

## Part I. On the physical characterization of ethene/propene/CO terpolymers: effect of composition

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### Abstract

A series of ethene/propene/CO terpolymers (PEPCO) with different ethene/CO (ECO) contents has been prepared and physically characterized. The ECO content varies between 0 and 80 wt%. Dielectric investigations have been carried out over wide ranges of frequency ( $10^{-1}$ – $10^6$  Hz) and temperature ( $-65$  to  $60^\circ\text{C}$ ). In addition, differential scanning calorimetry (DSC) and stress–strain measurements have been done. The dielectric results showed that all samples exhibit three or more relaxations, namely; local, glass and high-temperature process. The relaxation strength of the local process is found to increase with increasing the ECO contents and is attributed to the ECO blocks. DSC showed that the glass transition temperature decreases with increasing ECO content and varies between 3 and  $23^\circ\text{C}$ . The composition dependence of the glass temperature,  $T_g$ , follows a Fox behavior. In addition, DSC measurements showed an endothermic process with multiple peaks in the range  $30$ – $150^\circ\text{C}$ . The heat of melting increases slightly with increasing ECO content. The stress–strain behavior is similar to thermoplastic rubber for samples with ECO contents lower than 50 wt%. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Ethene/propene/CO terpolymer; Dielectric relaxation; Polymerization

### 1. Introduction

The first polyolefin ketone was prepared by Dintses [1] in 1939 through a high temperature and pressure radical polymerization. The carbon monoxide, CO, content was very low (10–20%). Since then several trials [2–26] over many years have been done to increase the CO content and to develop milder preparation conditions [7,8] through the use of new transition metal catalysts [6]. These trials led to the synthesis of strictly alternating ethene/CO copolymer, PECO [8]. In addition, successful attempts have been done to co-polymerize CO with ethene and  $\alpha$ -olefins like propene and styrene [10–18]. This is because the ethene/CO copolymer, PECO, is a highly crystalline material with high melting point, which limits any technical application of the material. In contrast, terpolymers of CO/ethene/propene with low propene contents exhibit low melting points and can be processed. This new class of material has been developed by Shell company as a replacement for nylon-6 and PET. It will be available in the near future under the trade

name Carilon. This material offers a new class of engineering thermoplastic due to its high performance over a wide range of temperatures, toughness, bio-compatibility, resistance to aggressive chemicals and low permeability especially for low hydrocarbon. This is in addition to the superior wear and friction properties. It has been proven that this material can be used in many applications like automotive, gas and oil electronic and medical industries. However, Carilon possesses high ECO content and is a thermoplastic material which is insoluble in common solvents. In addition, the molecular weight of these materials prepared with the currently available catalyst systems ranges between low and medium molecular weight [19,20] (about 50,000 g/mol) and copolymerization with higher  $\alpha$ -olefins yields even lower values [21–23] (practically oligomers).

A great achievement was done by Abu-Surrah [24,25] in 1996 to prepare a terpolymer of ethene/propene/CO with high molecular weight that can reach a value of  $1.2 \times 10^6$  g/mol by using dicationic palladium (II) phosphine catalysts and an optimized amount of water as activator. These materials with higher propene contents are soluble and show elastic properties. Therefore, we are expecting that these materials can cover a wider scope for

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Table 1  
Polymerization conditions and results

Sample	Propene (g)	Ethene (g)	Yield (g)	ECO (wt%)	$M_n$ (g/mol)	$M_w/M_n$
V6	58.7	0.8	3.54	35.2	120,000	1.93
V8	55.8	1.7	3.86	51.8	131,000	1.92
V10	56.5	2.4	5.22	57.6	141,000	1.90
V14	44.4	2.6	5.09	66.0	145,000	1.97
V19	47.2	4.2	6.48	80.0	228,000	1.77

technical application starting from thermoplastics to thermoplastic rubbers.

Therefore, in the frame of the present work a series of polyethene/propene/CO terpolymer are prepared according to Abu-Surrah [24,25] and investigated by dielectric

spectroscopy, differential scanning calorimetry (DSC) and stress–strain measurements. This work is aimed at shedding more light on the physical behavior in relation to the terpolymer composition. Dielectric spectroscopy is able to detect the molecular dynamics of the different constituents as it is

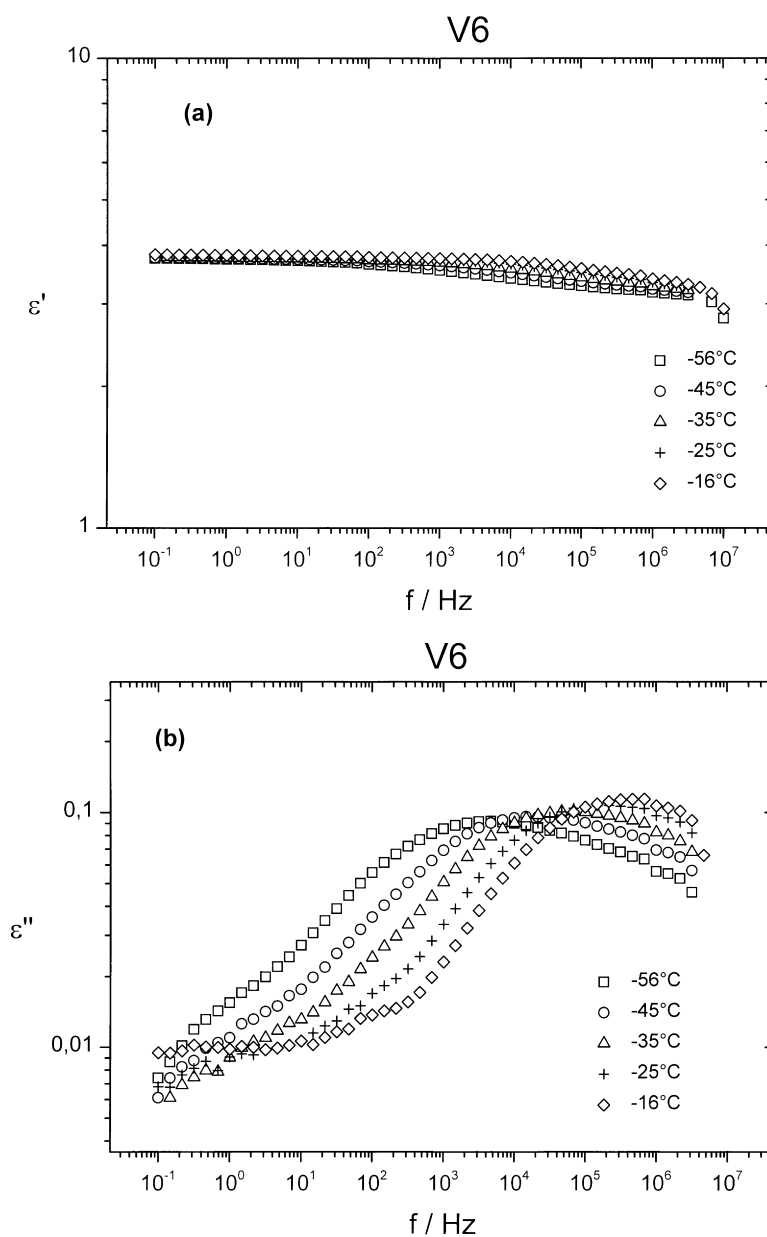


Fig. 1. Frequency dependence of (a) dielectric constant,  $\epsilon'$ ; and (b) dielectric loss,  $\epsilon''$  at low temperatures for sample V6.

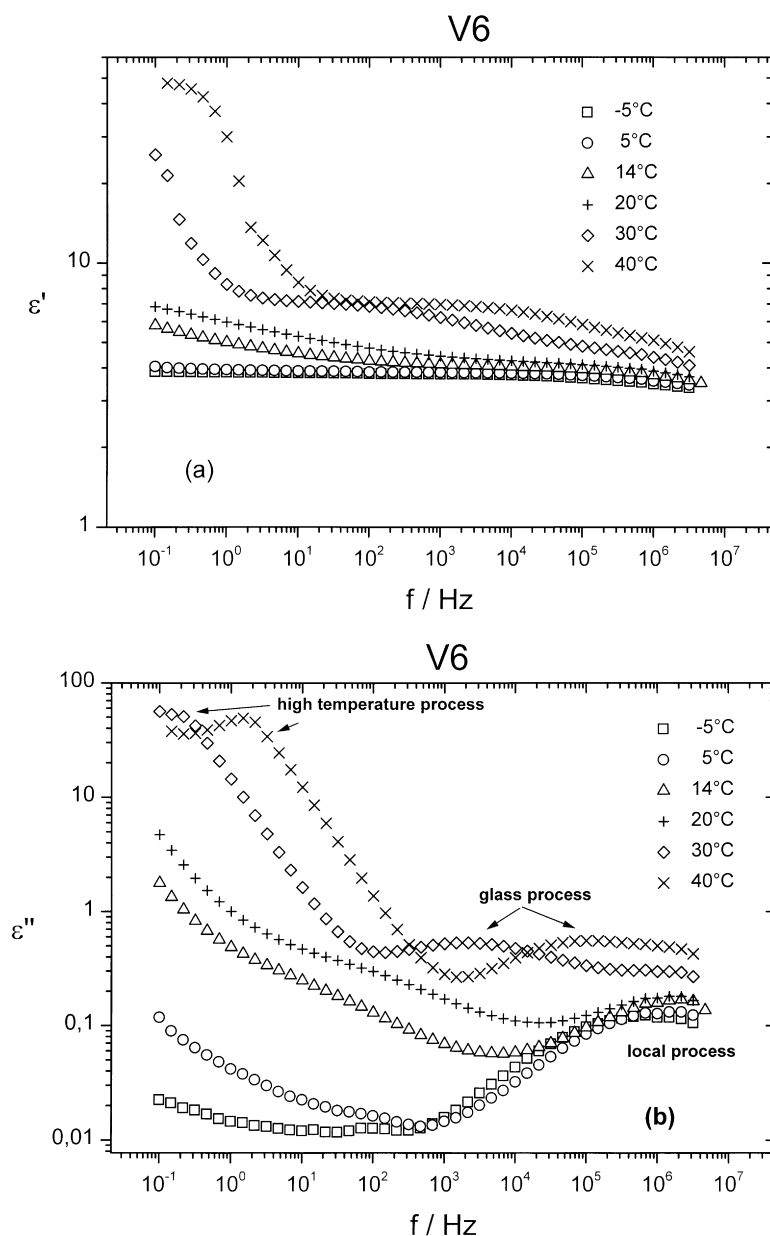


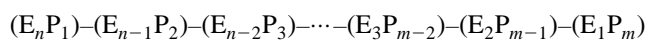
Fig. 2. Frequency dependence of (a) dielectric constant,  $\epsilon'$ ; and (b) dielectric loss,  $\epsilon''$  at high temperatures for sample V6.

sensitive to both local and cooperative segmental reorientation of the different blocks present within the terpolymer chains. It is thought that long sequences of ethene/CO exist in the polymeric chains, which are followed by a terpolymer sequence, that starts when the ethene concentration is low enough and the propene monomers will be able to compete in the polymerization.

This concept is based on the fact that ethene/CO polymerizes 10–25 times faster (depending on the reaction condition) than propene/CO and is supported by the NMR measurements [27,28]. Therefore, a tapered molecule could be formed as shown below:

E–EP–P

where E is polyethene/CO block  $(ECO)_l$ , P is polypropene/CO block  $(PCO)_q$ , and is tapered statistical terpolymer of ethene/propene/CO with the following structure:



Moreover, calorimetric and stress–strain measurements can supply information about the dependence of composition on glass temperature, crystallinity, as well as mechanical behavior of the resulting materials. The ultimate aim of this work is to develop a concept of molecular structure that leads to the preparation of polyketone rubbers.

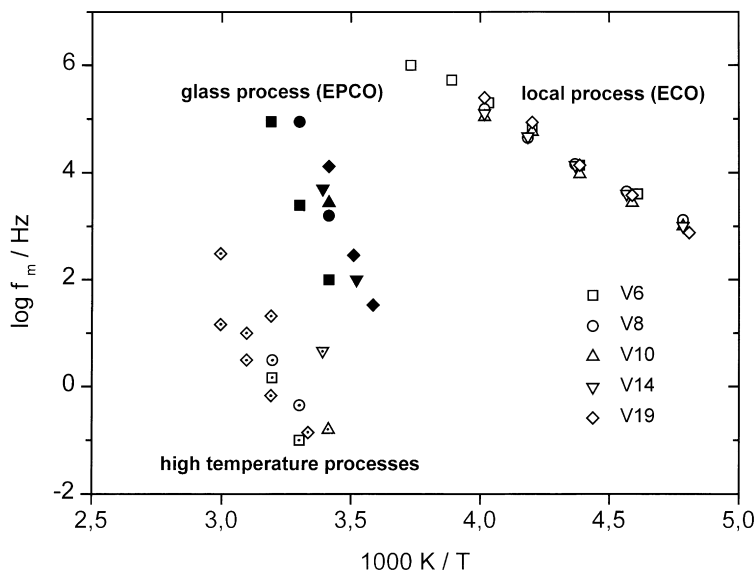


Fig. 3. Activation diagram of the frequency of dielectric loss maxima,  $f_m$ , for all processes observed in different samples (symbols of processes: local, open; glass process, solid; high-temperature processes, dot center).

## 2. Experimental

### 2.1. Preparation of samples

A solution of 150 ml  $\text{CH}_2\text{Cl}_2$ , 31 mg (40  $\mu\text{mol}$ )  $[\text{dpppPd}(\text{NCCH}_3)_2](\text{BF}_4)_2$  and 0.25 ml (10.3 mmol) methanol as activator was filled in the autoclave. In this solution about 50 g propene and various amounts of ethene are dissolved with stirring. The polymerization was performed at 60 bar CO pressure. After 21 h polymerization time, a clear, viscous solution was obtained. The polymer is precipitated in methanol, re-dissolved in  $\text{CH}_2\text{Cl}_2$  and stirred for 1 h with water to destroy the catalyst. After removal of the catalyst, a polymer film was prepared through slow evaporation of the solvent. Several samples were prepared from which only six samples (including pure propene/CO copolymer) have been thoroughly investigated dielectrically (see Table 1). The polypropene/CO, PPCO, has a molecular weight,  $M_n$ , of 79,000 g/mol and a polydispersity of 1.9. The ECO content in the polymer has been determined by elemental analysis and NMR measurements. The molecular weight was determined using gel permeation chromatography using chloroform as solvent. The NMR analysis showed the existence of long sequences of ethene/CO block in addition to the ethene/propene/CO terpolymer.

### 2.2. Measurements

The dielectric setup contains an impedance/gain analyzer SI 1260 (Schlumberger), an electrometer amplifier and measuring cell. The accuracy in  $\tan \delta$  is  $<10^{-3}$ . The measurements were carried out over wide ranges of frequency ( $10^{-1}$ – $10^6$  Hz) and temperature ( $-65$  to  $60^\circ\text{C}$ ). The calorimetric measurements were carried out using a

Perkin–Elmer DSC-7 differential scanning calorimeter. The calorimeter was calibrated according to the recommendations suggested by the GEFTA, Germany, for temperature, heat and heat flow rate [29,30]. The measurements were done with a heating and cooling rates of 10 K/min. The glass transition temperature was determined as the half-vitrification point. The stress–strain measurements were performed on a Zwick universal tensile test machine model 1445, Germany, at room temperature. The specimens ( $40 \times 5 \times 0.5 \text{ mm}^3$ ) were extended at 10 mm/min.

## 3. Results and discussion

The frequency dependence of the dielectric parameters,  $\epsilon'$  and  $\epsilon''$  are shown in Fig. 1 for the V6 sample at low temperatures ( $-56$  to  $-16^\circ\text{C}$ ), while Fig. 2 presents the high-temperature measurements ( $-5$  to  $60^\circ\text{C}$ ). Fig. 1a shows that  $\epsilon'$  exhibits a dispersion, indicating the presence of relaxation process at low temperatures. This process can be clearly seen in the frequency dependence of the dielectric loss,  $\epsilon''$ , shown in Fig. 1b at the same temperature range, where a well-defined relaxation process appears. On the other hand, Fig. 2 shows that this polymer exhibits another high relaxation process which has a strong temperature dependence that appears at 30 and  $40^\circ\text{C}$  at about 2 and 100 kHz. In addition, another strong relaxation process appears at low frequencies at the same temperatures, at frequencies of about 0.1 and 2 Hz, respectively. Therefore, it can be clearly stated that this polymer exhibits three relaxation processes appearing at different ranges of temperature and frequencies within the range of the current measurements. Similar findings are observed for all samples measured. However, it should be stated that additional

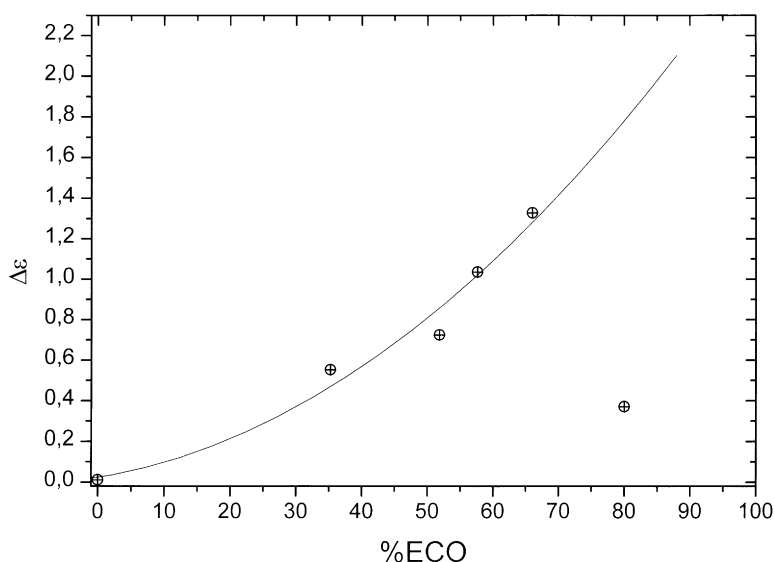


Fig. 4. Relaxation strength dependence on ethylene ketone (ECO) content.

relaxation processes were observed for some samples appearing at higher temperatures and lower frequencies (e.g. sample V19). Fig. 3 represents the activation diagram of the relaxation processes observed for all samples. In this diagram, the following can be seen:

1. the activation energy of the low-temperature process is 14 kcal/mol;
2. the activation behavior of the low-temperature relaxation process is almost independent of the ECO content;
3. the processes appearing at higher temperature have higher activation energies, which equal about 61 and 38 kcal/mol.

Finding 1 indicates that the low-temperature process has a local nature. It is generally accepted that the local relaxation process is attributed to limited reorientations of some loosely packed segments in the glassy state. This conclusion is supported by the fact that these polymers exhibit no glass transition at this range of temperatures as evidenced by the DSC measurements. However, Finding 2 is surprising because it is well known that the dynamics of local process (relaxation-frequency and distribution) is very sensitive to the changes in the local environment, where it depends on tacticity [31], substitution [31,32], chemical composition [33], additives [34–37] and crystallinity [31,35]. Furthermore, this finding implies that the origin of this process should be independent of the polymer composition. Such behavior has been observed in case of micro-phase separated systems and in polymer blends [32,38–40], which are compatible on the superstructural level [32,38,39]. In these cases, it has been found that the local relaxation of the bulk segments is not dependent on composition. Accordingly, it can be concluded that this process could be attributed to limited reorientation of some segments that are present in the ECO or PCO blocks at the ends of the chains, which can

make either micro-phase separation and/or short-range order on a length scale that can maintain the dynamics of the local process unchanged and can function as precursors of thin crystallites. However, micro-phase separation is not yet detected through microscopic examination. On the other hand, these materials can slowly crystallize with time or by annealing at 60–80°C. In addition, it is very interesting to observe that although some samples do not exhibit a melting peak or nano-structure (as evidenced microscopically and by DSC), they show elastic properties at room temperature indicating the presence of physical cross-links. Therefore, it is now of interest to know the origin of this local relaxation. Hence, the dielectric relaxation strength,  $\Delta\epsilon$ , of different samples have been determined from the relaxation spectra using the Kramers–Kronig equation [41]

$$\Delta\epsilon = \frac{2}{\pi} \ln 10 \int_{-\infty}^{\infty} \epsilon'' d \log f$$

where  $\Delta\epsilon$  is given as

$$\Delta\epsilon \propto ng\mu^2$$

where  $n$  is the number of dipoles with a dipole moment  $\mu$  and  $g$  is the association factor [41].

Fig. 4 shows that the dielectric relaxation strength of this low temperature-process increases with increasing ECO content. This experimental fact leads to the conclusion that the origin of this process should be the ECO segments in the ECO blocks, which remain undisturbed regardless of the ECO content so that the dynamics (relaxation frequency and distribution of relaxation times) remains unchanged. It could be of interest to mention that the half-width of this process is found to be almost independent on composition and equals about four decades. This value represents a narrow distribution for a local process as it is normally lying between 3 and 7 decades. Therefore, it can be envisaged that the ECO blocks form their own regions so that the

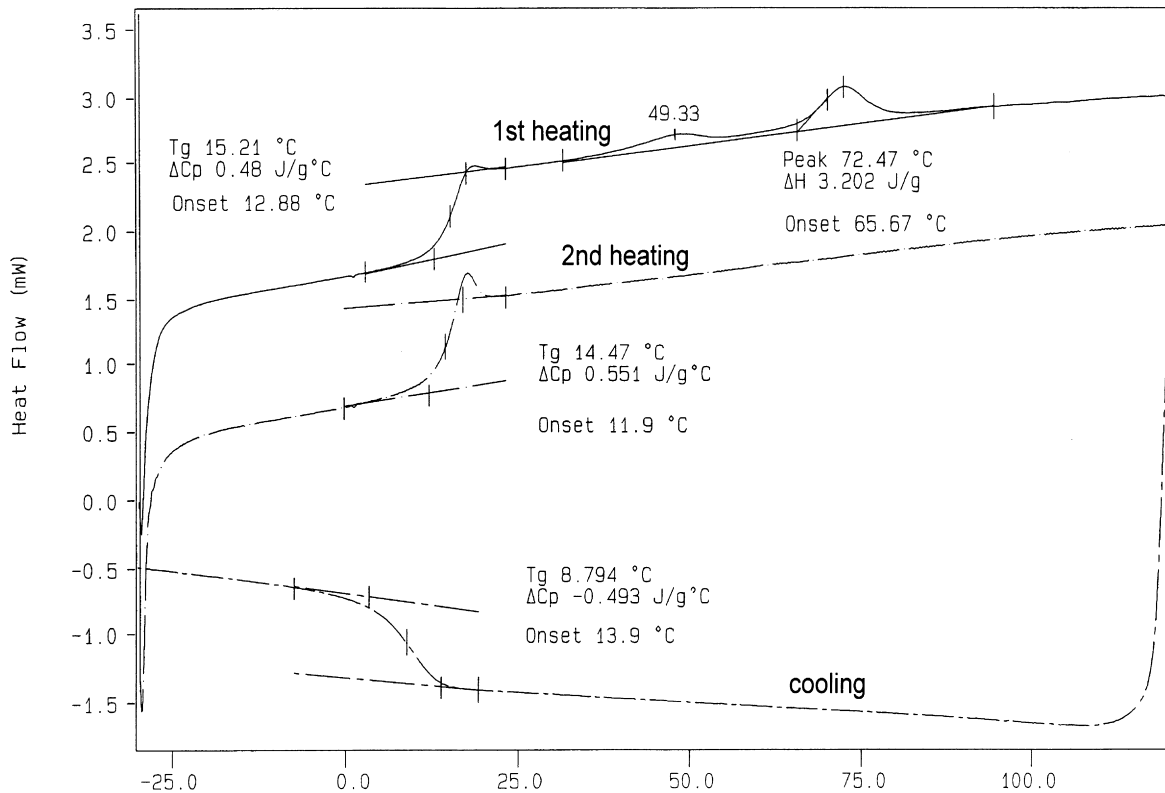


Fig. 5. DSC measurements of sample V6 at the first heating, cooling and second heating scans.

dynamics of this local process remains unaffected. It is worth noting to mention that pure propene/CO copolymer, PPCO, also exhibits the same process at the same position but with a very low relaxation strength ( $= 0.01$ ). This small peak can be attributed to residual trace of ethene which could be less than 0.5% of the used propene. It can be also seen in Fig. 4 that the sample with 80% ECO content

exhibits reproducible deviation of the relaxation strength,  $\Delta\epsilon$ , (low value). The reason of this anomaly is unclear. However, such decrease in  $\Delta\epsilon$  could be tentatively attributed to a better degree of molecular packing that could be attained at very high ECO contents due to the increase in the ECO sequence length, so that the number of loosely packed segments responsible for local process will decrease.

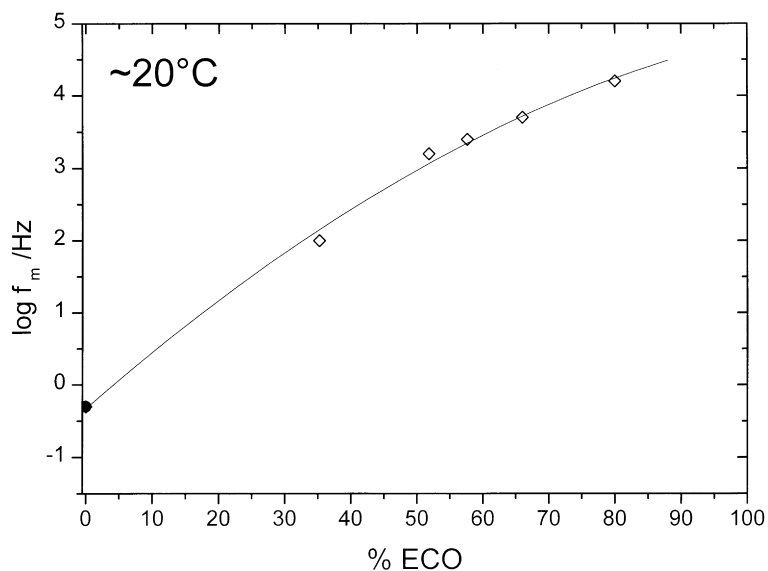


Fig. 6. Composition dependence of relaxation frequency on for the glass process observed at  $20^\circ\text{C}$ .

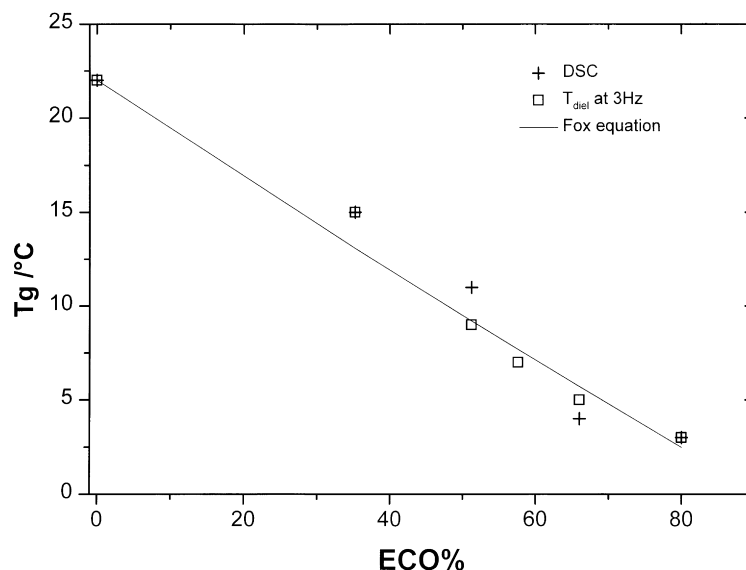


Fig. 7. Composition dependence of the glass transition temperature,  $T_g$ .

The high activation energy observed for the second process (starting from low temperature and upwards) indicates its cooperative nature [31]. Therefore, it can be concluded that the second relaxation process is the glass relaxation process of the polymer. This conclusion is supported by the DSC measurements which show the existence of a glass transition temperature in this temperature range as shown in Fig. 5. In order to understand the relation between the glass process and composition, it would be helpful to correlate the relaxation frequency observed at 20°C with the ECO content. The relation is presented in Fig. 6, which shows that the relaxation frequency of the glass process increases systematically by increasing the ECO content. Furthermore, Fig. 7 shows that the values of

$T_g$  calculated from the activation diagram at 3 Hz for all samples are in excellent agreement with those obtained from DSC [42]. Therefore, it can be concluded that this process is the glass process of the ethene/propene/CO terpolymer. It is also clear from Fig. 7 that the higher the ECO content in the terpolymer, the lower is the  $T_g$ . The composition dependence of glass transition temperature follows a Fox behavior

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

where  $T_g$  is the glass transition temperature of the random copolymer,  $T_{g1}$  and  $T_{g2}$  are the glass transition temperatures

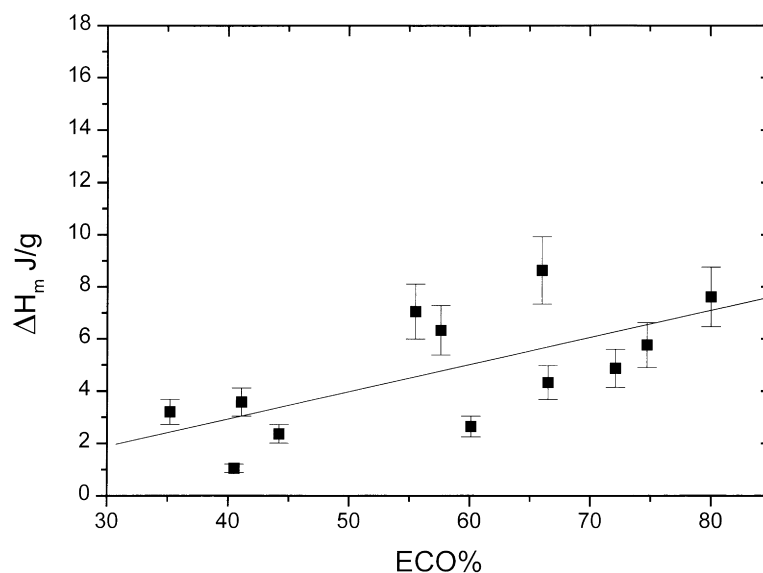


Fig. 8. Composition dependence of the heat of fusion,  $\Delta H_m$ .

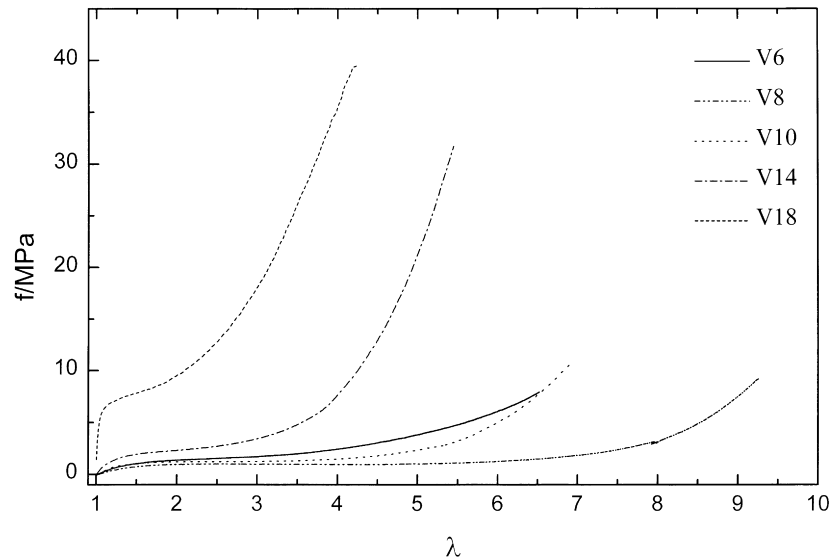


Fig. 9. Stress–strain behavior of different samples at room temperature.

of polymer 1 and 2, respectively;  $w_1$  and  $w_2$  are the weight fractions of monomer 1 and 2, respectively.

The high-temperature processes have an activation energy of 38 kcal/mol and appear at frequencies lower (higher temperatures) than those of the glass process of the terpolymer. The origin of the high-temperature processes is still unclear. Therefore, further investigations will be done to know if it is due to an ionic conductivity process or a relaxation in the crystalline regions like the high-temperature processes observed in polyethylene [43].

On the other hand, Fig. 5 shows that sample V6, as a representative example, exhibits multiple peaks at the melting process that appear at temperatures between 30 and 150°C. However, the number of the peaks and the relative heights vary from one sample to another. However, the general tendency of all samples is that these melting peaks

either completely disappear or become very weak at the second heating scan. These peaks can be observed again upon long annealing at room temperature and therefore indicate the tendency of the samples for slow crystallization. In order to get an impression about the heat of melting,  $\Delta H_m$ , a relation between this parameter versus the ECO content is presented in Fig. 8. The value of  $\Delta H_m$  is taken for all peaks. This figure shows that the general tendency is a slight increase in  $\Delta H_m$  by increasing the ECO content. It seems that these fine lamellae are responsible for the elastic properties observed in these materials at room temperature.

Fig. 9 represents the stress–strain behavior of different samples. It is clear that this material behaves as cross-linked rubber with different degrees of cross-linking density. The higher the ECO content, the higher is the stiffness of the material. This can be seen in Fig. 10 which shows that

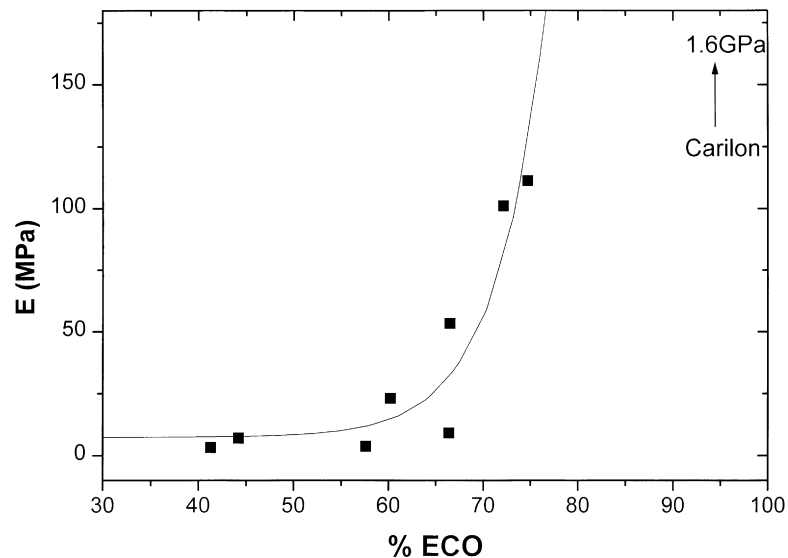


Fig. 10. Composition dependence of Young's modulus,  $E$ .



Young's modulus,  $E$ , increases rapidly at ECO contents higher than 50% over more than three orders of magnitude if one compares the value of Carilon, Shell (1.6 GPa) [44].

The modulus  $E$  of styrene–butadiene–styrene, SBS 1102, block copolymer (typical example of thermoplastic rubbers) is 3.9 MPa. It is worth noting that the current polyketones range between thermoplastics and thermoplastic rubbers with different  $E$  moduli and deformabilities.

Therefore, it seems that these materials are very promising to get a wide variety of properties.

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