

Dielectric Behavior of Alternating Ethylene, Propylene, and Carbon Monoxide Co- and Terpolymers via Impedance Spectroscopy

Saadi Abdul Jawad,¹ Adnan S. Abu-Surrah,² Mufeed Maghrabi,¹ Ziad Khattari¹

¹Department of Physics, Hashemite University, Zarqa-13115, Jordan

²Department of Chemistry, Hashemite University, Zarqa-13115, Jordan

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ABSTRACT: Dielectric behavior of alternating ethylene–carbon monoxide (ECO) and ethylene–carbon monoxide/propylene–carbon monoxide elastic terpolymer (EPEC-48) (48% mole ratio of ECO) have been investigated by impedance spectroscopy. At intermediate frequencies, the co- and terpolymer samples display a relaxation peak with an activation energy of 1.40 and 1.12 eV, respectively, due to a rotational motion of the carbonyl groups in the relatively more polar ECO block. However, at low frequency, a relaxation peak was observed only in the EPEC-48 terpolymer im-

pedance and admittance spectra due to the rotational motion of the polar groups of propylene–carbon monoxide (PCO) block which is attached to ECO repeating units. In addition, it has been found that below 100°C the ECO material is highly resistive, and both dielectric constant and loss factor are dependent on frequency and temperature. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2020–2026, 2012

Key words: impedance; dielectric constant; loss factor; alternating polyketone; copolymers; terpolymers

INTRODUCTION

After about 60 years of research, ethylene-*alt*-carbon monoxide copolymer (ECO) and related terpolymers have grown up and reached industrial ranges like Carilon[®] from Shell¹ or Ketonex[®] from British Petroleum.^{2–4} The catalysts chosen are based on palladium(II) complexes, together with diphosphine chelate ligands. One of the most significant benefits of the olefin-CO copolymerization is the cost of the monomers. Simple olefins and carbon monoxide are abundant and inexpensive. ECO alternating copolymers have physical and mechanical properties in some range comparable with nylon.⁵ In addition, terpolymers of ethylene, propylene, and carbon monoxide are examples for the combination of a polar polyolefines with polar functions to prepare polyolefines with intrinsic hydrophilic properties.

Developments in palladium(II) catalyzed copolymerization of olefins with carbon monoxide that led to co- and terpolymers with highly defined molecular weight, and stereo- and regioregularity.^{6–9} The choice of appropriate reaction conditions and the design of metal catalyst allow tailoring the copolymer structure and, as a result, the bulk properties of the

material: from highly crystalline thermoplastics to high molecular weight elastomers. Ethylene-CO/propylene-CO (EPEC) terpolymers containing less than $\cong 30$ mol % PCO are typical thermoplastic materials^{10,11} whereas EPECs with a propylene content $> \cong 50$ mol % display thermoplastic elastic behavior.¹²

The elasticity of these materials is due to the block-structure of the polymeric chain, which leads to a phase-separated morphology consisting of a continuous flexible phase and a dispersed hard phase. For EPEC terpolymers soft and hard phases can be assigned to the constituent materials on the basis of the material properties of the pure polymers. Pure propylene-*alt*-carbon monoxide (PCO) is mainly amorphous with a glass transition temperature T_g close to room temperature.¹³ Thus, the PCO-block will form the soft matrix. Since the regular ECO chain¹⁴ can easily crystallize, it is likely that the ECO chain segments create the dispersed, hard phase, which mainly consists of small ECO crystallites or parallel-aligned ECO chain segments.

Recently, we reported on the dielectric behavior of the thermoplastic terpolymer, ethylene–carbon monoxide/propylene–carbon monoxide with 69% ECO units (EPEC-69) using impedance spectroscopy.¹⁵ Two distinct regions were observed, the first is characterized by the slight change in the ac and dc conductivity with temperature and frequency at temperatures less than its T_m . Above this temperature (the second region) a dramatic change in all the dielectric variables with

Correspondence to: S. Abdul Jawad (saadi@hu.edu.jo).

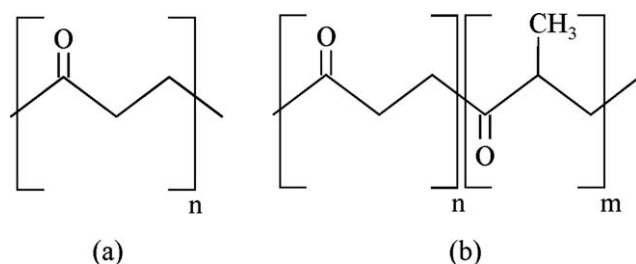


Figure 1 Structure of (a) alternating ethylene-carbon monoxide copolymer (ECO), (b) ethylene-carbon monoxide/propylene-carbon monoxide elastic terpolymer (EPEC-48).

frequency and temperature was observed. In the present work we report on the dielectric behavior of both ethylene-carbon monoxide alternating copolymer (ECO) and the terpolymer, ethylene-carbon monoxide/propylene-carbon monoxide thermoplastic elastomer, with 48% ECO units (EPEC-48).

EXPERIMENTAL

Methods

Infrared spectra (KBr, cm^{-1}) were measured on a Nicolet-Magna-IR 560 Spectrophotometer. Thermal gravimetric analysis was carried out on a NETZSCH STA 409 PC LUX instrument at a heating rate of 10 K min^{-1} . Molecular weight (M_w) and molecular weight distributions (M_w/M_n) (M_w : weight average molecular weight; M_n : number average molecular weight) were measured by gel permeation chromatography (GPC) relative to polystyrene standards.

Materials

Ethylene-CO (ECO)/propylene-CO (PCO) terpolymer with 48% ECO units [Fig. 1(a)] and ethylene-CO (ECO) [Fig. 1(b)] were prepared following a previously published procedure.^{10,16}

ECO/PCO

IR spectra (neat) of the terpolymer display a strong absorption band at 1705 cm^{-1} , which can be ascribed to poly(1,4-ketone) carbonyl. GPC measurements showed that the material has a molecular weight (M_w) = 1.90×10^5 and a molecular weight distribution = 2.4. According to differential scanning calorimetry (DSC), the polymer sample exhibit a glass transition temperature (T_g) at 10.3°C and a melting transition (T_m) at 51.0°C . Thermal gravimetric analysis (TGA) indicate that the terpolymer is stable up to $\cong 400^\circ\text{C}$.

ECO

IR spectra (neat) of the copolymer display a strong stretching frequency absorption band at 1691 cm^{-1} ,

which can be ascribed to poly(1,4-ketone) carbonyl, which is at lower frequency compared with ECO/PCO. This shift can be attributed to strong dipolar interactions between the polar carbonyl groups in the alternating ethylene-CO (ECO) copolymer. DSC diagram show a glass transition temperature at 54.2°C and two melting transitions at 113.1 and 252.5°C . Thermal gravimetric analysis (TGA) indicate that the terpolymer is stable up to $\cong 407^\circ\text{C}$.

Impedance measurements

ac impedance measurements were carried out in the frequency range $1\text{--}10^5 \text{ Hz}$ and in the temperature range 30 (above T_g and less than T_m) to 140°C for EPEC 48 and to 170°C for ECO, using a Solartron-1260 impedance/gain phase analyzer with a 1296 dielectric interface. Two software packages, Z-60 and Z-View were used to maximize the performance and data handling of the system. By measuring the amplitude and the phase shift of the resulting current, one can calculate the real (Z') and imaginary (Z'') components of the complex impedance. The real and imaginary components of dielectric constant, and admittance were determined from the calculated values of Z' and Z'' .

Instruments

Infrared spectra were measured on a Nicolet-Magna-IR 560 spectrophotometer. Molecular weight and molecular weight distributions were measured by gel permeation chromatography (GPC) relative to polystyrene standards. Thermal gravimetric analysis was performed on a NETZSCH STA 409 PC LUX instrument (heating rate 10 K min^{-1}).

RESULTS AND DISCUSSION

Impedance spectroscopy

Impedance technique is suitable for the resistive and/or capacitive analysis when long range conductivity is dominated. While dielectric permittivity and modulus are appropriate only when localized relaxation dominates.¹⁷ In this study both impedance and permittivity will be discussed.

The electrical impedance spectra for EPEC-48 and ECO are shown in Figure 2(a,b), respectively. For the terpolymer, EPEC-48, four distinct regions in Z' spectrum could be observed. In the frequency range $0.1\text{--}1 \text{ Hz}$, there is steep increase in impedance at low frequency indicating that the material is highly resistive but then becomes nearly independent of frequency, followed by a significant impedance decrease as the resistance drops due to its predominant capacitive behavior. At high frequencies (more than 10^4 Hz), Z' merges for all temperatures, and

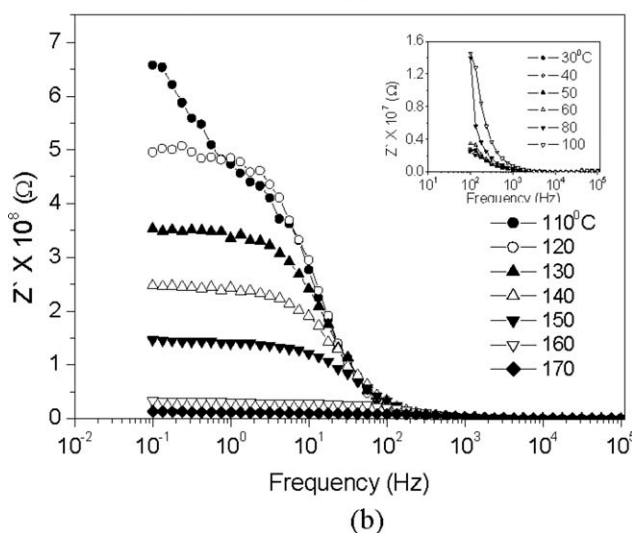
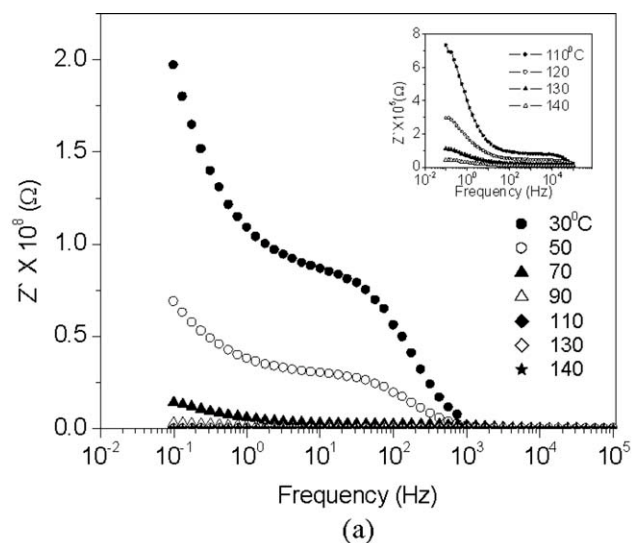


Figure 2 Frequency dependence of the real part of impedance (Z') at different temperatures (a) EPEC 48 (b) ECO.

becomes almost independent of both the frequency and the temperature indicates disappearance of space charge polarization.^{18,19}

However, for ECO copolymer, the feature of Z' spectrum is similar to that observed for the terpolymer, EPEC-48, at temperature more than 100°C and in the frequency range 10 Hz to 10⁵ Hz. However, an independent frequency region in the plot Z' versus temperature was observed in the frequency range 0.1–10 Hz, and decreases with increasing temperature. The magnitude of Z' in this region represents the bulk resistance of the material.

The plot of imaginary part of impedance for EPEC-48 [Fig. 3(a)] exhibits a well-defined peak and an indication of low frequency peak associated with the dispersion regions observed in the plot of Z' versus frequency. The peak which was observed at intermediate frequencies in both EPEC-48 and ECO decreases in magnitude with increasing temperature and shifts to a higher frequency. The existence of a

temperature-dependent electrical relaxation phenomenon could be the reason for this shift. The observation of these peaks in both co- and terpolymer suggests that this relaxation is due to a rotational motion of polar groups in the ECO segments. In the low frequency region (0.1–10 Hz) the plot of Z'' versus frequency for EPEC-48 indicates the presence of another relaxation peak. This relaxation peak is mainly due to the rotational motion of polar segments of PCO block which is attached to ethylene-CO block. However, for ECO the plot of imaginary part of impedance (Z'') versus frequency [Fig. 3(b)] shows a single relaxation peak shifts to higher frequencies with increasing temperature. The appearance of the peak at temperature above 100°C in the copolymers indicates that the polymer chains are nearly rigid below this temperature and this rigidity hinders the motion of polar segments in ECO block.

The presence of PCO block attached to ECO copolymer chain results in an increase in the elasticity of the

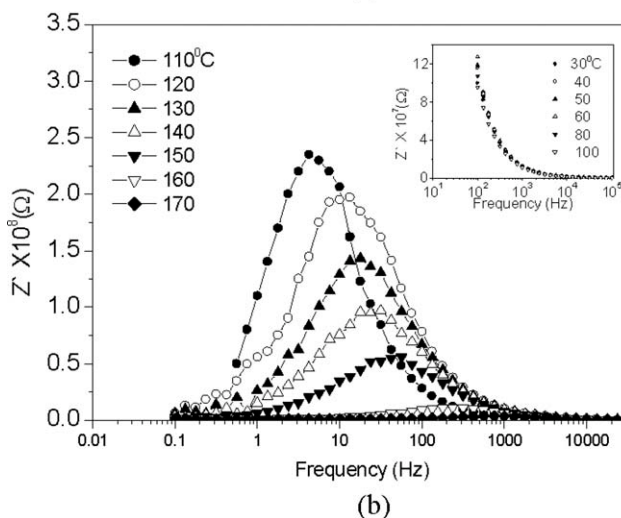
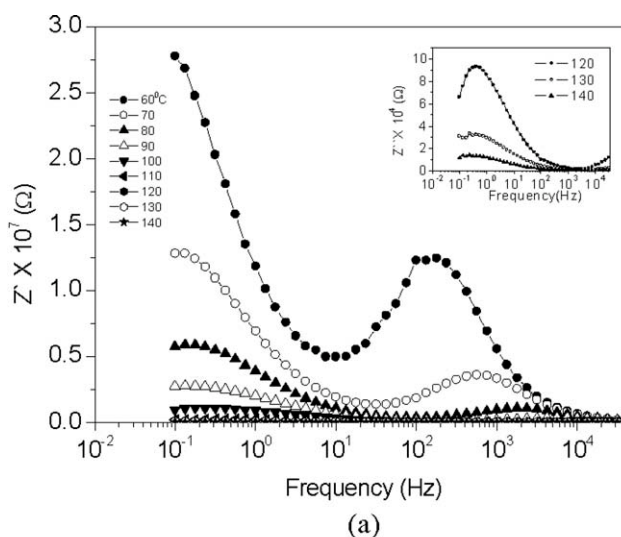


Figure 3 Frequency dependence of imaginary part of impedance (Z'') at different temperatures (a) EPEC 48 (b) ECO.

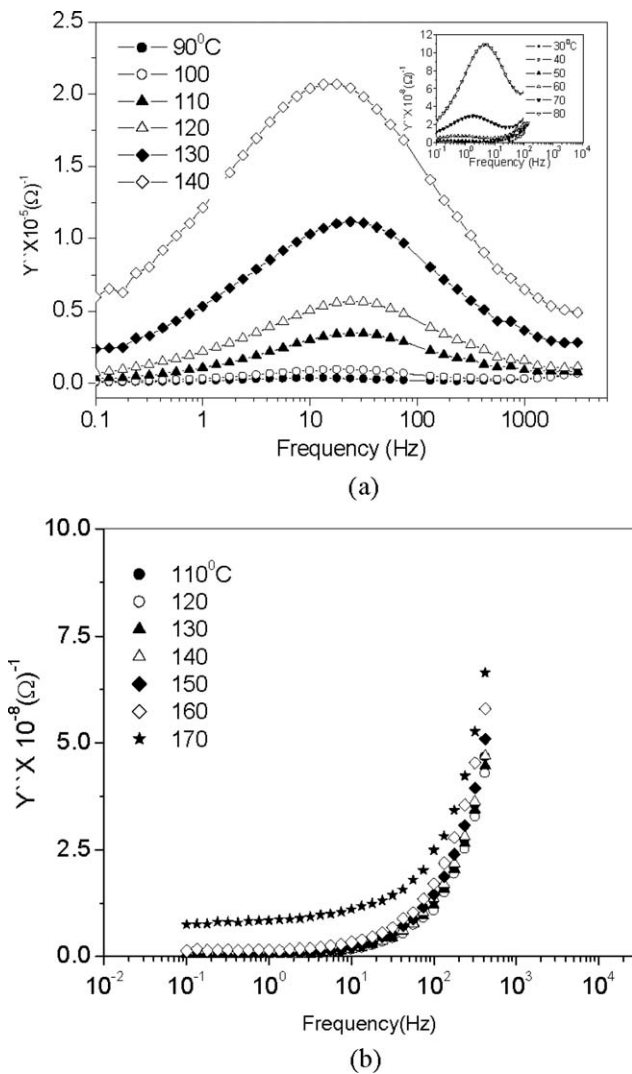


Figure 4 Frequency dependence of imaginary part of admittance (Y'') at different temperatures (a) EPEC 48 (b) ECO.

material (EPEC-48) and leads to a phase-separated morphology consisting of a continuous flexible phase and a dispersed hard phase. This will allow the polar units to rotate freely and give rise to the observed relaxation peak in the plot of Z'' versus frequency. To observe the low frequency relaxation peak in the EPEC-48 terpolymer, the bulk and the surface phenomenon effects on the dielectric dispersion at low frequencies should be separated, this can be achieved using the imaginary part of the complex admittance. The real and imaginary parts of the complex impedance are related through the relation.^{20–22}

$$Y_* = \frac{1}{Z_*} = Y' - iY''$$

$$Y' = \frac{Z'}{Z'^2 + Z''^2}$$

$$Y'' = \frac{Z''}{Z'^2 + Z''^2}$$

In these equations Z' appears in Y'' equation in the denominator to the second power, its density to overwhelm the loss factor is minimized, therefore, a plot of Y'' as a function of frequency in the frequency range 0.01–10 Hz is shown in Figure 4(a), where a well-defined relaxation peak was observed in the low-frequency region. However, no such peak was observed in the ECO copolymer [Fig. 4(b)], which confirms that this peak is due to a rotational motion of the polar units of PCO block which is attached to ECO segments.

On the other hand, the plot of complex plan (Z' vs. Z'') as shown in Figure 5(a,b) for EPEC-48 and ECO, respectively, yield two semicircles for EPEC-48 terpolymer. The high frequency semicircle is related to the conduction mechanism and the low frequency arc is attributed to the block structure (ECO and

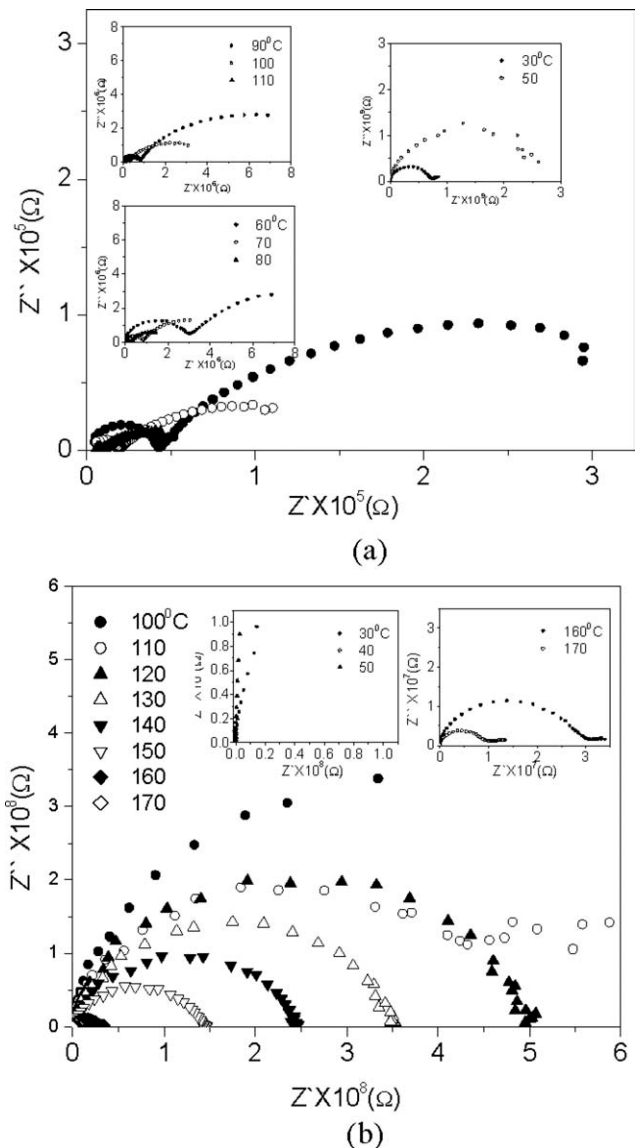


Figure 5 Complex impedance plot at different temperatures. (a) EPEC 48 (b) ECO.

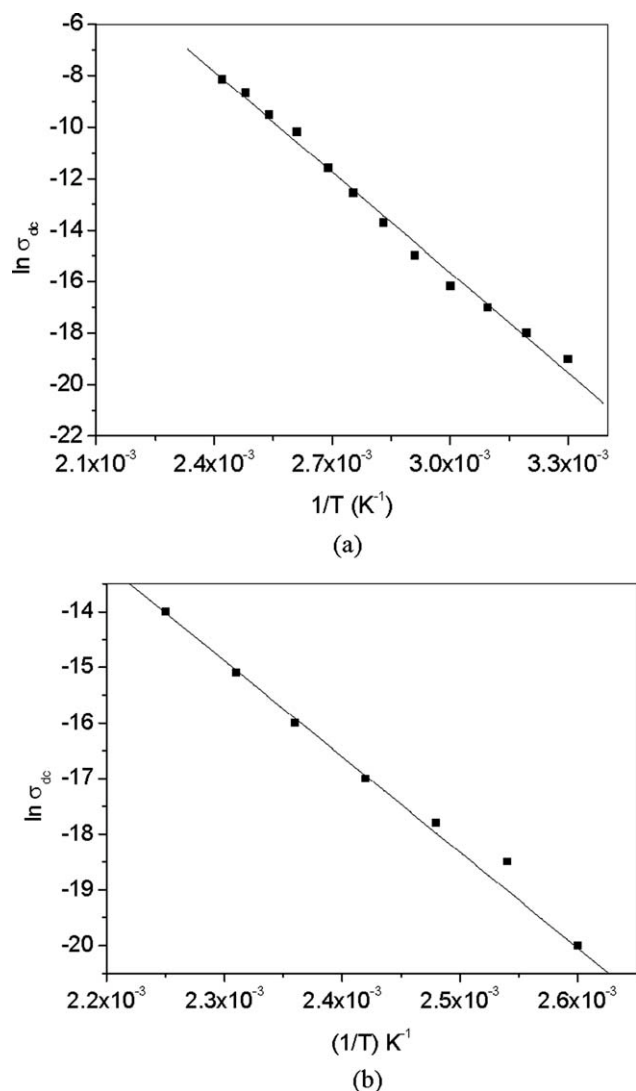


Figure 6 Variation of dc conductivity with $1/T$ calculated from Z'' vs. Z'' . (a) EPEC 48 (b) ECO.

PCO blocks) in the terpolymer (EPEC-48). For ECO sample, a single semicircle was observed at temperature higher than 100°C . Below this temperature the plot yields a straight line with a large slope indicating an insulating behavior. The material is highly capacitive with very high resistance. Above this temperature a tendency to a semicircle behavior is observed indicating the presence of both localized and nonlocalized conduction process.²¹ At higher temperatures the arcs transformation to a nearly semicircle indicates the occurrence of a single relaxation process characterized by a distribution relaxation time. Measuring the diameter of the semicircles allow us to calculate dc-conductivity of the material from the relation $\sigma = 1/R_p (A/d)$, where A is the area of the sample and d is the thickness.

The dc-conductivity dependence on temperature was found to follow an Arrhenius equation in the form $\sigma = \sigma_0 \exp(-\Delta E/kT)$ where ΔE is the activation energy, k is the Boltzmann constant, and T is

the absolute temperature. Figure 6(a,b) shows the logarithmic plot of the dc-conductivity as a function of the reciprocal temperature.

The nature of conductivity variation with rise in temperature together with a typical Arrhenius-type behavior suggests that the electrical conduction in both materials is thermally activated. The activation energy, calculated from the slope of the graph, was found in the order of 1.12 eV for EPEC-48, and 1.40 eV for ECO copolymer. From these values we can conclude that adding PCO units to the ECO copolymer facilitate the rotation of the dipole in the main chains of the terpolymer.

Dielectric constant and dielectric loss

Dielectric constant (ϵ') for EPEC-48 and ECO was calculated from the impedance measurements and plotted as a function of frequency at various temperatures as shown in Figure 7(a,b), respectively. In

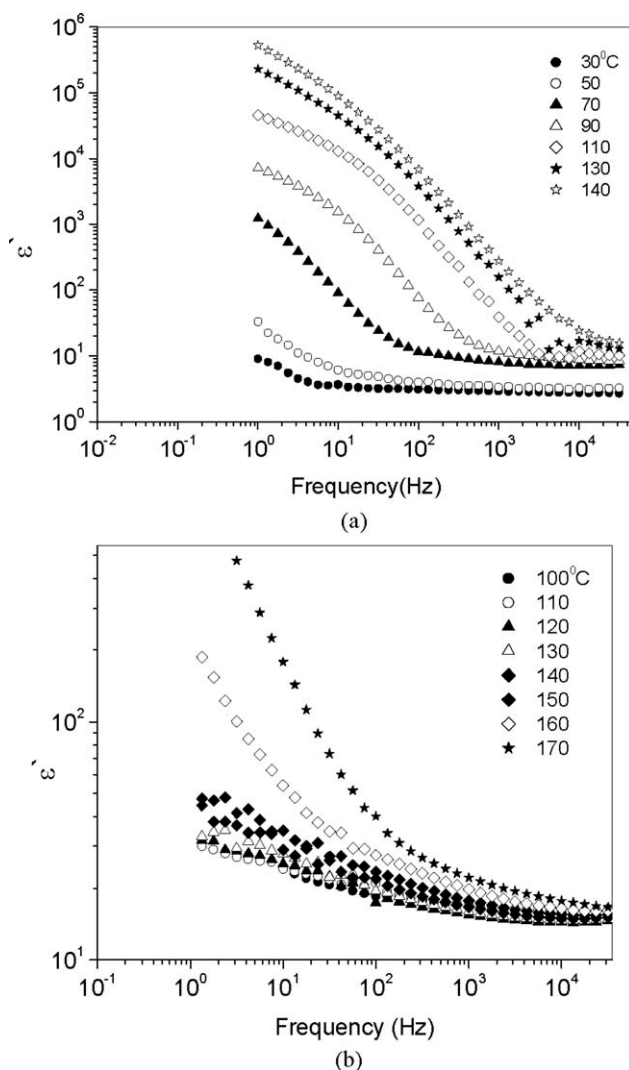


Figure 7 Frequency dependence of dielectric constant at different temperatures. (a) EPEC 48 (b) ECO.

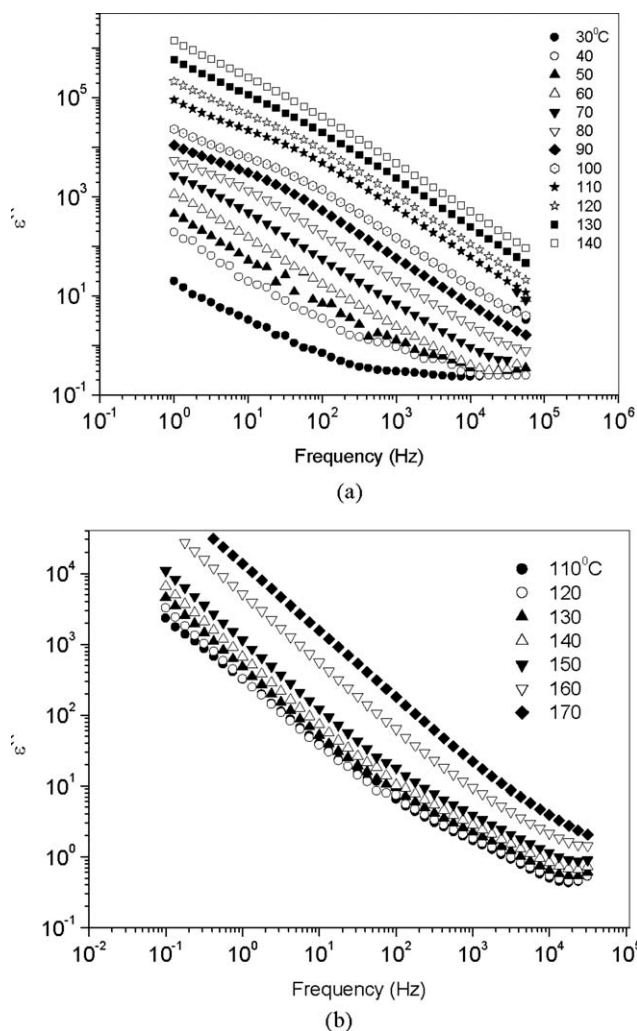


Figure 8 Frequency dependence of dielectric loss at different temperatures. (a) EPEC 48 (b) ECO.

both polymers the dielectric constant decreases with increasing frequency in the region of low frequencies and becomes almost constant at higher frequencies.

The increase in ϵ' with increase in temperature is associated with the decrease in bond energies.²³ This behavior is typical to the polar dielectrics in which the orientation of dipoles is facilitated with rising temperature and thereby the dielectric constant increased. However, ϵ' decreases dramatically with increasing frequency and attain a constant value at high frequencies which is similar to that observed in many polymers. The decrease in ϵ' with increasing frequency could be due to electrode polarization effects. This is due to the blocking of charge carriers at an electrode–dielectric interface when migrated under the influence of an electric field.^{24–27}

The feature of the dielectric loss (ϵ'') curves (Fig. 8) are similar for both co- and terpolymer. In the low frequency domain the loss factor reached high values which drop to normal values, as frequency increased, indicating the existence of dielec-

tric relaxation. The decrease in ϵ'' with decreasing frequency may be interpreted as the accumulation of charges at the interface between the sample and the electrodes which gives a space charge polarization. The slope of the curves in the low frequency region in the log plot is nearly equal to -1 which is typical for dc conductivity effect²⁸

Figure 9(a,b) shows the plot of normalized impedance (Z''/Z''_{max}) and normalized M'' (M''/M''_{max}) at different temperatures. In ECO copolymer, there is a separation between normalized M'' and Z'' which is an evidence of localized conduction and departure from an ideal Debye-like behavior. According to ideal Debye's theory of dielectric relaxation, the impedance (Z^*) and modulus (M^*) maxima are supposed to peak at the same frequency at a given and/or measured temperature, which is not observed in the present case.^{29–31} The separation in Normalized

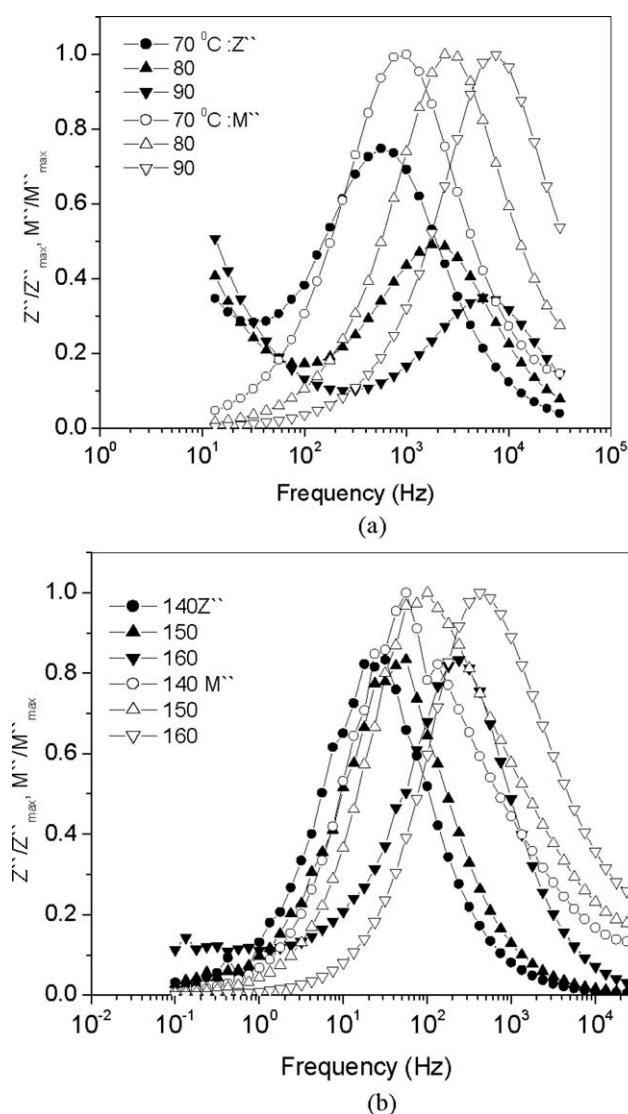


Figure 9 Frequency dependence of normalized modulus at different temperatures.

Z'' and M'' for EPEC-48 is less pronounced, which is nearly close to Deby-like behavior.

CONCLUSIONS

The present work reports the results of dielectric behavior for alternating ethylene, propylene, and carbon monoxide co- and terpolymers via impedance spectroscopy technique. The results reveal that below 100°C the ECO material is highly resistive. The observation of relaxation phenomena in both co- and terpolymer suggests that, this relaxation is due to a rotational motion of polar groups in the ECO segments. The low frequency relaxation peak in EPEC-48 terpolymer is due to a rotational motion of the polar units of PCO block which is attached to ECO segments. Both dielectric constant and loss factor are dependent on frequency and temperature.

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