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Surface characterization of photocured aromatic methacrylate resins by inverse gas chromatography

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The surface properties of a commercially available photocured resin were investigated using a combination of inverse gas chromatography (IGC) and X-ray photoelectron spectroscopy (XPS). Results were compared with those obtained from a sample of a modified resin, in which one of the components was removed from the formulation, and poly(methyl methacrylate). IGC results indicated that modification of the resin produced differences in the acid–base properties of the material, with the modified resin behaving in a less basic manner. XPS data revealed very little difference between the two resins.

(Keywords: photocured resins; inverse gas chromatography; surface energy; dispersive interactions; acid–base interactions)

INTRODUCTION

The importance of acid–base interactions in the adhesion of polymers to ceramic substrates is well documented[1,2]. Since the initial application of acid–base theory to the study of adhesion phenomena, a series of techniques has been used in order to characterize the acid–base properties of polymers, with varying degrees of success[3], e.g. X-ray photoelectron spectroscopy (XPS)[4], infra-red spectroscopy[3], flow microcalorimetry and inverse gas chromatography (IGC)[5]. In IGC the term 'inverse' means that the stationary phase is the main object of investigation rather than the mobile phase. Molecular probes of known physico-chemical properties are injected at infinite dilution and the measurement of their retention times permits the characterization of the surface or bulk properties of the packing material under test. Over the last two decades IGC has been demonstrated as an effective means of characterization of conventional homopolymers, copolymers[5], conducting polymers[6], inorganic fillers, reinforcing fibres, clays[7] and so on. It has recently been applied to the study of photopolymerized methacrylates and their thermal treatment[8,9]. The increasing demand for materials characterization by IGC lies in the fact that it is a fast,

versatile and inexpensive method to investigate thermodynamic properties of both the bulk and the surface of finely divided materials.

The aim of this work has been to carry out IGC studies on a fully-formulated (and therefore multicomponent) system. The product chosen was a commercially available photocured resin, produced by Zeneca Specialities under the tradename of Luxtrak™. These resins are of particular interest to manufacturers of both microelectronic and fibre-optic components, as they offer several advantages over the more conventional, thermally cured systems. The Luxtrak™ series of resins may be cured 'on command' using visible light (of optimum wavelength 470 nm). Photocured resins offer the additional advantages of rapid cure times (seconds at standard ambient temperature and pressure), plus the ability to cure through translucent (e.g. alumina), in addition to optically transparent, materials. These properties are beneficial in areas such as surface mount technology and in joining fibre-optic connectors, as they minimize the risk of component misregister.

Substrates frequently encountered in microelectronics applications include various compositions of alumina (ranging from 80 to 99.6% purity), single crystal silicon (plus its layer of native oxide) and quartz. There is a marked difference in the acid–base properties of the substrate materials, signified by the variation in values of *IEPS* (isoelectric point of the

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solid surface): alumina has a value of 8 and silica, 2. The potential to detect changes in acid–base properties of various resin formulations is therefore of interest to the manufacturers, who wish to tailor the resins for specific applications by maximizing acid–base interactions.

Experiments were carried out on a standard formulation (available under the product designation LCR000) and subsequently on a modified resin, ModLCR. Surface analysis by XPS was also carried out in order to compare surface chemical compositions with the surface thermodynamic characteristics determined by IGC.

EXPERIMENTAL

Resin preparation

The LCR resin was the commercially available product supplied by Zeneca pre-packaged in syringes. The modified resin, ModLCR, was specially formulated for this work and was essentially the LCR material minus the ethoxylated methacrylate monomer (EMM) component. This modification was undertaken in order to study the effect of its removal on interphase formation and the consequential adhesion to ceramic substrates, work that is reported in detail elsewhere[10]. In this paper it is the effect of this modification on the acid–base properties of the system that is the subject of investigation.

Samples of resin were cured under Melinex film (to prevent oxygen inhibition of the cure process at the surface) using an intense blue light as recommended by the manufacturers. Following cure, the crosslinked resins were ground to a coarse powder suitable for packing into the IGC column.

Inverse gas chromatography

Teflon columns, of 6 mm outside diameter and 1 m long, were packed with 9 and 14 g of LCR and ModLCR, respectively. The resins were crushed and sieved to 100–200 μm before packing. For comparison with these methacrylate resins, a Teflon column of the same dimensions was packed with 10 g of poly(methyl methacrylate) (PMMA) beads. A Girdel 330 gas chromatograph fitted with a flame ionization detector and a flow rate regulator was used. Methane (Alltech) was the non-interacting marker and a high purity grade nitrogen (Air Liquide) was the carrier gas. The flow rate was 18.5 and 5.5 cm^3 min^{-1} for the resins and PMMA, respectively, as measured by a soap-bubble flowmeter. A very low flow rate was used for the PMMA measurements in order to obtain retention times, of the probes, significantly different from that of methane. This results from the very low adsorptive capacity of the PMMA beads which yield very short retention times and thus does not allow the use of higher flow rates of the level used for the LCR resins. The oven temperature was 25°C as measured by a

digital thermometer inserted through the oven wall. The injector and detector temperatures were approximately 110°C. The columns were conditioned at 110°C and under a stream of nitrogen for 16 h prior to chromatographic measurements. All measurements were made at 25°C, well below the glass transition temperature (T_g) of the polymers involved which was approximately 100°C for all three materials studied. The temperature of analysis, relative to T_g, is important because, when semi-crystalline or amorphous materials are characterized at temperatures above T_g, both surface adsorption and bulk absorption of the probes contribute to their retention times[11,12]. It is only when IGC experiments are performed well below the T_g of the polymer under consideration that the kinetics of the bulk absorption process become low enough to be neglected and the net retention time may be regarded as solely attributable to surface adsorption phenomena[13]. This is one of the important advantages of IGC over static methods for the study of polymer adsorption.

Probe vapours were injected manually at least in triplicate by a Hamilton gas-tight syringe. To achieve extreme dilution of the probes, the syringe was purged as many times as necessary. The retention data were collected with a Delsi 21 digital recorder and the retention times determined graphically according to the tangents method of Conder and Young[13]. An example of the gas chromatogram obtained is given in *Figure 1*, where a mixture of alkane probes have been injected together to illustrate the different retention times within the column; as methane is the non-interacting probe this defines zero retention time.

In this work the probes used were apolar n-alkanes, and an acidic, a basic and an amphoteric species. All were of an AnalR (high purity analytical reagent) grade. The thermodynamic properties of the probes are reported in *Table 1*, where DN (ref. 14) and AN (ref. 15) stand for Gutmann's donor and acceptor numbers. Note that the values of AN were corrected for van der Waals' interactions[15] and are abbreviated to AN^*.

X-ray photoelectron spectroscopy

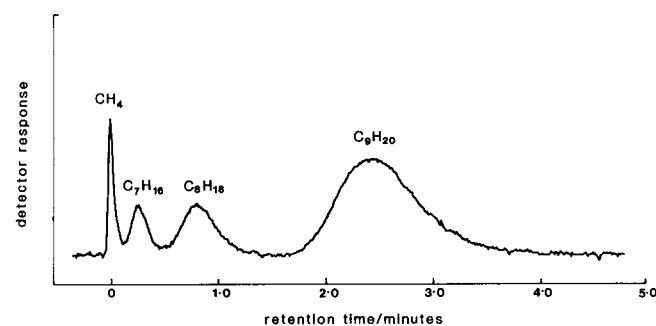XPS analysis was carried out using a VG Scientific ESCALAB MkII system interfaced to a VGS 5000-S

Figure 1 Output from the IGC detector following the injection of a mixture of CH$_4$, C$_7$H$_{16}$, C$_8$H$_{18}$ and C$_9$H$_{20}$ n-alkanes. The methane is assumed to have a retention time of zero and provides the calibration point for the abscissa

Table 1 Probes used to characterize the photocured resins and PMMA

Molecular probe		T_b (°C)	DN	AN*	DN/AN*	Supplier
Heptane	(C_7H_{16})	98.4				Prolabo
Octane	(C_8H_{18})	125.7				Fluka
Nonane	(C_9H_{20})	150.8				Fluka
Decane	$(C_{10}H_{22})$	174.1				Fluka
Trichloromethane	(TCM)	61.2	0	22.6	0	Aldrich
Ethyl acetate	(EtAc)	77.1	77.1	6.3	11.4	Prolabo
Tetrahydrofuran	(THF)	66.0	83.7	2.1	39.9	Prolabo

DN and *AN** are in kJ mol⁻¹

datasystem based on a DEC PDP11/73 computer. Small plaques (approximately 1 cm²) were prepared for analysis by scraping using a clean scalpel blade under flowing argon in the fast entry lock of the ESCALAB. Each sample was analysed using Al $K\alpha$ X-rays, the analyser being operated in the constant analyser energy mode at a pass energy of 50 eV for the survey spectra and 20 eV for the high resolution C 1s and O 1s spectra. Quantification was achieved using the manufacturer's software and peak areas of the C 1s and O 1s regions following the removal of a linear background.

RESULTS AND DISCUSSION

Measurements of adsorption behaviour of the probes

In IGC, probes are injected at infinite dilution in order to favour probe molecule–stationary phase interactions and thus minimize lateral probe–probe interactions which can be neglected in subsequent calculations. Their retention on the solid surface therefore results only from their interaction with the solid stationary phase. The volume of carrier gas required to sweep out an adsorbed species is V_N, the net retention volume:

$$V_N = j F_C t_N$$

where j is the compression correction factor, F_C the corrected flow rate and t_N the net retention time. At infinite dilution and in the case of adsorption phenomena only, the free energy of adsorption (ΔG_a) is related to V_N in the following manner:

$$-\Delta G_a = RT \ln V_N + C$$

where R is the gas constant, T is the column temperature and C is a constant which takes into account the weight and specific surface area of the packing material and the standard states of the probes in the mobile and the adsorbed phases[16].

London dispersion interactions. The potential of solid materials to undergo London dispersion interactions is usually described by the dispersive component of the surface energy (γ_S^d). A standard method to determine γ_S^d relies on the use of the n-alkane series[17]. In practice, for these probes, ΔG_a or simply $RT \ln V_N$ values were plotted against n_C, the number of carbon atoms in the series. The slope of the linear correlation

is referred to ΔG^{CH2}, the free energy of adsorption of a methylene group, from which γ_S^d will be derived as described in the next section. *Figure 2* shows the excellent correlation obtained in the $RT \ln V_N$ versus n_C plot for both LCR and ModLCR at 25°C. The slopes are very slightly different which indicates that the dispersive properties are similar but slightly stronger in the case of the LCR resin at the test temperature.

Acid–base interactions. Several approaches have been proposed to distinguish between the dispersive and acid–base contributions to ΔG_a (ref. 18). In this work we simply rely on the approach of Brookman and Sawyer[19] in which ΔG_a (or $RT \ln V_N$) values are related to the boiling point of the injected probes. As shown above, n-alkanes produce a linear plot which will constitute a reference for London dispersion interactions. For polar probes interacting specifically with the stationary phase, ΔG_a values are expected to show a positive deviation from the linear correlation defined by the n-alkanes. Assuming that dispersive and acid–base (AB superscript) interactions are additive, the subtraction of ΔG_a^{AB} from ΔG_a is straightforward and corresponds to the vertical distance between the n-alkane reference line and the molecular probe of interest in the following manner:

$$-\Delta G_a^{AB} = -(\Delta G_a - \Delta G_a^d) = RT \ln(V_N / V_{Nref})$$

where V_N and V_{Nref} are the net retention volumes of the polar probe and a hypothetical reference n-alkane having the same boiling point (T_b), respectively. *Figure 3*
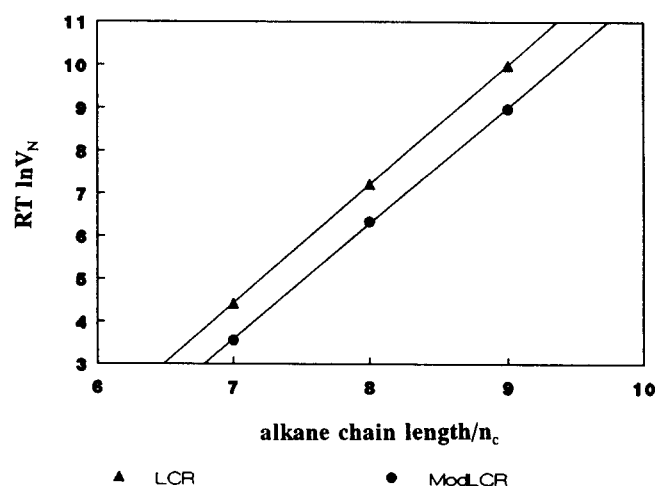

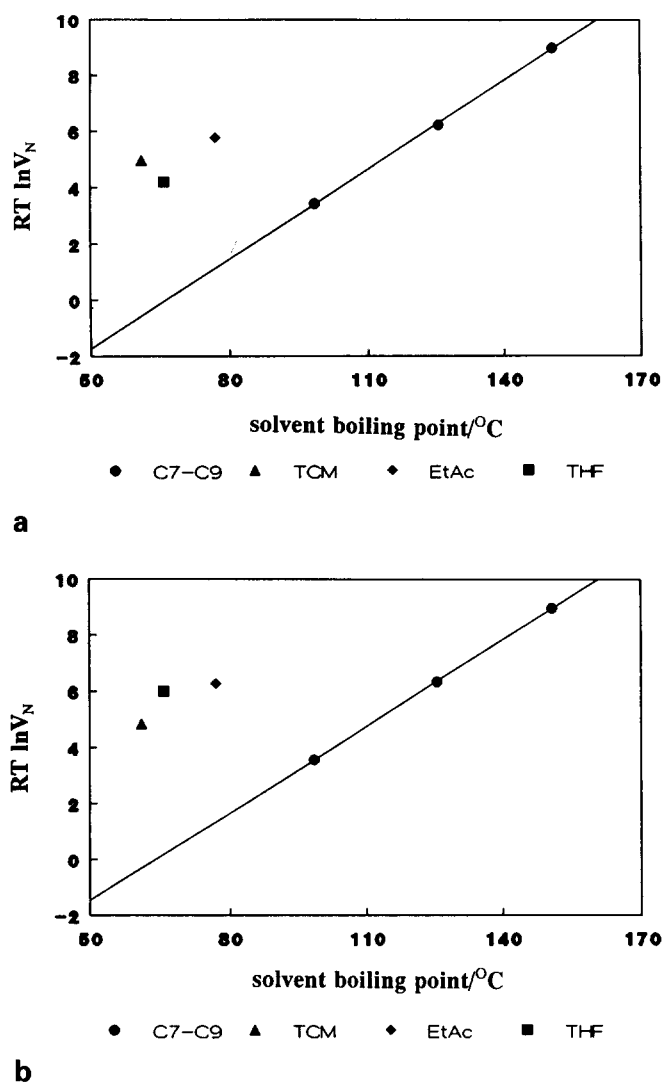**Figure 2** Adsorption of n-alkanes on LCR and ModLCR resins

a

b

Figure 3 Adsorption of n-alkanes and polar probes (trichloromethane, ethyl acetate and tetrahydrofuran) on (a) LCR and (b) ModLCR, at 25°C

Table 2 Measurements of the adsorption behaviour of the probes (at 25°C)

Material	$-\Delta G_a^{CH2}$	$-\Delta G_a^{AB}$		
		TCM	EtAc	THF
LCR	2.79	5.5	4.6	4.2
ModLCR	2.71	5.1	4.9	5.8
PMMA	2.68	6.3	4.7	4.4

ΔG_a values are in kJ mol^{-1}

modification of the LCR material by the removal of the aliphatic methacrylate component.

Determination of the materials' thermodynamic properties

Using the adsorption thermodynamics data for both the polar and non-polar probes, it is possible to derive material properties of the resins under test. Based on the Fowkes' method[20] to evaluate the dispersive contribution to the work of adhesion between two materials, Dorris and Gray[17] suggested the determination of γ_S^d using ΔG^{CH2}:

$$\gamma_S^d = (\Delta G^{CH2}/Na_{CH2})^2/4\gamma_{CH2}$$

where N is the Avogadro number, a_{CH2} the cross-sectional area of an adsorbed CH_2 group (6 Å^2) and γ_{CH2} is the surface free energy of a solid containing only methylene groups such as polyethylene ($\gamma_{CH2} = 36.8 - 0.058T$ mJ m^{-2}, T is in °C).

Following the approach of Saint-Flour and Papirer[21] we have determined acid–base constants K_D and K_A, where D and A stand for donor and acceptor, respectively, using values reported in *Table 2*:

$$-\Delta G_a^{AB} = K_D AN^* + K_A DN$$

This equation can be rewritten as:

$$-\Delta G_a^{AB}/AN^* = K_A(DN/AN^*) + K_D$$

Plotting $-\Delta G_a^{AB}/AN^*$ against (DN/AN^*) usually produces a linear correlation of which slope and intercept are K_A and K_D, respectively. The determination of these acid–base constants for LCR and ModLCR is shown in *Figure 4*. Although fundamentally this approach is not correct because it combines ΔG and Gutmann's numbers derived from ΔH terms, it has proved to be effective in monitoring changes in the surface properties of similar materials, as indicated by Papirer and co-workers[21,22].

The material properties as described by γ_S^d and acid–base constants K_D and K_A are presented in *Table 3*. For comparison with the methacrylate resins, we also report i.g.c. data on PMMA beads. Note that our value of γ_S^d for PMMA beads is comparable to that of 34 mJ m^{-2} obtained by Jacob *et al.* using IGC[23] for PMMA powder at 40°C and a flow rate of 7.6 cm^3 min^{-1}. The γ_S^d values for LCR and ModLCR are consistent with methacrylate-based polymers and comparable to that of PMMA.

shows the variation of $RT \ln V_N$ *versus* T_b for LCR and ModLCR at 25°C. $RT \ln V_N$ values for all the polar probes lie significantly above the reference lines defined by the n-alkanes. This is an indication that both resins have acidic and basic characteristics since they interact specifically with both Lewis base (THF and EtAc) and Lewis acid (TCM) species. Therefore the behaviour of both resins can be described as amphoteric in nature. A significant change in the position of the THF datum point for the LCR (*Figure 3a*) and ModLCR (*Figure 3b*) plots indicates that the ModLCR is somewhat more acidic than LCR at 25°C.

Table 2 reports the ΔG^{CH2} and ΔG_a^{AB} values for the n-alkane series and the polar probes adsorbed on LCR and ModLCR at 25°C. Comparison of the adsorption of the basic probe, THF, on LCR and on ModLCR shows that there is a significant difference of 1.6 kJ mol^{-1} at 25°C, as can be seen in *Figures 3a* and *3b*. This is in contrast to the behaviour obtained with acidic (TCM) and amphoteric (EtAc) probes. Nevertheless, the slight changes in the behaviour of these probes are consistent with a decrease in surface basicity on
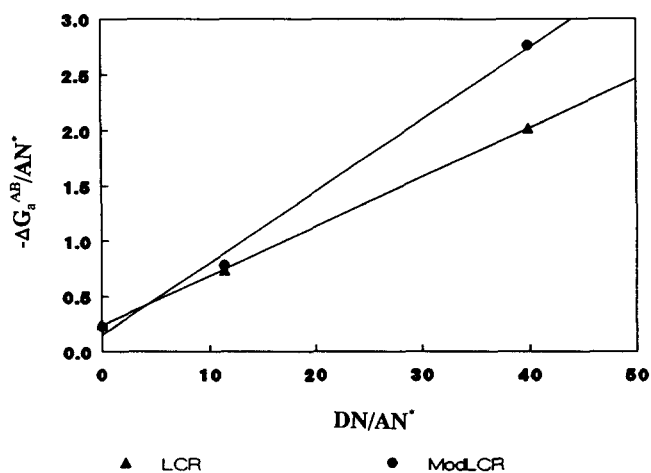
Figure 4 Evaluation of K_D and K_A (respectively the intercept and slope of the graph) for LCR and ModLCR at 25°C
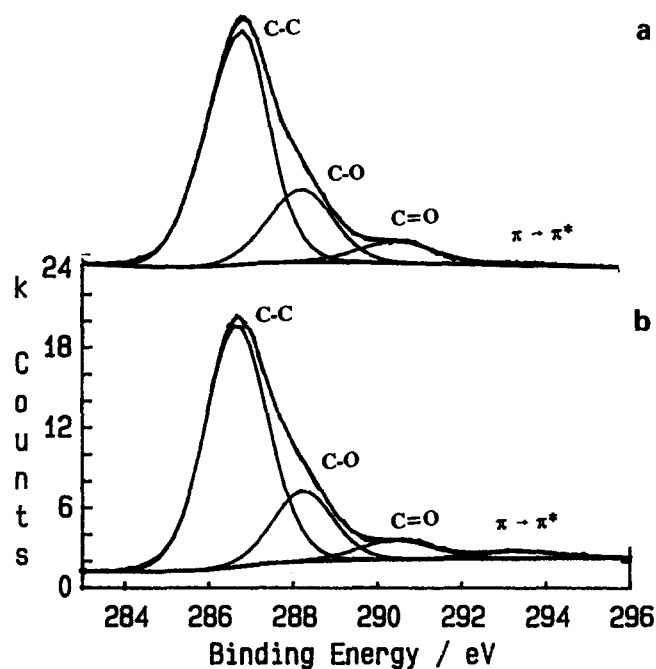
Table 3 Materials properties of LCR, ModLCR and PMMA (at 25°C)

Material	γ_S^d (mJ m^{-2})	$K_D \times 100$	$K_A \times 100$	K_D/K_A
LCR	42.0	23.7	4.5	5.3
ModLCR	39.8	15.1	6.5	2.3
PMMA	38.8	25.5	4.6	5.5

The basicity constant K_D at ambient temperature decreases in the order PMMA > LCR > ModLCR, whilst ModLCR is slightly more acidic than LCR and the reference material PMMA. The overall acid–base ratio K_D/K_A decreases in the same trend as K_D and firmly indicates that ModLCR is the less basic resin. These observations show that the reformulation of LCR is reflected in the surface properties since IGC permits the subtle variations in surface energetics to be detected.

X-ray photoelectron spectroscopy

The XPS results for the two materials are presented in *Figure 5*, which shows the C 1s spectra and the composition in terms of atomic percentage of oxygen and each carbon species. The C 1s spectra are very similar although there is a slight difference in the intensity of the $\pi \rightarrow \pi^*$ shake-up satellite, which is diagnostic of the phenyl group. The intensity of this feature, relative to the alkyl/phenyl component at 285.0 eV, is 1.5 and 4.5% for the LCR and ModLCR resins, respectively, a variability that is probably only just within the accuracy (reproducibility) of the XPS method itself. This is reflected in the quantitative surface analyses; the C/O ratios for the two resins are LCR = 3.83 and ModLCR = 4.32. Thus it is possible to distinguish between the two resins using XPS by resorting to a study of the $\pi \rightarrow \pi^*$ feature, and as expected, the C/O ratios differentiate between the two formulations quite readily. Consideration of the concentration of the individual species shown in *Figure 5* indicates the problem if any degree of chemical speciation is attempted by XPS: once again

Figure 5 C 1s XPS spectra (uncorrected for electrostatic charging) of freshly scraped surfaces of (a) LCR and (b) ModLCR. The inset table shows the surface compositions (in atomic%), and the relative intensity of the $\pi \rightarrow \pi^*$ shake-up satellite

Resin	Atomic %				Relative intensity of $\pi \rightarrow \pi^*$ satellite (%)
	O	C–C/C–H	C–O	C=O	
LCR	20.7	57.2	17.2	6.5	1.5
ModLCR	18.8	58.6	16.7	5.9	4.5

the values all fall within the 10% error bars generally quoted for XPS. The use of the $\pi \rightarrow \pi^*$ shake-up satellite is appropriate in some cases to determine the level of aromaticity, but as it only represents about 10% of the C–H/C–C intensity for a fully aromatic compound this approach was not thought to be viable. However, the situation is very different when the resins form an interface with alumina, where substantial enhancement of the EMM component is seen in the case of the LCR material[10].

CONCLUSIONS

From this study, it can be seen that IGC is a simple but effective means of studying differences in the surface chemistry of polymers. IGC can monitor changes in the surface properties of materials which might be too slight to detect using techniques such as XPS. These changes may have a profound effect on the surface thermodynamic characteristics of polymers, which is not reflected in their surface composition. The combination of IGC with XPS provides a detailed understanding of both the physics and chemistry of polymer surfaces.

The commercial resin (LCR) was found to behave in a largely amphoteric manner, but modification by removal of the EMM component led to a slight

increase in surface acidity. The data obtained were shown to be consistent with materials of this general type by comparison with PMMA.

ACKNOWLEDGEMENTS

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