

Utilization of Some Oligomers Based on Poly(ethylene terephthalate) Wastes as Modifiers for Polyvinyl Chloride

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ABSTRACT: Two glycolized products, PET-TEG and PET-BD, were prepared by depolymerization of PET wastes using 30 wt % triethylene glycol (TEG) and 40 wt % 1,4-butanediol (BD). In this work we investigated how the mechanical and electrical properties of PVC and PVC/EPDM blend were affected by mixing them with different concentrations of the two obtained glycolized products. Dynamic mechanical, DSC, and dielectric behaviors of PVC containing various amounts of the two modifiers were studied. The present data confirm that the α -relaxation dynamic of PVC at constant frequency shifts to a lower temperature with increasing modifier content. PVC samples containing 5 phr of the two modifiers show the highest impact strength at -30°C . It was noted that addition of PET-TEG to PVC or PVC/EPDM blend led to end products with enhanced insulating properties, which makes them suitable for industrial applications. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2501–2509, 2002

Key words: 1,4-butanediol; EPDM rubber; glycolysis; PET wastes; PVC; triethylene glycol

INTRODUCTION

The effective utilization of polyethylene terephthalate (PET) and polyvinyl chloride (PVC) wastes is of considerable commercial and technological significance. However, there are technical difficulties in obtaining a final product with acceptable mechanical properties. PET and PVC wastes are chemically incompatible and their processing temperatures are different. The aim of our work is to find a method to obtain PET products compatible with PVC.

Various recycling processes for PET wastes are available and most of them consist of depolymer-

ization of the polyester by hydrolysis,^{1–4} methanolysis,^{5–7} or glycolysis.^{8,9} The PET conversion products are used as raw materials for further synthesis of PET or new products such as polyesters, polyurethanes, or polyisocyanurate foams.¹⁰

The simplest example of the degradative transesterification of PET is the reaction between long chain alcohols and PET wastes. The products obtained serve as plasticizers for PVC.^{11–14}

Lusinchi et al.¹⁵ also investigated the depolymerization of PET and the polycondensation of its reaction products with ϵ -caprolactone to obtain a new polymer that is compatible with PVC.

The glycolysis of PET wastes using 1,4-butanediol (BD) and triethylene glycol (TEG) has recently been studied and the products identified.¹⁶ The objective of this work is to investigate the effect of depolymerization products of PET using 1,4-BD and TEG on the mechanical and electrical

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Table I Formulations of PVC/EPDM Blends

Ingredient	Formulations (phr)				
	100	75	50	25	0
PVC	100	75	50	25	0
EPDM	0	25	50	75	100
DOP	30	30	30	30	30
Dibutyltin maleate	3	3	3	3	3
Stearic acid	0.3	0.3	0.3	0.3	0.3
PET-TEG	25	25	25	25	25
Peroxide	4	4	4	4	4

properties of PVC and PVC/ethylene-propylene-diene terpolymer (EPDM) blend.

EXPERIMENTAL

Materials

The two glycolized products PET-TEG and PET-BD were obtained by depolymerization of PET wastes using 30 wt % TEG and 46 wt % BD. The PET-TEG and PET-BD glycolized products consist mainly of hydroxyl-terminated oligomers with number-average molecular weight of 881 and 497 g/mol and polydispersity of 1.22 and 1.29, respectively, and could be represented by the following structures:

- $\text{H}-(\text{OCH}_2\text{CH}_2)_3-[\text{OOC}-\text{C}_6\text{H}_4-\text{CO}-(\text{CH}_2\text{CH}_2\text{O})_3-]_n\text{OH}$
- $\text{HO}-(\text{CH}_2)_4-[\text{OOC}-\text{C}_6\text{H}_4-\text{COO}-(\text{CH}_2)_4-]_n\text{OH}$

The PVC resin used in this study was a white powder made by suspension polymerization with a *K* value of 67.

Dibutyltin maleate, dioctyl phthalate (DOP), and stearic acid were of technical grades.

EPDM rubber (ethylene-propylene-diene terpolymer) was a white rubberlike solid, commercially known as Vistalon 7500.

Preparation of Samples

PVC Modified with Glycolized Products

PVC resin (100 parts by weight) was mixed with each of the two PET-TEG and PET-BD oligomers at different concentrations. Three parts of dibutyltin maleate, 30 parts of DOP, and 0.3 parts of stearic acid were added to all formulations. The blends were prepared by mixing all the components in an electrically heated chamber of the Brabender Plasti-corder at a constant temperature of 180°C for 5 min.

Samples of appropriate thickness for various measurements were prepared by pressing the mixture under pressure of about 40 kg/cm² and a temperature of 180°C, then cooling to room temperature.

PVC/EPDM Blends Modified with PET-TEG Oligomers

The PVC resin and EPDM rubber were blended in different ratios. The oligomers and the other ingredients shown in Table I were added to a PVC/

Table II Mechanical Characteristics of PVC Modified with Different Oligomers

Property	PVC	Concentration of the Added Oligomers (phr)							
		PET-TEG				PET-BD			
		5	15	25	30	5	15	25	30
Tensile strength (MPa)	27.03	24.00	26.19	25.75	23.61	24.69	24.01	24.41	24.45
Elongation (%)	181.99	195.00	201.40	214.04	249.40	190.00	177.95	220.31	224.52
Impact strength (kJ/m ²)	29.72	38.01	31.03	19.11	18.16	38.99	32.00	—	32.22

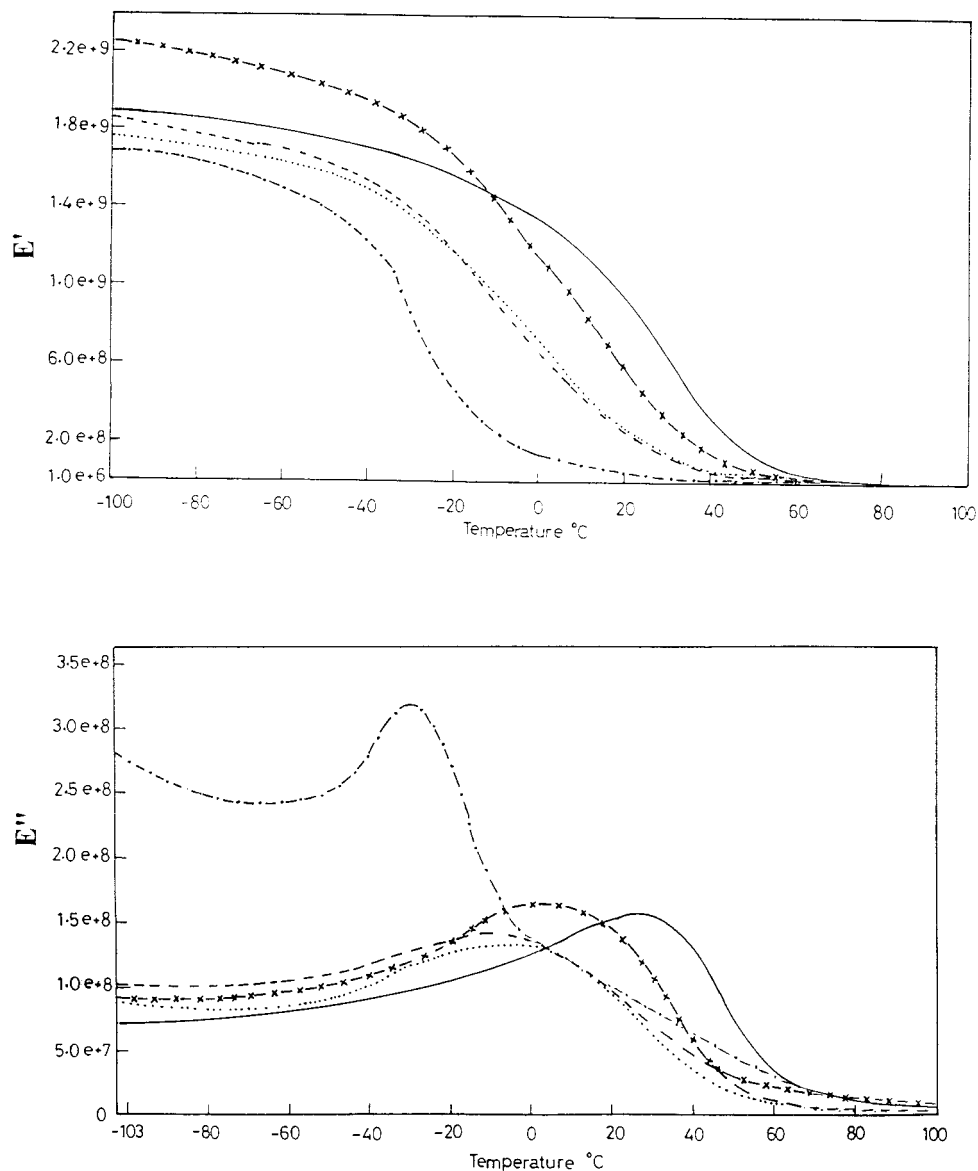


Figure 1 Temperature dependency of the storage modulus E' and loss modulus E'' of PVC modified with different concentrations of PET-TEG (in phr): (—), 0; (—x—) 5; ($\cdot\cdot\cdot$), 15; (— — —), 25; (— · —), 100.

EPDM system such that the ratio was kept constant. All components were mixed in a Brabender Plasti-corder at 170°C for 5 min. The blends were compression molded at 170°C under pressure of 40 kg/cm².

Measurements

The mechanical properties were determined using a tensile-testing machine (Zwick 1101) according to ASTM D 412.

Izod impact strength was performed according to ISO 180/4 at -30°C.

The dynamic mechanical analyses (DMA) were measured using a Perkin-Elmer DMA-7e instrument (Perkin Elmer Cetus Instruments, Norwalk, CT). The experiments were carried out in a tensile mode over a temperature range of -100 to 120°C at a heating rate of 5°C and frequency of 1 Hz. The temperature at the maximum point of the loss modulus (E'') was taken as the measure of glass-transition temperature T_g .

DSC measurements were performed using a Perkin-Elmer (PYRIS) differential scanning calorimeter calibrated for temperature and enthalpy

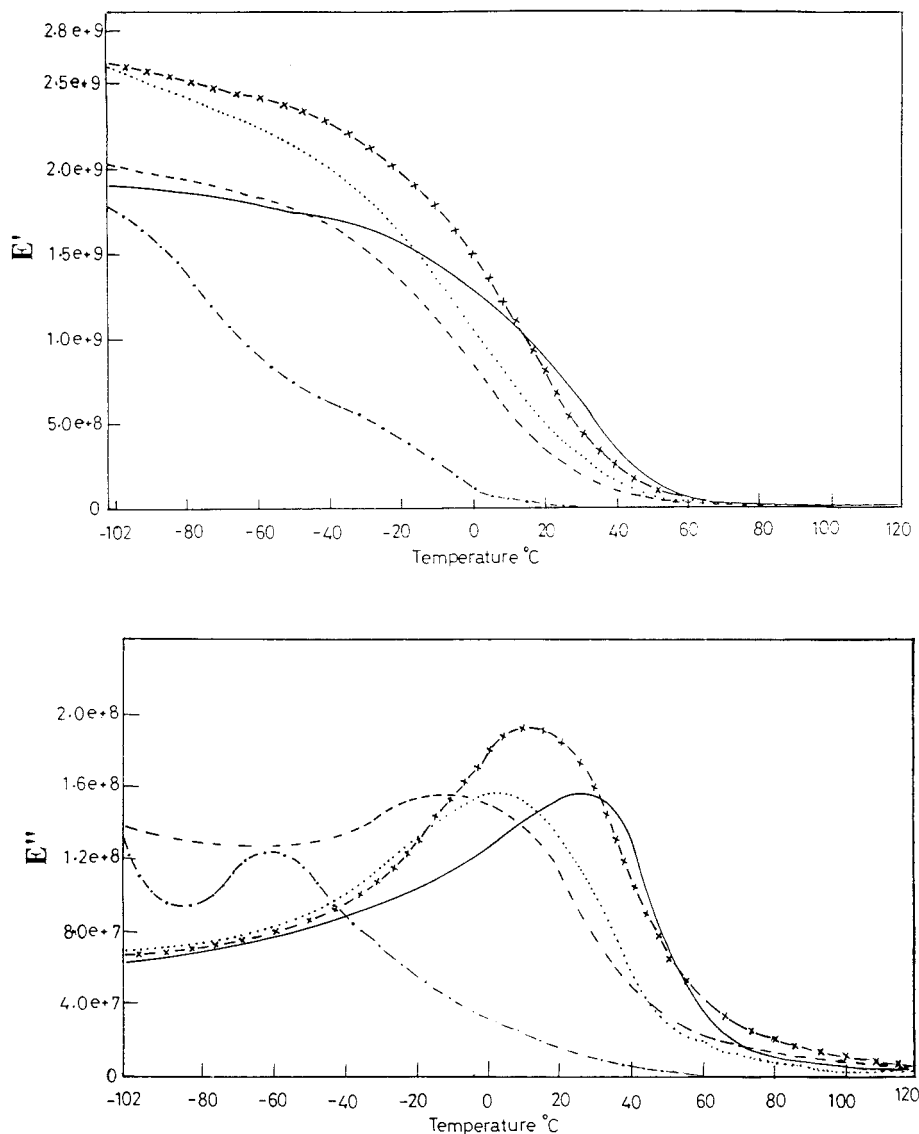


Figure 2 Temperature dependency of E' and E'' of PVC modified with different concentrations of PET-BD (in phr): (—), 0; (—x—), 5; (···), 15; (---), 25; (-·-), 100.

with water and indium. All scans were obtained by heating from -100 to 120°C at a heating rate of $10^{\circ}\text{C}/\text{min}$.

Dielectric measurements were carried out in the frequency range 100 Hz to 100 kHz by using an LCR meter (type AG-411 B; Ando Electric, Japan). The capacitance C and the loss tangent $\tan \delta$ were obtained directly from the bridge from which the permittivity ϵ' and dielectric loss ϵ'' were calculated. A guard ring capacitor [type NFM/5T; Wiss. Tech. Werkstätten (WTW) GmbH, Germany] was used as a measuring cell. The cell was calibrated by using standard materials (trolitul, glass, and air) of varying thickness

ranging from 1 to 5 mm. For each sample, a relation between the thickness d and its capacitance C_M was plotted as a standard curve. The capacitance C_M for the standard materials obtained from the standard curves is plotted versus the known permittivity ϵ' of each material ($\epsilon' = 2.5, 7, 1$ for trolitul, glass, and air, respectively). The relation between C_M and ϵ' was found to be linear and, thus, the permittivity corresponding to any measured capacitance can be deduced. To check the standard curve, two Teflon samples ($\epsilon' = 2.0$)¹⁷ of varying thickness were used. The experimental error in ϵ' and ϵ'' was found to be ± 3 and 5%, respectively.

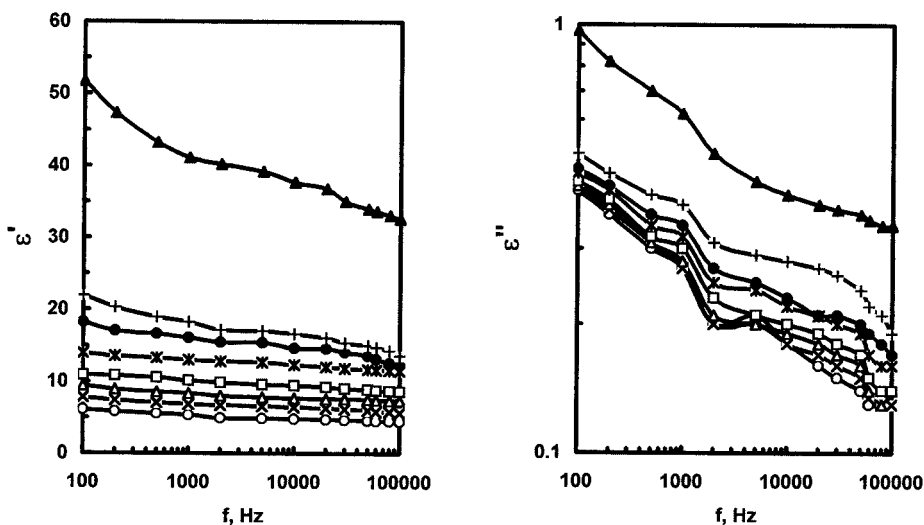


Figure 3 Permittivity ϵ' and dielectric loss ϵ'' for PVC modified with different concentrations of PET-TEG (in phr): 0 (○); 5 (×); 10 (△); 15 (□); 20 (*); 25 (●); 30 (+); 100 (▲).

RESULTS AND DISCUSSION

The main objective of this work was to reuse the glycolized products of PET wastes in the design of polymer blends suitable for some applications. For this purpose different samples of PVC modified with PET-BD and PET-TEG oligomers were prepared. Table II contains the composition of these samples together with the mechanical characteristics before and after the addition of the two modifiers.

Mechanical Properties

It is quite evident from the data in Table II that the mechanical properties are directly affected by the modifier content, that is, the more the modifier used, the greater the elongation at break and the smaller the tensile strength. This may be related to the plasticizing action of the added oligomers.¹⁸

It is also obvious that the addition of PET-BD generally has an impact strength increasing effect. However, it is interesting to observe that the impact strength very slightly decreases when the samples contained higher amounts, although it is still comparable to that of the unmodified sample.

On the other hand, higher impact strength values are obtained at a PET-TEG concentration of 5 and 15 phr, whereas any further increase in modifier concentration results in a decrease in impact strength values.

The energy level is raised initially when polymer molecules are instantaneously deformed. A relaxation process involves some form of energy loss under the imposed force and the damping properties of a polymer are dominated by its T_g .

The plots of the dynamic storage and loss moduli versus temperature for PVC with varying amounts of PET-TEG and PET-BD oligomers are shown in

Table III Glass-Transition Temperatures of PVC Modified with Different Oligomers

Concentration of Added Oligomers (phr)	PVC		PET-TEG		PET-BD	
	DMA	DSC	DMA	DSC	DMA	DSC
0	27.9	28.5	—	—	—	—
5	—	—	8.9	9.3	14.5	13.3
15	—	—	1.9	1.3	-1.6	-0.6
25	—	—	-6.6	-7.5	-4.2	-5.2
100	—	—	-32	-30	-50	-46

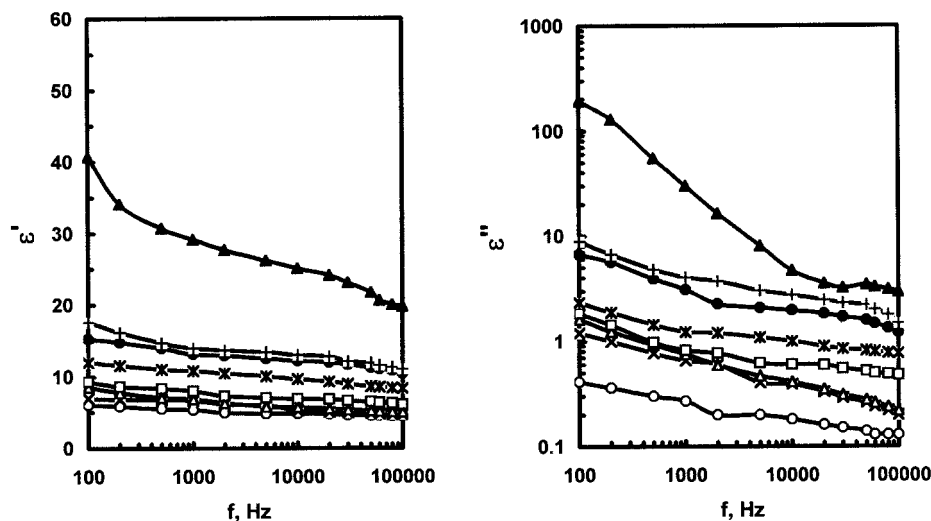


Figure 4 Permittivity ϵ' and dielectric loss ϵ'' for PVC modified with different concentrations of PET-BD in phr): 0 (O); 5 (x); 10 (Δ); 15 (\square); 20 (\star); 25 (\bullet); 30 (+); 100 (\blacktriangle).

Figures 1 and 2, respectively. All curves exhibit a common feature, that is, the loss modulus (E'') curves are broad and generally have only a single peak, which is an indication of a relaxation process. This peak can be related to the main dynamic glass-transition α -relaxation, which is usually explained by cooperative diffusional motion of main-chain segments. It is worth mentioning that the shape of the dispersion does not change and only its position shifts with composition. Adding the PET-TEG and PET-BD oligomers to PVC shifts the storage modulus and loss modulus toward lower temperatures. This is expected, given that the glass-transition temperatures for oligomers are lower than that of PVC and the dynamics of the α -relaxation of PVC becomes faster when mixed with the two oligomers.

The broadening of the main peak may be related to the increase of interdomain spacing be-

cause the distance between domains would be expected to become larger as more modifier is added to the amorphous matrix. Similar effects on dynamic properties of PVC are observed by using different plasticizers. It has been reported that the interdomain spacing increases as the plasticizer content increases.¹⁹ Moreover, no other relaxation processes (i.e., no phase separation) were detected, indicating miscibility between PVC and the added oligomers. This could be attributed to the existence of specific interaction between the carbonyl groups of the oligomers and the PVC molecules²⁰: dipole-dipole interaction between C=O and C-Cl groups or hydrogen bonds between the C=O and or α -H atom of PVC.

DSC Analysis

It should be noted that the parallel DSC studies (Table III) show a similar trend. The most rele-

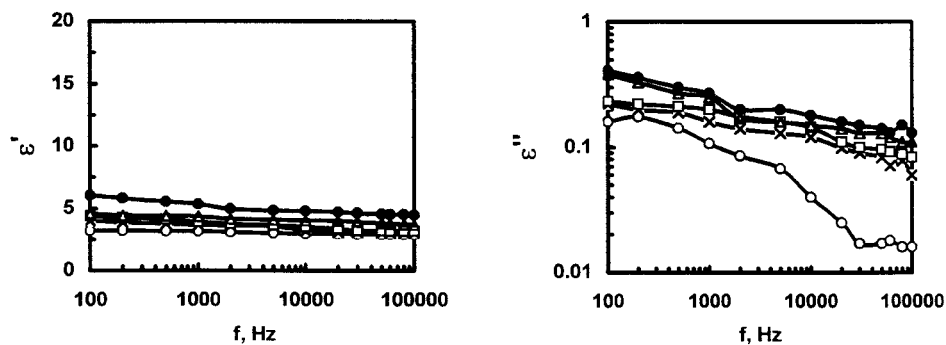


Figure 5 Permittivity ϵ' and dielectric loss ϵ'' for EPDM/PVC blend (in phr of EPDM): 100 (O); 75 (x); 50 (\square); 25 (Δ); 0 (\bullet).

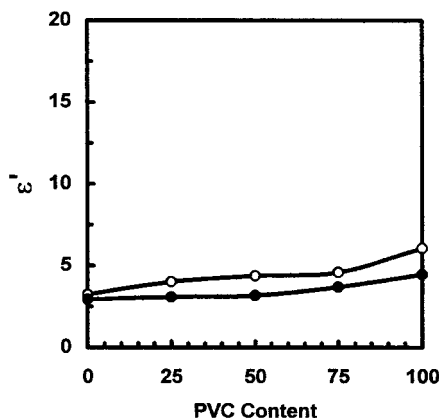


Figure 6 Relation between PVC content and ϵ' at 100 Hz (○) and 100 kHz (●).

vant feature of the DSC measurements for the two systems in all compositions is the prominence of the single glass-transition temperature, confirming the miscibility of the PVC with the added oligomers. It is also found that the T_g values are shifted on the temperature scale in proportion to the relative concentration of the two modifiers. From DMA and DSC data, there is reasonably good agreement in the T_g values obtained from the two techniques.

Dielectric Properties

The permittivity ϵ' and dielectric loss ϵ'' for different ratios of PVC and PET-TEG and PET-BD mixtures as well as pure PVC and pure oligomers were measured over a frequency range of 100 Hz to 100 kHz at room temperature. The obtained data are illustrated graphically in Figures 3 and 4 versus the applied frequency f . From these figures it is clear that ϵ' values decrease by increasing the

applied frequency, thus showing anomalous dispersion. It is also noticed that the values of the permittivity ϵ' in the whole range of frequency increase by increasing the percentage of the added oligomers. This increase is slightly higher in the case of adding PET-TEG than of PET-BD oligomers. The value of the permittivity for pure PVC ($\epsilon' = 5.33$ at 1 kHz) is found to be in fair agreement with values found in the literature,²¹⁻²³ where $\epsilon' = 4.5-6.5$ at 1 kHz for PVC-DOP samples.

The absorption curves relating ϵ'' and the applied frequency are found to be flatter than the Debye curve, indicating more than one relaxation process. In addition to the relaxation mechanisms ascribed to the orientation of the main chain and its related motions,²⁴⁻²⁸ another mechanism expected at the lower frequency range due to these mechanisms is the Maxwell-Wagner effect, which could be attributed to the multiphase of the investigated systems.²⁹ The ion mobility also plays an important role in such mechanisms.^{30,31} The conductivity σ was calculated from the measured resistance R using the equation $\sigma = RA/L$, where A is the area of the sample and L is its thickness. The data obtained for σ are found to be $1 \times 10^{-11} \Omega^{-1} \text{ cm}^{-1}$ for the samples containing different concentrations of PET-TEG, whereas it ranges from 0.6 to $4.4 \times 10^{-10} \Omega^{-1} \text{ cm}^{-1}$ for different concentrations of PET-BD. These results could lead to the conclusion that the investigated systems are considered to be insulating materials, given that their conductivity values are in the order of those found in the literature ($10^{-8}-10^{-12} \Omega^{-1} \text{ cm}^{-1}$).³²

By inspection of Figures 3 and 4 it is clear that the values of ϵ'' increase by increasing the modifier content. This increase is found to be small in

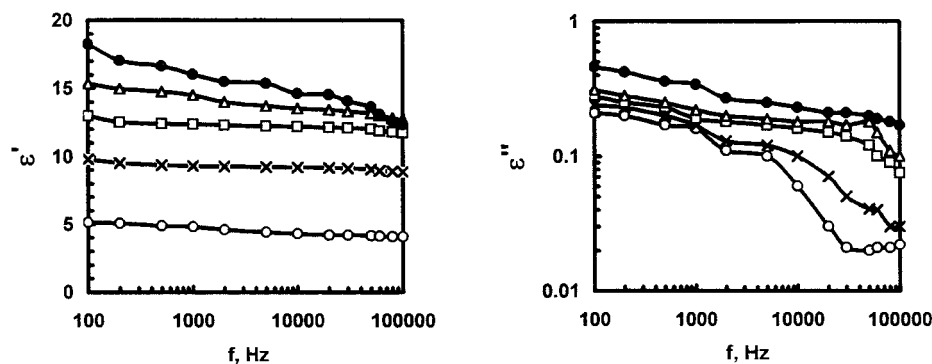


Figure 7 Permittivity ϵ' and dielectric loss ϵ'' for EPDM/PVC blends modified with 25 phr PET-TEG (in phr of EPDM): 100 (○); 75 (×); 50 (□); 25 (△); 0 (●).

the case of adding PET-TEG oligomers ($\epsilon'' = 0.41$ for PVC and $\epsilon'' = 0.5$ for PVC + 25 phr PET-TEG at 100 Hz), whereas a higher increase in ϵ'' is noticed in the case of the samples containing PET-BD oligomers ($\epsilon'' = 0.41$ for PVC and $\epsilon'' = 6.73$ for PVC + 25 phr PET-BD at 100 Hz).

It is interesting to note that the addition of 25 and 30 phr PET-TEG to PVC improves to some extent the insulating properties of the system, opposite to what was found in the PET-BD/PVC system, which achieves very high losses.

In view of the above discussion, it could be concluded that the addition of PET-TEG to PVC led to end products with enhanced insulating properties, which makes them suitable for some industrial applications.

EPDM is considered to be a good insulating material, given its ϵ' ranging from 3.5 to 2.5 and ϵ'' , from 0.16 to 0.016.³³ Thus, it was chosen to be blended with different concentrations of PVC after the addition of 25 phr PET-TEG as a recommended concentration to achieve more improvement for its insulating properties. The formulations of such blends are given in Table I.

The permittivity ϵ' and dielectric loss ϵ'' were measured at the same range of frequency and at room temperature for EPDM/PVC blend without PET-TEG oligomer and the obtained data are illustrated graphically in Figure 5. From this figure it is clear that the values of ϵ' increase by increasing PVC content in the blend and decrease by increasing the applied frequency, which shows anomalous dispersion. From this figure it is also found that the values of ϵ'' increase slightly by increasing the PVC content in the blend. The absorption curves relating the dielectric loss and the applied frequency are found to be flatter than the Debye curve, indicating more than one relaxation process.

Figure 6 represents the variation of ϵ' versus PVC content at two fixed frequencies, 100 Hz and 100 kHz, respectively. It may be noted that the values of ϵ' are not represented by a straight line and the deviation from linearity is negative. This negative deviation indicates poorer properties for the polymer blend than those of the individual components.

The permittivity ϵ' and dielectric loss ϵ'' were also measured at the same range of frequency and at room temperature for EPDM/PVC blend after the addition of 25 phr PET-TEG and the obtained data are illustrated graphically in Figure 7. It is clear that the values of ϵ' increase by increasing PVC content in the blend and decrease by increas-

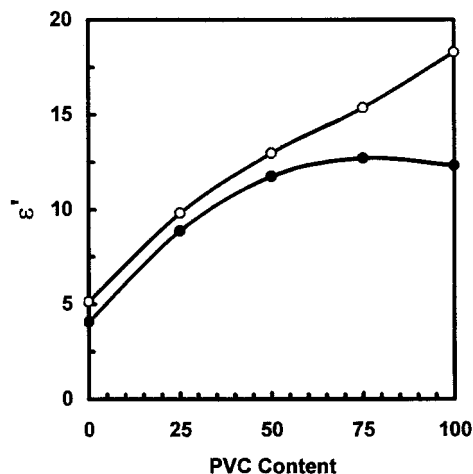


Figure 8 Relation between the content of PVC modified with 25 phr PET-TEG and ϵ'' at 100 Hz (○) and 100 kHz (●).

ing the applied frequency, thus showing anomalous dispersion. This increase is found to be much higher than that noticed before the addition of 25 phr PET-TEG. From this figure it is also found that the values of ϵ'' increase slightly by increasing PVC content in the blend. The dielectric loss ϵ'' is found to be slightly higher than that detected for samples free from PET-TEG.

Figure 8 represents the variation of ϵ' versus PVC content at two fixed frequencies, 100 Hz and 100 kHz, respectively. It is obvious that this relation is not represented by a straight line, although the deviation from linearity is positive. This means that the polymer blend may exhibit insulating properties better than those of either EPDM or PVC, which suggests a major synergistic improvement in practical utility for insulating purposes.

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