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Dielectric behaviour of glycidyl methacrylate–butyl methacrylate copolymers

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Different copolymers of glycidyl methacrylate and butyl methacrylate with various compositions have been prepared by free radical polymerization. The composition of these copolymers was determined by ^{1}H nuclear magnetic resonance technique. The dielectric properties of these compositions have been studied over a frequency range from 100 Hz to 50 kHz and at different temperatures from 20 to 60° C.

1. Introduction

Acrylic copolymers that contain epoxy functional groups as pendant units have become increasingly important in many applications, e.g. coatings and biomaterials [1], and as bases for the production of photo-cross-linkable polymers [2]. The copolymers of glycidyl methacrylate can be used for controlling fouling on shiphulls and other surfaces in contact with the marine environment [3]. They could also have better mechanical and electrical properties after cross-linking of the epoxy pendant groups [3].

Dielectric measurements of some homopolymers having different alkyl methacrylate [4] and their copolymers either in solid form [5] or in dilute solution [6] were carried out to study the dielectric behaviour and the relaxation process involved during heating or increasing the applied frequency.

This work was directed to investigate the dielectric behaviour of glycidyl methacrylate–butyl methacrylate copolymers having different contents of epoxy groups.

2. Experimental details

2.1. Materials

Glycidyl methacrylate (GMA, Aldrich, England) was distilled twice under reduced pressure. Butyl methacrylate (BuMA, Aldrich) was used after distillation under reduced pressure. 2,2-Azobisisobutyronitrile (AIBN) initiator (Merck, West Germany). It was recrystallized twice for methanol (m.p. 105° C).

2.2. Copolymerization procedure

Ampoules of pyrex glass were charged with the monomer mixtures, the solvent and the initiator (AIBN). The ampoules were then cooled and closed with a rubber stopper through which passed a needle to be used for purified nitrogen bubbling. The copolymerization was carried out in a water thermostat adjusted to 65° C with periodical stirring. After around 6 h the reaction was stopped by opening the glass ampoules and pouring the contents into a large excess of cold methanol. The copolymers obtained were purified by reprecipitation from acetone solution in a mixture of methanol/water (1 : 1 volume). The precipitated copolymers were dried to constant weight in a vacuum oven at 40° C.

Butyl methacrylate homopolymer, was prepared in a similar manner.

2.3. Preparation of the copolymer films

Homopolymer (5 g) and different copolymers (5 g) were separately dissolved in 100 ml distilled chloroform solution. The dry films of these homopolymer and copolymers were obtained by casting their chloroform solution on a mercury surface, then drying in a vacuum oven at room temperature for about 10 d (film thickness ~ 2 mm).

2.4. Dielectrical measurements

The permittivity, ε', and dielectric loss, ε'', were measured using an NF Schering bridge-type decameter in the frequency range between 100 Hz and 50 kHz. A guard-ring capacitor type NFM/5T was used. The accuracy of the measurements of ε' was $\pm 1\%$ while for ε'' it was $\pm 2\%$. A description of the instrument and methods used for measurements and calculations are given in the instruction sheet by Wiss. Techn. Werkstten. Weilheim. OB. West Germany (WTW) [7]. Measurements were carried out at temperatures between 20 and 60° C using an ultrathermostat.

2.5. Conductivity measurements

To measure the d.c. conductivity, the direct current power supply unit GMU 516/01 (Philips, Holland) was used. This gives a stable d.c. voltage between 0 and 200 V with a maximum permissible loading current of 1 mA. The voltage across the sample and the current flowing through it were measured using a multimeter

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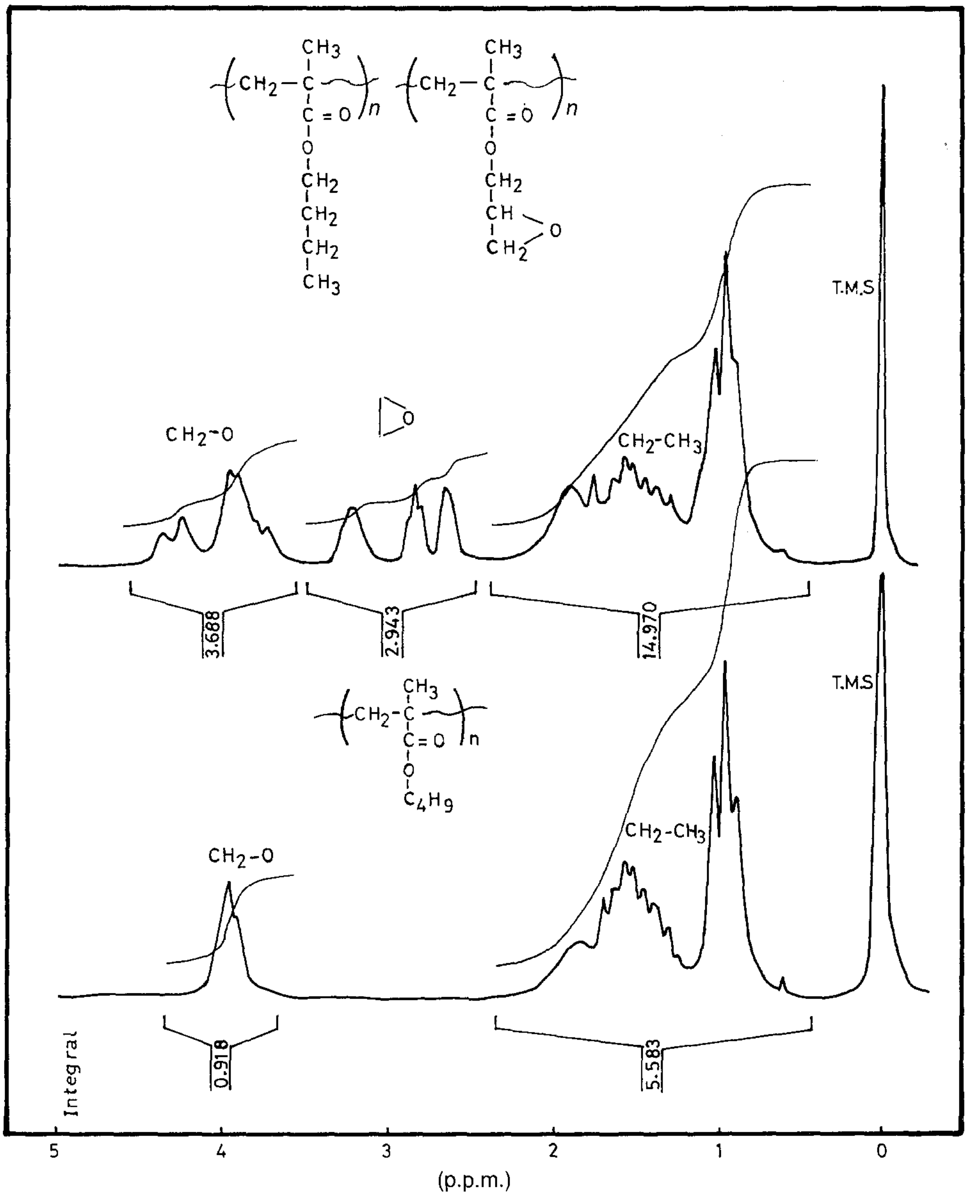

Figure 1 ¹H NMR spectra of butyl methacrylate homopolymer and glycidyl methacrylate–butyl methacrylate copolymer (copolymer 3).

type WRI BN 1050 from Rhode & Schwarz, West Germany.

2.6. Spectral measurements

The compositions of the copolymers were determined using ¹H nuclear magnetic resonance (NMR). BRUKER. W.H. 90 MHz Spectrometer (West Germany).

3. Results and discussion

Polybutyl methacrylate and copolymers having different concentrations of glycidyl methacrylate and butyl methacrylate were prepared in benzene solution at 65° C in the presence of AIBN as initiator. The total concentration of both monomers was $2\,\mathrm{mol\,l^{-1}}$; the two monomers are incorporated into the copolymers depending on their relative concentrations and reactivities [8]. The composition of the copolymers of glycidyl methacrylate–butyl methacrylate were determined quantitatively by ¹H NMR spectrometry as shown in Tables I and II. The spectra of the homopolybutyl methacrylate and that of the used copolymers (copolymer 3) are given in Fig. 1. The calculated copolymer compositions are depicted in Table III.

For butyl methacrylate homopolymer and the different investigated copolymer samples, the frequency dependence of permittivity, ε', and dielectric loss, ε'', at various temperatures are shown in Fig. 2. For butyl methacrylate homopolymer, ε' and ε'' at 100 Hz are comparable with those found in the literature [9]. ε' is found to decrease by increasing the applied frequency, f. The rate of this decrease becomes higher with increasing temperature.

From the absorption curves relating ε' and $\log f$ it is found that there is a peak whose maximum lies around 1 kHz as shown in Fig. 2. This peak is found to be independent of either temperature or the concentration of copolymer in the sample leading to the

TABLE I Chemical shifts of butyl methacrylate homopolymer

Resonance signal δ (p.p.m.)	Proton	Peak area integration	Assignment
0.8–2.4	12 H	5.583	CH_3-CH_2-CH_2 CH_2-$\overset{CH_3}{C}$
3.8–4.4	2 H	0.918	CH_2-O

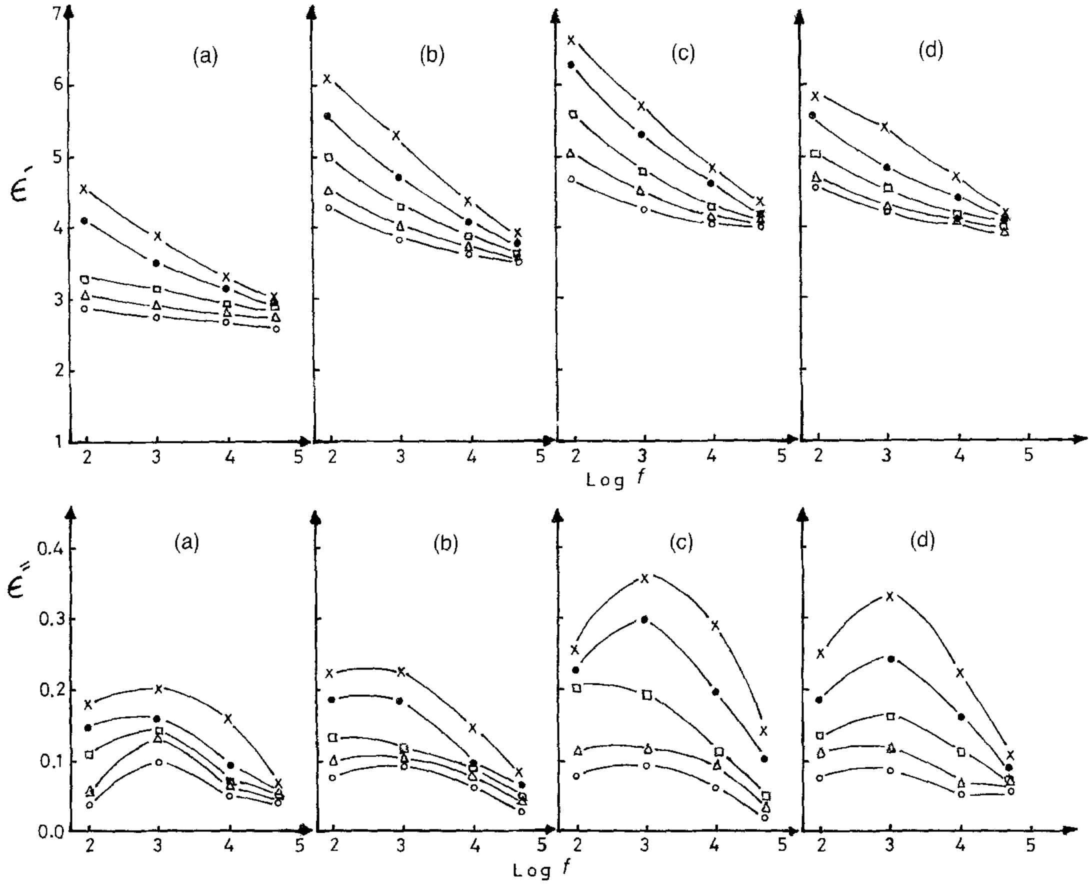

Figure 2 Variation of the permittivity ε' and dielectric loss, ε'', with frequency at different temperatures, for (a) homobutyl methacrylate (b) (GMA-BuMA) copolymer 22.2 : 77.8, (c) (GMA-BuMA) copolymer 32 : 68, (d) (GMA-BuMA) copolymer 53.55 : 46.45. (x) 60° C, (●) 50° C, (□) 40° C, (△) 30° C, (○) 20° C.

Maxwell–Wagner effect [10]. This effect may be due to an a.c. current which is in phase with the applied potential. This current results from the difference in the conductivities and the permittivities of the different constituents of the copolymer samples. Anyhow, it is worth checking that these losses in that range of frequency are not due to d.c. conductivity. Ohm's law was applied to direct currents flowing through the samples at different voltages ranging from 0 to 195 V. No detectable current is seen to flow through the samples, indicating that they have no d.c. conductivity. From Fig. 2 it is also seen that the increase in the epoxy content in the copolymer samples may be the cause of the increase in permittivities and in Maxwell–Wagner losses which are more detectable at higher temperatures. This increase is

TABLE II Chemical shifts of glycidyl methacrylate–butyl methacrylate copolymers

Resonance signal, δ (p.p.m.)	Proton	Assignment	Remarks
		$CH_2\text{-}\overset{CH_3}{\overset{\vert}{C}}$	5 GMA
0.8–2.3	17 H	$CH_2\text{-}\overset{CH_3}{\overset{\vert}{C}}$ + $CH_2\text{-}CH_2\text{-}CH_3$	12 BuMA
2.4–3.6	3 H	$\underset{O}{CH_2\text{-}CH}$	3 GMA
3.8–4.4	4 H	$CH_2\text{-}O$ $CH_2\text{-}O$	2 BuMA 2 GMA

TABLE III Initial monomer concentration and molar composition of gycidyl methacrylate–butyl methacrylate copolymers

Copolymer	Initial concentration (mol %)		Peak area intergration			Copolymer composition	
	M_1 (GMA)	M_2 (BuMA)	3 H	17 H	4 H	(mol l^{-1})	
1	20	80	0.679	10.002	2.162	22.2	77.8
2	30	70	4.069	39.447	8.806	32	68
3	50	50	2.943	14.970	3.688	53.55	46.45

Total concentration = 2 mol l^{-1}; solvent, benzene. Temperature, 65° C; initiator, AIBN.

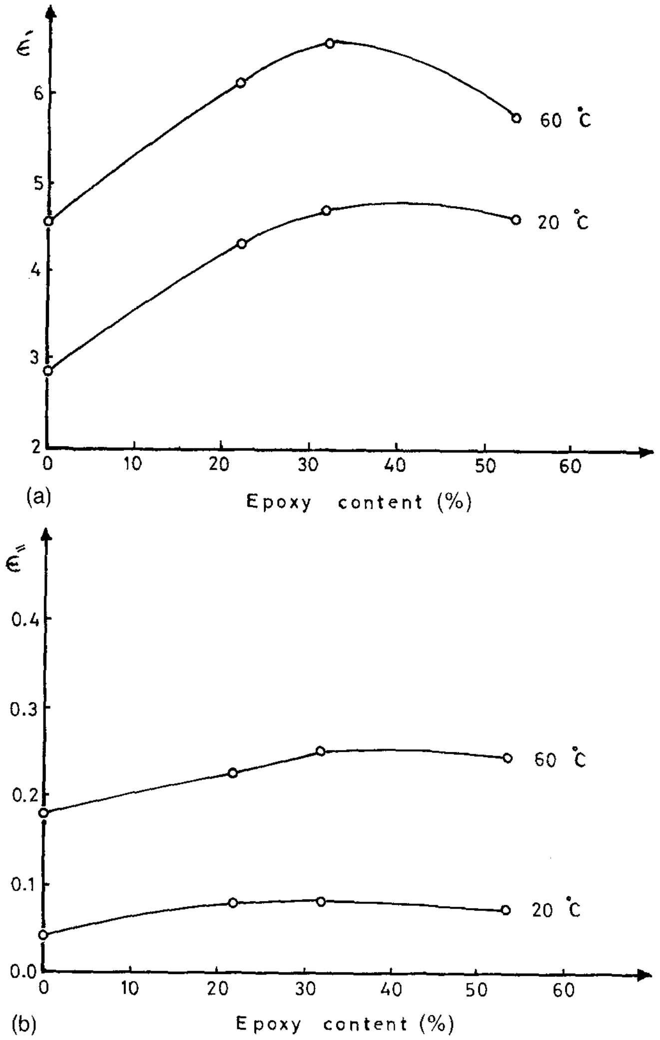

Figure 3 The dependence of (a) permittivity, ε', and (b) dielectric loss, ε'', on the epoxy contents in glycidyl methacrylate–butyl methacrylate copolymers at 20 and 60° C.

only noticed up to 32% epoxy concentration. When the concentration of epoxy in the copolymer samples reaches 53.55%, ε' and ε'' start to decrease as shown in Fig. 3 at a frequency of 100 Hz. This decrease, which is supposed to start at that concentration, may be due to the formation of partial cross-linking between some of the epoxy rings, which is followed by a decrease in ε' and ε''.

For all the investigated copolymer samples, it was also found that ε' and ε'' increase with increasing temperature of the samples as shown in Fig. 2. This trend is similar to that found before in the case of some polyamides [11]. So, it could be concluded that ε' and ε'' increase on increasing the epoxy content in the glycidyl methacrylate–butyl methacrylate copolymers up to certain concentrations, and then they decline.

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