



Dielectric Relaxation Behaviour of Glycidyl Methacrylate (GMA) and 3-methoxy-4-(2-hydroxy-3-methacryloyloxy-propoxy) Benzaldehyde (MH) and their copolymers.

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KEYWORDS

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ABSTRACT:

Research has been done on the dielectric characteristics of GMA-MH and its copolymers at a wide range of frequencies, including 100Hz to 100kHz and room temperature to 180°C. It has been investigated how the dielectric loss and dielectric constant change with frequency, and temperature. The dielectric constant falls with temperature and frequency increases. The data was computed and examined by the AC Conductivity. The AC conductivity rises with rising frequency and temperature. Glycidyl methacrylate copolymers with epoxy functional groups as pendant units have become increasingly important in a variety of applications. For instance. The epoxy pendant group can enhance the mechanical and electrical characteristics of coatings and biomaterials. The present report is centred on the methodical examination of GMA, MH, and their copolymers' dielectric properties with respect to temperature and frequency. Two relaxation peaks are present, one at a temperature marginally above room temperature (β -relaxation) and the other at a higher one (α -relaxation). The main chain segments' micro Brownian movement (α -relaxation) and the epoxy and carbonyl pendant groups are believed to be the causes of the peaks. MH is restricted to a single set of i.e., the α -relaxation peaks. The dielectric property consistently decreases as the non-polar MH content rises. The results are discussed by studying the segmental motion of the main chain and increasing the MH content in copolymers and pendant groups within the copolymer.

1. INTRODUCTION

The reactive epoxide ring present in glycidyl methacrylate (GMA) based copolymers is drawing a lot of attention because it allows the copolymer to participate in a variety of chemical reactions and can be used to improve mechanical and electrical properties after the epoxy pendant group is cross-linked[1-2]. With a broad range of industrial applications, glycidyl methacrylate, or GMA, is an intriguing functional monomer. Surface coatings have been made using polymers based on GMA[3], leather adhesives[4], Pharmaceutical drug delivery[5] dental composites, super absorbents, ion exchanger resin, nonlinear optical material [6] compatibilizer and surface modifier. the easily transformable epoxy group present in GMA-based polymers allows for a wide range of chemical reactions, which is their main advantage. The base

polymer can be chemically modified by the interaction of an oxidane group with different nucleophiles; long alkyl side chains can crystallise despite having an amorphous backbone, which reduces their oil absorbency. Amorphous copolymers can be produced by using the technique of copolymerization with additional monomers to lessen the unwanted effect [7]. Epoxy functional groups as pendant units in acrylic copolymers have gained importance in a variety of applications, such as coatings and biomaterials, as well as serving as building blocks for the synthesis of photo-cross-linkage polymers. Glycidyl methacrylate copolymers can be utilised to prevent fouling on ship hulls and other surfaces that come into touch with the sea. After the epoxy pendant groups are cross-linked, they may also have improved electrical and mechanical properties[8]. The dielectric behaviour and relaxation process involved in heating with an increase in applied



frequency were studied by conducting dielectric measurements of a few homopolymers with various alkyl methacrylate and their copolymers, either in solid form or in diluted solution[9]

This present work was directed to investigate the dielectric behavior of Glycidylmethacrylate(GMA)-3-methoxy-4-(2-hydroxy-3-methacryloxy-propoxy) Benzaldehyde (MH)Copolymers having different compositions were carried out. Polymers of GMA and its modified forms were found to have specific applications. Hence GMA has been modified to obtain 3-methoxy-4-(2-hydroxy-3-methacryloxy-propoxy) Benzaldehyde (MH) containing aldehyde functional group by condensing it with vanillin. The aim of this manuscript is to investigate the relaxation process of GMA- MH copolymers.

2.METHODOLOGY- EXPERIMENTAL

The powdered homopolymers and their copolymer samples of GMA and MH were utilised to create pellets with the following dimensions: 1-2 mm in thickness and 1 cm in diameter.Using a three terminal cell and a GR-1620A capacitance measuring assembly, the dielectric constant and loss were determined for these pellets. A CERAMO (REX-P90) temperature controller is used to regulate the temperature in the temperature range of room temperature to 180°C, as well as in the frequency range of 200 Hz to 105 Hz. The glass transition temperature (Tg) was ascertained using the Mettler Toledo Sr System's Differential Scanning Calorimetry (DSC) technique. The dielectric constant and loss were measured with an overall accuracy of 1% and 2%, respectively..

3.RESULTS &DISCUSSION

Dielectric Analysis

The study of dielectric relaxation provides valuable and sufficient information about the orientational and translational motion of mobile charge carriers in the dielectric. The dielectric constant (ϵ') changes with the frequency dispersion of the applied field and is also dependent on the physical properties of the dielectric. The variation of dielectric constant (ϵ') arose in different frequency domains due to different dielectric polarizations such as ionic, electronic, interfacial and orientation. The dielectric constant (ϵ') expresses the charge stored in the material at the dielectric loss ϵ'' . It

expresses the loss of energy during the rapid reversal of the electric field [10] .

The complex dielectric permittivity ϵ^* can be calculated by $\epsilon^* = \epsilon' - j \epsilon''$. Where ϵ' is the real(relative permittivity or dielectric constant) and ϵ'' is the imaginary(dielectric loss) parts of the complex dielectric permittivity, The dielectric permittivity analysis provides information on the transport properties of ions in the polymer. The real part of the permittivity measures the alignment of dipoles and the imaginary part represents required to align the dipoles and to move ions [11]. The low frequency dispersion region is due to the accumulation of charges at the electrode-polymer interface. In the low frequency region, conductance losses predominated due to unavoidable electrode polarization. In the high frequency region, both spectra show decreasing magnitude that is saturated at very high frequency in the frequency range studied. This is due to the rapid, periodic reversal of field applied at the electrode-polymer interface which reduces the contribution of carriers to the dielectric permittivity. The formula for calculating the complex dielectric permittivity ϵ^* is $\epsilon^* = \epsilon' - j \epsilon''$. Dielectric permittivity analysis provides information on the transport properties of ions in a polymer, where ϵ' is the imaginary (dielectric loss) part of the complex dielectric permittivity and ϵ' is the real (relative permittivity or dielectric constant) part. Permittivity's real component measures dipole alignment, while its imaginary component indicates the necessity of both ion movement and dipole alignment [11].The electrode-polymer interface is the site of the charge accumulation that results in the low-frequency dispersion region. Because of the electrodes' inevitable polarisation, conduction losses predominated in the low frequency range. Both spectra exhibit a decreasing magnitude in the high-frequency region, which is saturated at a very high frequency within the investigated frequency range.

Table 1 lists the findings of the dielectric constant (ϵ) measurements for the room temperature homopolymers of GMA and MH as well as their copolymers at various compositions. In every instance, the ϵ decreases in a typical manner with frequency (Fig. 1a). The graph (Fig. 1b) illustrates the nonlinear variation of $\tan\delta$ at room temperature as a function of



frequency. This results in a decreasing magnitude peak at 1 kHz for GMA and MH-GMA (10/90, 30/70, and 50/50), respectively. Regarding MH, a typical behaviour is observed.

The findings regarding the dielectric constant (ϵ) measurements at room temperature for GMA and MH homopolymers as well as their copolymers at various compositions

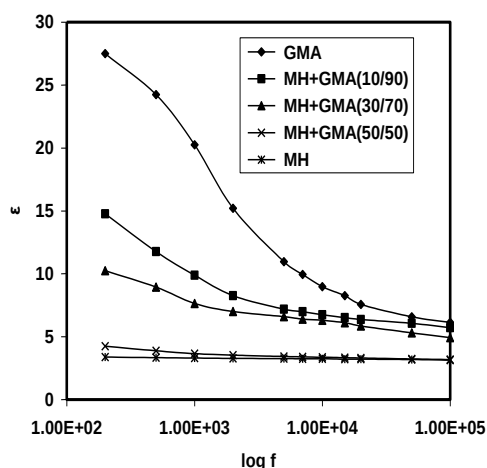


Fig.1(a)-Variation of ϵ with log f for GMA, MH and their copolymers

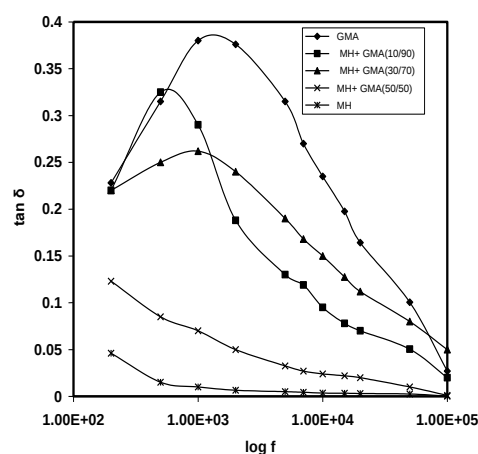


Fig.1 (b)-Variation of $\tan \delta$ with log f for GMA, MH and their copolymers

Table 1. Values of dielectric constant (ϵ) for GMA, MH and their copolymers at room temperature

S.NO	SAMPLE (wt %)	ϵ at 200Hz	ϵ at 100kHz
1	GMA	27.50	6.15
2	90GMA -10MH	14.76	5.71
3	70GMA-30 MH	10.25	4.92
4	50GMA-50 MH	4.25	3.18
5	MH	3.37	3.14

For frequencies below 10 KHz, the higher magnitudes of ϵ are ascribed to spurious effects and space charge polarisation. Beyond 10 KHz, the combined effect of various polarisation types is responsible for the ϵ [12]. The peak appearance in $\tan \delta$ at 1 KHz is attributed to interfacial relaxation (Maxwell-Wagner effect) [13]. The variation of ϵ and $\tan \delta$ at room temperature as a function of frequency show a constant decreasing trend with increase of non-polar content of MH.

The typical variation of ϵ and $\tan \delta$ with temperature for GMA at four different frequencies is depicted in Figures 2(a&b). The data indicates that there are two sets of peaks in the temperature variation of ϵ and $\tan \delta$: one set is slightly above room temperature, while the other is above the glass transition temperature. The ϵ versus temperature plot shows that the peaks materialised at the same temperature. A shift in relaxation frequencies is only seen at higher

temperatures when $\tan \delta$ is plotted against temperature. However, at room temperature, the difference might not be noticeable. Copolymers of MH-GMA (10/90, 30/70, and 50/50) exhibit comparable behaviour. However, at high temperatures, MH only exhibits one set of peaks.

The β - and α - relaxations are responsible for the high and low temperature peaks, respectively. The micro-Brownian motion of the pendant epoxy and carbonyl groups of the GMA polymer backbone, combined with the local distortion of the main chain, causes β - relaxation peaks to appear without any shift in peak positions with frequency. Segmental motion of molecular chains is known to cause α - relaxation peak, or dipolar relaxation, above T_g with shift in peak position [14–16]. For higher frequencies, the peaks further shift towards higher temperatures. $\tan \delta$ was observed to rise with increasing frequency at each temperature until it reached a maximum value



($\tan\delta_{\max}$), after which it began to decrease with additional frequency increases. Low frequencies allow dipoles to alter the electric field's phase, which results in minimal power losses. The maximum power loss occurs when the frequency increases because the dipole cannot reorient in the allotted time and becomes out of

phase with the electric field. The internal friction causes heat to be produced. Moreover, a higher frequency means that there is less time for a significant dipole moment, which lowers power losses. Moreover, a decrease in the maximum of $\tan\delta$ is noted.

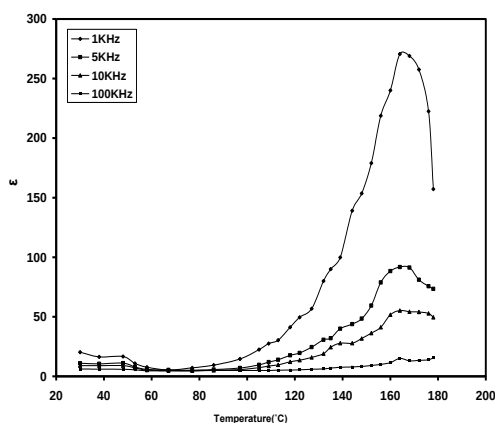
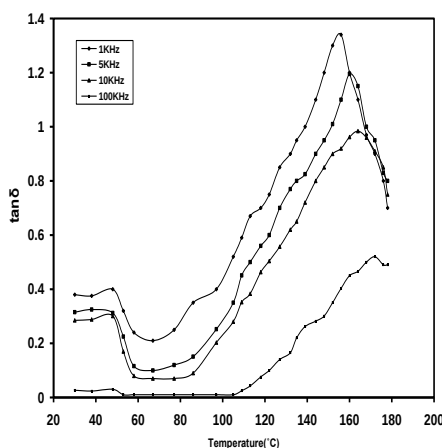
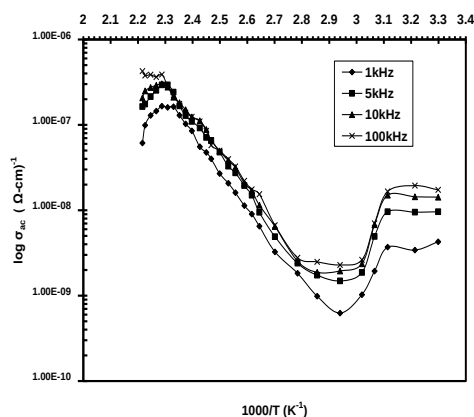
Fig. 2(a) - Variation of ϵ with temperature for GMAFig. 2(b) - Variation of $\tan \delta$ with temperature for GMA

Fig. 2(c) - Variation of ac conductivity with reciprocal temperature for GMA

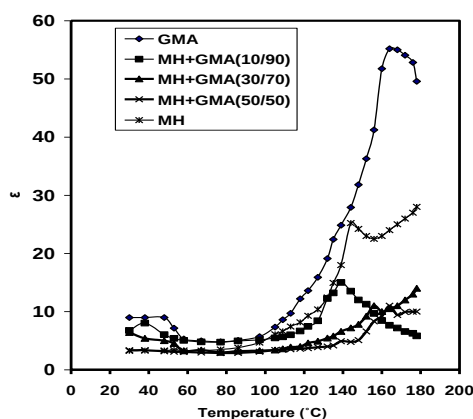
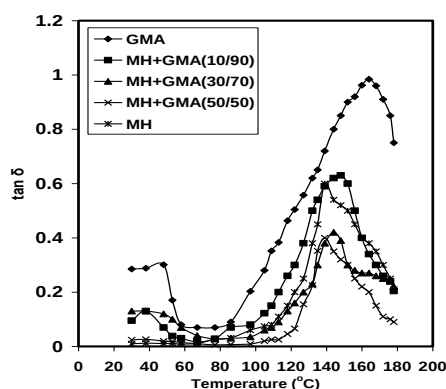
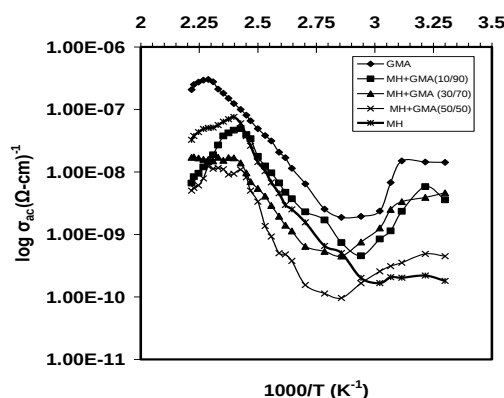
Fig. 3- Variation of ϵ with temperature for GMA, MH and their copolymers at 10 kHzFig. 4- Variation of $\tan \delta$ with temperature for GMA, MH and their copolymers at 10 kHz

Fig. 5- Variation of ac conductivity with reciprocal temperature for GMA, MH and their copolymers at 10kHz



Additionally, it is clear from fig. 2(a&b) that the dielectric constant rises as temperature does. The dielectric behaviour of the polymers is clearly determined by the charge distribution and the statistical thermal motion of the polar groups. In the case of polar polymers, the dielectric constant begins to decrease at a particular critical frequency, and the dipole molecules are unable to orient themselves at lower temperatures. The known phenomenon of increasing polarisation with increasing temperature, which is seen in many materials, may be connected to the dielectric constant's temperature increase[21–25]. Raising the temperature will enhance the segmental mobility of the polymer, which will help with the orientation of the dipoles and raise the dielectric constant.

It is also evident that strong temperature dependence begins for lower frequencies at lower temperatures and for higher frequencies at higher temperatures. The temperature coefficient of dielectric constant ($TC\epsilon$) is computed for 1kHz at different temperature intervals (Table-2) in order to comprehend the nature of temperature dependence. Using the formula $TC\epsilon = 1/\epsilon \cdot m.p. \cdot d\epsilon/dt$, the temperature coefficient of dielectric constant ($TC\epsilon$) has been calculated from room temperature T_{rt} to the glass transition temperature T_g . The dielectric constant at the midpoint of T_g and T_{rt} is denoted by $\epsilon_{m.p.}$, where $d\epsilon$ represents the difference between the dielectric constants.

Table 2. Variation of temperature coefficient of dielectric constant ($TC\epsilon$) for GMA at 1kHz.

Sno	Temperature(°C)	$TC\epsilon$ (°C) ⁻¹
1	30-48	0.013
2	48-78	-0.056
3	78-105	0.038
4	105-132	0.053
5	132-165	0.059
6	165-178	-0.030

The variation of dielectric property of the present polymer system is shown in Figs.3, 4 ,5. The following conclusions are drawn:

1.Variation in ϵ with increasing temperature shows a persistent downward trend as MH content increases in the series at all frequencies. Except for 1 kHz in MH+GMA(50/50), for which case an enhanced variation is observed at elevated temperatures. In case of MH there is a slow variation at low temperatures and large variation at elevated temperatures beyond 100°C.

2.Variation in $\tan \delta$ with temperature shows a an ongoing downward trend as MH content rises from GMA homopolymer to MH+GMA (50/50) copolymer at all frequencies. But for MH though $\tan \delta$ values are less than that for GMA, the values are higher than MH+GMA copolymers of different compositions. There could be some kind of compensating effect in copolymers of various compositions for decreasing

trend in $\tan \delta$. The amplitude of relaxation peaks obtained for various frequencies as a function of temperature decrease with increasing content of MH, due to decrease in polar nature from GMA to MH.

AC Conductivity

Many studies have been conducted on the electrical conductivity of polymers in order to understand the nature of charge transfer in the materials. The micro electronics industry is interested in polymers because they are low conductivity, good insulators. Polymers' electrical conductivity is dependent on the charge carriers that are produced thermally. The variation of AC conductivity with reciprocal temperature is depicted in Figure 2(c).

The plot displays two conductivity regions that are temperature and frequency dependent up to 85 °C and frequency independent between 85 °C and 160 °C. Above this temperature, conductivity varies randomly, signifying the disordered state of the copolymer. Figure



2(c) shows that the AC conductivity of GMA is one order of magnitude higher than that of the other samples under investigation. This trend may be caused by the polarity of GMA's declining content in copolymers. With an increase in MH content, the activation energies measured from Arrhenius plots at high temperatures (130–150 degrees Celsius) rise. This pattern might result from the polar copolymers' declining GMA content[19–21].

The change in ac conductivity for GMA with temperature reciprocal. Since the conductivity was calculated using the dielectric data, the variation with temperature represents the combined effect of ϵ and $\tan\delta$. The formula $\sigma_{ac} = \omega \epsilon' \epsilon'' \tan\delta$ can be used to determine the AC conductivity, where $\epsilon_0 = 8.854 \times 10^{-12}$ F/m represents the absolute permittivity of the free space and $\omega = 2\pi f$ represents the angular frequency. The slope of the linear portion of the graph in the temperature range of 130°C to 150°C is used to estimate the activation energy for the conduction process. 1.03 eV is the obtained activation energy.

4.CONCLUSION

The dielectric characteristics of GMA-MH homopolymers and their copolymers have been studied. Furthermore, it was found that ϵ' and ϵ'' increased along with the temperature of the samples. This pattern is similar to the glycidyl methacrylate-butyl methacrylate copolymer scenario. Thus, it follows that ϵ' and ϵ'' increase in proportion to the epoxy content in the GMA-MH copolymer. Together with the assessment and analysis of AC conductivity, the conduction mechanism, molecular movements and relaxations inside the polymer, and the character of ϵ' 's temperature dependence are also looked at.

At room temperature and at elevated temperatures, two sets of relaxation peaks are observed. The peaks are ascribed to micro Brownian motion of the copolymer's main chain segments (α -relaxation) and epoxy and carbonyl pendant groups. However, in the case of MH, α - relaxation peaks a single set are seen. With an increase in non-polar MH content, a steady decline in the dielectric property has been noted. The findings are examined in relation to the growing MH

content in copolymers, the presence of pendant groups in the copolymer, and the segmental motion of the copolymer's main chain.

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