiness within hours due to formation of insoluble oxyhalides. Water penetration in the polymeric samples is much slower. For example, a 10 wt% $BiBr_3$/PMMA specimen exposed to air remains clear for many months. Haziness develops more rapidly at higher bismuth halide content or when the specimen is in immediate contact with water, especially at elevated temperature. The loss of transparency does not appear to alter the radiopacity, and no halide is leached into the water, probably because the oxyhalides are water insoluble. A cross-linked PMMA/$BiBr_3$ specimen was significantly less sensitive to water penetration and remained transparent for a much longer time than a comparable non-crosslinked material.

In addition to their moisture sensitivity, bismuth halides interact with amines[21], and, therefore, interfere in the room temperature curing of dental plastics with amine accelerators in combination with a peroxide initiator. This problem could conceivably be solved by using sterically hindered amine accelerators. The bismuth halides do not affect the polymerization of acrylates with common radical initiators at elevated temperatures. The decrease in the number average molecular weight of PMMA obtained by bulk polymerization of MMA containing 40 wt% $BiBr_3$ is only a factor 1.5 relative to that of PMMA made under identical conditions but in the absence of the halide[8]. A distinct advantage of the bismuth trihalides for application *in vivo* is their biocompatibility. The bismuth-containing PMMA materials were found to exhibit negative Ames mutagenicity, and cytotoxicity tests confirm that the radiopaque materials are non-toxic and non-carcinogenic[22].

CONCLUSIONS

Homogeneous and perfectly transparent blends of poly(methyl methacrylate) or poly(ethyl methacrylate) with $BiBr_3$ or $BiCl_3$ exhibiting radiopacities exceeding that of aluminium by at least a factor two can be made under controlled conditions. The radiopacities are proportional to the molar concentration of the bismuth halide. The materials are biocompatible but moisture sensitive, and homogeneity is limited to carbonyl or phosphonate containing polymers. Recent studies have shown that triphenylbismuth is compatible with a much wider variety of polymers and overcomes most of the problems encountered with the bismuth halides[6,7]. As an organic compound it can be modified for permanent incorporation into a polymer which eliminates the possibility of leaching[23].

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