Electrical and Mechanical Properties of Ethylene Propylene Diene Monomer–Chloroprene Rubber Blend Loaded with White and Black Fillers

A. F. YOUNAN,[1] S. L. ABD-EL-MESSIEH,[2] A. A. GASSER[3]

[1] Polymer and Pigments Department, National Research Centre, Dokki, Cairo, Egypt

[2] Microwave Physics Department, National Research Centre, Dokki, Cairo, Egypt

[3] National Institute for Standards, Giza, Cairo, Egypt

Received 1 October 1997; accepted 20 March 1998

ABSTRACT: The permittivity ε' and dielectric loss ε'' for different ratios of an ethylene propylene diene monomer (EPDM)–chloroprene rubber (CR) blend ranging from 0 to 100 phr were measured over a frequency range from 400 Hz to 60 kHz. The measurements were carried out at room temperature (25°C). The values of ε' and ε'' were found to decrease with increasing EPDM content in the EPDM–CR blend. The sample which possesses the best mechanical and electrical properties was a 50 EPDM–50 CR blend. This sample was chosen to be loaded with 40 phr of some white fillers, namely, calcium carbonate, silica, silitan z, and talc. From the electrical and mechanical investigations, it was found that the use of silica and calcium carbonate in these blends could improve these properties. The electrical and mechanical properties were also studied for the investigated blends loaded with both silica and calcium carbonate with different contents (10–40 phr). It was found that 20 phr is the most promising concentration which can possess better properties. The same trend was obtained by the addition of 20 phr SRF black in addition to the white fillers to the above blends. On the other hand, from the compatibility study between both investigated rubber, it is found that both types are incompatible, in which some improvement may occur by the addition of PVC. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2061–2068, 1998

Key words: EPDM; chloroprene rubber; silica; calcium carbonate

INTRODUCTION

Raw rubber, either polar or nonpolar, has poor physicomechanical properties. To improve these properties, some ingredients such as accelerators, activators, antioxidants, and softeners should be added to the raw rubber. The addition of these materials in small quantities with respect to raw rubber could affect the electrical and mechanical properties[1,2] of the mixes. Many investigations on ethylene propylene diene monomer rubber (EPDM) blends have been reported,[3,4] while few investigations have been carried out to study the effect of carbon black on the electrical properties as well as on the mechanical properties of EPDM.[5,6]

Recently, the electrical and mechanical properties of EPDM loaded with different quantities of up to 60 phr SRF black[7] were studied. This investigation led to an increase in tensile strength, permittivity ε', and dielectric loss ε'' by increasing the SRF content, while elongation at break and equilibrium swelling decreased by increasing the percentage of SRF. The absorption curves relat-

Correspondence to: S. L. Abd-El-Messieh.

Journal of Applied Polymer Science, Vol. 70, 2061–2068 (1998)

ing ε'' and log f revealed the presence of three absorption regions relating to the Maxwell Wagner effect in the low-frequency region followed by the orientation of the large and small aggregates which were caused by the movement of the main chain in the intermediate and high-frequency regions.

The permittivity ε' of chloroprene rubber is moderately high, which makes it useful for the manufacture of wires, cables, and jackets for electrical conductors. Schneider et al.[8] studied the dielectric behavior of neoprene mixed with 50 phr channel black at frequencies between 500 and 10^8 Hz and temperatures between 20 and 60°C. They observed only α absorption (high-temperature absorption). Hanna et al.[9] made an extensive dielectric study on neoprene rubber loaded with four different types of carbon black in increasing quantities over a wide range of frequency (1 kHz to 40 MHz) and at room temperature. ε' and ε'' are found to increase by increasing the carbon concentration. The curves relating ε'' and log f were analyzed into three absorption regions. The low-frequency absorption region is attributed to the polarity of the ingredients added to rubber and was found to be the same for all investigated samples. The second absorption region which was observed at 5 MHz was associated with the Debye dispersion due to dipole rotation caused by movements of the main backbone carbon. The third relaxation process observed in that range of frequency was ascribed to rotations which can occur by segmental rotations or the local twisting motion of the main chain.

The aim of this work was to study systematically the dielectric properties of the EPDM, chloroprene rubber (CR), and their blends; therefore, it was also aimed to study the effect of SRF in addition to white fillers on the electrical and mechanical properties of the blend containing 1 : 1 EPDM–CR.

As the dynamic method discussed before[10] needs intensive work to be carried out in order to study the compatibility of the polymers, therefore, the aim here was to find a rapid dielectric method to study the compatibility of the blends. As EPDM–CR blends are considered to be incompatible,[11] therefore, it is reasonable to improve such compatibility by some additives.

EXPERIMENTAL

Materials

Polychloroprene (Neoprene) was the WRT type with a specific gravity of 1.23 g/cm^3 and Moony viscosity M(1 + 4) equal to 48 at 100°C. The EPDM 447 had a specific gravity of 0.86 g/cm^3 and a Moony viscosity M(1 + 4) of 48 at 85°C. The poly(vinyl chloride) (PVC) emulson was from BDH with a k value of 70.

Blend Preparation

The mixing was carried out in a Brabander plasticorder at 130°C and a rotor speed of 30 rpm. The mixing was continued for 5 min, and then peroxide was added to the mix on a laboratory two-roll mill (470-mm diameter; 300-mm working distance; speed of the slow roll, 24 rev/min; gear ratio, 1 : 1.4). The compounded blends were left overnight before vulcanization.

Vulcanization

ASTM determination of the rheometric characteristics, maximum torque M_H, minimum torque M_L, scorch time t_{s2}, optimum cure time t_{c90}, and cure rate index (CRI), was done using a Monsanto oscillating disc rheometer 100. The vulcanization was carried out in a heated flatten press under a pressure of about 40 kg/cm^2 and a temperature of 162 ± 1°C.

Techniques

The mechanical properties were measured at room temperature using a tensile testing machine (Zwick 1101) according to ASTM D 412–661 (1967). The permittivity ε' and dielectric loss ε'' in the frequency range (400 Hz to 60 kHz) were measured using an LCR meter type AG-4311 B Ando Electric LTB. The capacity C and the loss tangent tan δ were obtained directly from the bridge from which ε' and ε'' were calculated. The cell was calibrated using standard samples with known permittivity according to the method discussed before.[12]

RESULTS AND DISCUSSION

EPDM–CR Blend

The EPDM and CR were blended in different ratios and mixed with the rubber additives as shown in Table I. The rheometric characteristics were determined at 162 ± 1°C and are listed in the same table. The obtained data show that increase of the CR ratio decreases both the maximum and minimum torque while it increases the optimum cure time. Also, the

Table I Rheometric Characteristics and Mechanical Properties of EPDM and CR Blends

Ingredients	Sample				
	M_1	M_2	M_3	M_4	M_5
	Formulation				
EPDM	100.0	75.0	50.0	25.0	—
CR	—	25.0	50.0	75.0	100.0
	Rheometric Characteristics at 162 ± 1°C				
M_H (dN m)	98.0	87.0	85.0	75.0	83.0
M_L (dN m)	8.5	8.3	7.5	4.5	6.0
t_{c90} (min)	20.0	22.0	24.0	34.0	36.0
t_{s2} (min)	1.3	2.0	2.3	2.0	2.3
CRI (min^{-1})	5.3	5.0	4.5	3.1	3.0
	Mechanical properties				
M-200 (MPa)	2.1	2.3	3.0	3.2	2.9
Tensile strength (MPa)	11.2	10.5	9.7	9.5	9.2
Elongation (%)	450.0	470.0	480.0	565.0	550.0
Swelling (%) (toluene)	80.4	88.0	98.7	100.3	115.5
Swelling (%) (oil)	133.2	102.6	68.0	46.2	13.6

Base recipe: EPDM 50 : CR 50; stearic acid 1.5; zinc oxide 5; Magnesum oxide 4; salitan z 40; paraffin wax 3; sulfur 1; zinc diethyl thiocarbamate (ZDEC) 0.8; isopropyl phenylenediamine (IPPD) 1; tetramethylthiuram disulfide (TMTD) 0.3.

cure rate index was decreased by increasing the CR content. The rubber mixes were vulcanized at their optimum cure time and the physicomechanical properties were determined and are collected in Table I. From these data, it is clear that the increase of the CR content slightly decreases the tensile strength and increases the elongation at break. On the other hand, the equilibrium swelling in toluene slightly increases with increase of the CR, which can be

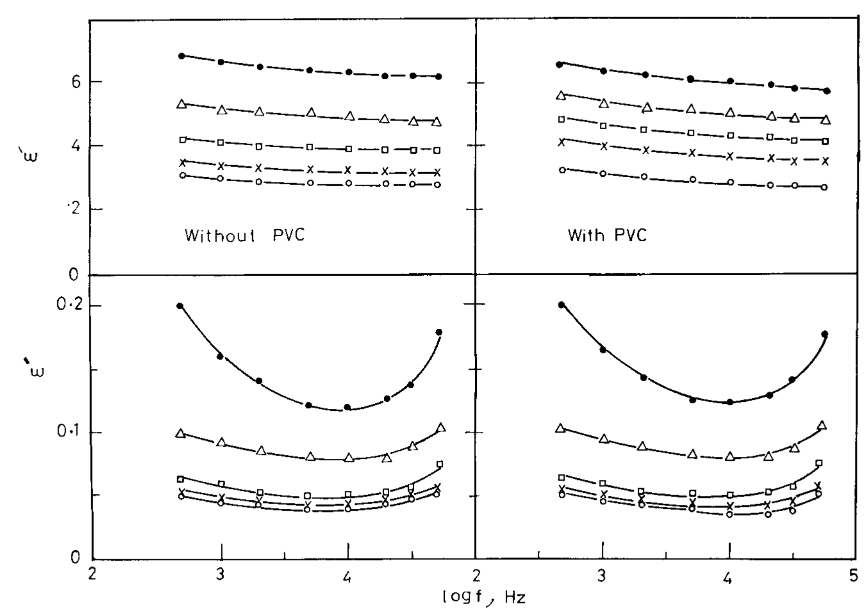

Figure 1 Permittivity ε′ and dielectric loss ε″ versus frequency for EPDM–CR blends: (○) 100 EPDM; (x) 75 EPDM; (□) 50 EPDM; (△) 25 EPDM; (●) 0 EPDM.

explained by the polarity of CR. This polarity highly reduces the swelling in motor oil.

The permittivity ε' and dielectric loss ε'' for different ratios of EPDM–CR rubber blends were measured over a frequency range from 400 Hz to 60 kHz. The measurements were carried out at room temperature ($\cong$ 25°C). The measured values of ε' and ε'' are illustrated graphically in Figure 1 versus log f, where f is the applied frequency. From this figure, it is clear that the permittivity ε' in the whole range of frequency increases with increasing CR content and shows an anomalous dispersion. The absorption curves relating ε'' and log f shown in Figure 1 seem to be broad, indicating the presence of more than one absorption region. These regions could be attributed to the rotation of the main chain[9] and the rotations which can take place by segmental rotations or the local twisting motion of the main chain.[9] On the other hand, the increase in ε'' in the lower-frequency range indicates the presence of an absorption region in such a range of frequency. This absorption region is considered to be due to the Maxwell Wagner effect, the origin of which is an ac current which is in-phase with the applied potential. This current results from the difference in permittivity and resistivity of the blends and the ingredients added to the rubber.

From Figure 1 it is noticed that the values of ε' and ε'' decrease by increasing the content of the nonpolar rubber (EPDM) in the blend. As the sample containing 50% EPDM is found to possess proper electrical and mechanical properties, therefore more measurements are advised on that sample when it is loaded with some types of white fillers in addition to SRF black.

EPDM–CR Blend 1 : 1 Loaded with Different White Fillers

To improve the properties of the above-mentioned blend, four different types of white fillers (silitan z, calcium carbonate, silica, and talc) with a constant ratio (40 phr) was added to the blend containing EPDM–CR (1 : 1). The rheometric characteristics were determined and are listed in Table II. From these data, it is shown that the addition of white fillers increases both the maximum and minimum torque, especially the silica which has a retarding effect as shown from the increase of both the scorch time and the optimum cure time. The rubber mixes were vulcanized at 162 ± 1°C for their optimum cure time. The me-

Table II Rheometric Characteristics and Mechanical Properties of EPDM–CR Blends with White Fillers and SRF Added

Ingredients	Sample No. M_{10}	M_3	M_{12}	M_{13}	M_{14}	M_{15}	M_{16}	M_{17}	M_{18}
Formulation									
White filler[a]	—	40.0 (1)	40.0 (2)	40.0 (3)	40.0 (4)	40.0 (1)	40.0 (2)	40.0 (3)	40.0 (4)
SRF	—	—	—	—	—	20.0	20.0	20.0	20.0
Rheometric characteristics at 162 ± 1°C									
M_H (dN m)	73.0	85.0	85.0	108.0	101.0	128.0	128.0	136.0	126.0
M_L (dN m)	5.0	7.5	7.5	8.5	5.5	11.5	14.5	14.5	11.5
t_{c90} (min)	22.5	24.0	27.0	26.5	26.5	26.0	26.5	31.5	25.5
t_{s2} (min)	1.7	2.3	2.0	2.5	2.3	1.8	2.0	1.7	2.0
CRI (min^{-1})	4.8	4.6	4.0	4.2	4.1	4.1	4.1	3.4	4.3
Mechanical properties									
M-200 (MPa)	1.4	3.0	2.1	4.6	2.3	8.3	6.0	8.2	5.7
Tensile strength (MPa)	9.1	9.7	8.5	9.7	8.1	13.5	12.1	11.3	13.4
Elongation (%)	530.0	480.0	485.0	425.0	470.0	325.0	270.0	230.0	295.0
Swelling (%) (toluene)	117.0	88.0	94.0	78.0	91.0	61.0	70.0	70.0	69.0
Swelling (%) (oil)	90.0	60.0	60.0	58.0	57.0	43.0	47.0	48.0	45.0

Base recipe: EPDM 50 : CR 50; stearic acid 1.5; zinc oxide 5; magnesium oxide 4; paraffin wax 3; sulfur 1; zinc diethyl thiocarbamate (ZDEC) 0.8; isopropyl phenylenediamine (IPPD) 1; Tetramethylthiuram disulfide (TMTD) 0.3.

[a] White fillers: (1) silitan Z; (2) calcium carbonate; (3) silica; (4) talc.

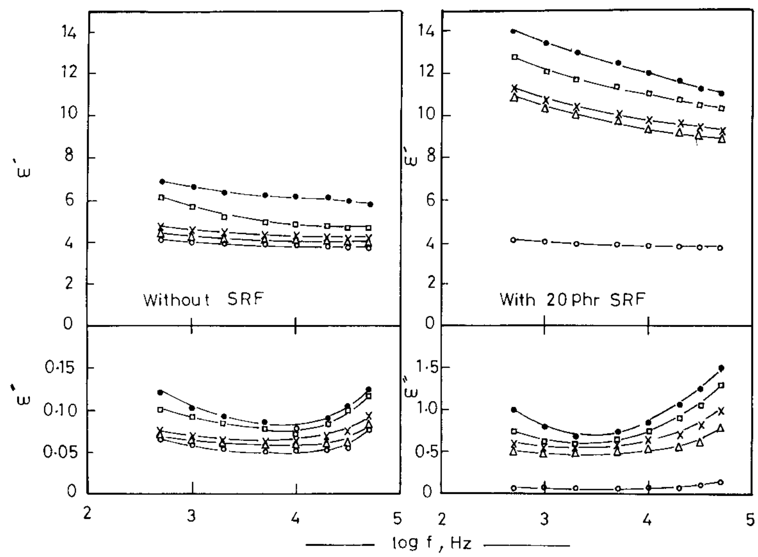

Figure 2 Permittivity ε' and dielectric loss ε'' versus frequency for (○) EPDM–CR blend 1 : 1 loaded with 40 phr of (△) silitan z, (X) talc, (□) calcium carbonate, and (●) silica.

chanical properties were determined and are collected in Table II. From these data, it is clear that the addition of white fillers improves the mechanical properties as well as the swelling resistance in both polar and nonpolar solvents as shown in Table II.

The permittivity ε' and the dielectric loss ε'' were measured for the EPDM–CR blend loaded with different types of white fillers. The measurements were carried out at the same range of frequency used in the previous measurements. The data are illustrated graphically in Figure 2. From this figure, it is clear that the values of ε' and ε'' at the whole frequency range increase in the order silica > calcium carbonate > talc > silitan z. The higher values of ε'' in the lower-frequency range could be attributed to the Maxwell Wagner effect, which usually appears in such a range of frequency due to the difference of permittivity of the ingredients added to the investigated rubber blend. In addition to that range, the flatness of the curves relating ε'' and log f indicates that there is more than one relaxation process. These processes may be due to the main chain and its related motions.[13] From the above study, it is clear that both silica and calcium carbonate possess very promising dielectric and mechanical properties. So, it could be concluded that the blends loaded with either silica or calcium carbonate are recommended to be used for insulating purposes. This result is comparable with that found before[4] in the case of butyl rubber loaded with some white fillers.

So, it was interesting to vary the percentage of both silica and calcium carbonate and to study their electrical and mechanical properties. For this purpose, four different concentrations ranging from 0 to 40 phr of either silica or calcium carbonate were added to the blend of EPDM–CR (1 : 1). Table III represents the prepared mixes as well as their rheometric characteristics. From the obtained data, it can be seen that the increase of calcium carbonate concentration slightly increases both the maximum and minimum torque while the increase of silica highly increases the torque but with a vulcanization retarding effect. The physicomechanical properties of the above samples were determined and are collected in Table III. It is clear that the increase of both types of fillers improves the mechanical properties and reduces the swelling percentage in both toluene and oil.

The permittivity ε' and dielectric loss ε'' were measured in the same way as discussed before. The obtained data are illustrated graphically in Figure 3. From that figure, it is clear that the values of ε' and ε'' increase by increasing the percentage of either silica or calcium carbonate. This increase is found to be much higher in the case of samples containing silica than in those containing calcium carbonate. This result is found to be comparable with that obtained before in the case of butyl rubber.[13] From Figure 3, it is also seen that the sample containing 20 phr of either silica or calcium carbonate can be recommended to possess better insulating properties as the ε''

Table III Rheometric Characteristics and Mechanical Properties of EPDM–CR Blends with Calcium Carbonate and Silica Added

Ingredients	Sample No.									
	M_{10}	M_{12a}	M_{12b}	M_{12c}	M_{12}	M_{13a}	M_{13b}	M_{13c}	M_{13}	M_{19}
Formulation										
Calcium carbonate	—	10.0	20.0	30.0	40.0	—	—	—	—	20.0
Silica	—	—	—	—	—	10.0	20.0	30.0	40.0	20.0
Rheometric characteristics at 162 ± 1°C										
M_H (dN m)	73.0	76.0	76.0	78.0	85.0	106.0	118.0	122.0	108.0	114.0
M_L (dN m)	5.0	5.5	6.0	6.0	7.5	6.0	7.0	8.0	8.5	6.0
t_{c90} (min)	22.5	23.0	23.0	26.5	27.0	28.0	29.5	31.5	26.5	31.0
t_{s2} (min)	1.7	2.0	2.0	2.0	2.0	2.3	2.3	2.0	2.5	1.5
CRI (min^{-1})	4.8	4.8	4.8	4.1	4.0	3.9	3.7	3.4	4.2	3.4
Mechanical properties										
M-200 (MPa)	1.4	1.6	1.6	1.4	2.1	1.8	2.3	3.0	4.6	1.7
Tensile strength (MPa)	9.1	9.5	9.2	7.4	8.5	8.1	7.2	8.0	9.7	7.0
Elongation (%)	530.0	440.0	455.0	430.0	485.0	480.0	415.0	385.0	425.0	350.0
Swelling (%) (toluene)	117.0	102.0	102.0	98.0	94.0	104.0	91.0	86.0	78.0	82.0
Swelling (%) (oil)	90.0	85.0	79.0	77.0	60.0	74.0	69.0	69.0	58.0	65.0

Base recipe: EPDM 50 : CR 50; stearic acid 1.5; zinc oxide 5; magnesium oxide 4; paraffin wax 3; sulfur 1; zinc diethyl thiocarbamate (ZDEC) 0.8; isopropyl phenylenediamine (IPPD) 1; tetramethylthiuram disulfide (TMTD) 0.3.

are not much higher than 30 and 40 phr. This result is also supported by the data given in the mechanical part.

EPDM–CR Blends 1 : 1 Loaded with Different White Fillers in Addition to 20 phr SRF

Semireinforcing furnace SRF, 20 phr, was added to the above samples loaded with the same white fillers. The rheometric characteristics were determined and are listed in Table II. From this table, it is clear that the addition of SRF black increases the torque due to its reinforcing effect. The rubber mixes were vulcanized at 162 ± 1°C at their optimum cure times. The mechanical properties were determined and are listed in Table II. From these data, it is clear that the addition of SRF black improves the mechanical properties as well as the swelling results in both polar and nonpolar solvents as shown in Table II.

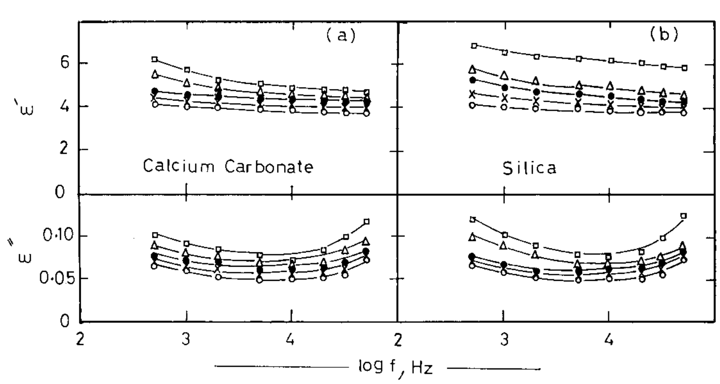

Figure 3 Permittivity ε′ and dielectric loss ε″ versus frequency for (○) EPDM–CR blend 1 : 1 loaded with (a) calcium carbonate (x) 10, (●) 20, (△) 30, and (□) 40 phr and (b) silica [same notations as (a)].

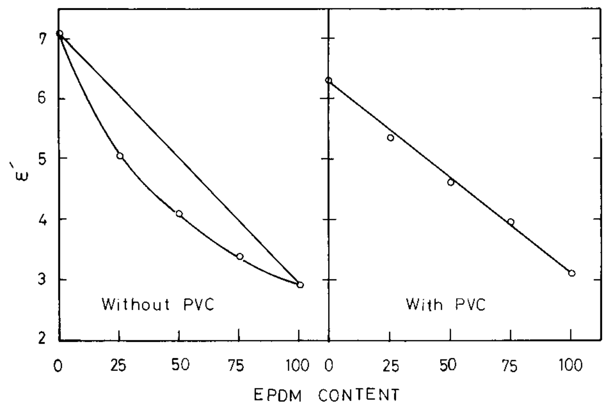

Figure 4 Relation between the permittivity ε' and rubber content.

The permittivity ε' and dielectric loss ε'' were measured for those samples containing SRF black in addition to the white fillers at the same range of frequency of 400 Hz to 60 kHz and the obtained data are illustrated graphically in Figure 2. From this figure, it is seen that the values of ε' and ε'' are much higher than those before adding the SRF black. This increase may be due to the presence of the conductive SRF black which provides interfaces and charge carriers which may be the cause of such increase. Also, from this figure, it is clear that both ε' and ε'' increase in the same way as noticed before the addition of SRF black. So, despite the higher increase in ε'' after the addition of 20 phr SRF, which may affect the insulating properties of the rubber, it is noticed that both calcium carbonate and silica possess the most proper insulating parameters.

Compatibility Study

To test the compatibility between the two types of rubber in the blend, the permittivity ε' is plotted graphically in Figure 4 versus the content of EPDM in the EPDM–CR blend at the frequency of 1 kHz. From this figure, it is clear that the values of ε' do not coincide with the line connecting the values of ε' for the two individuals (EPDM and CR). This indicates that the two types of rubber are incompatible since the deviation from that line is about 30%, which is considered to be higher than the promising experimental error. This presumption finds justification through the calculation of the heat of mixing,[10] which may be an approximate method for measuring the polymer–polymer compatibility using the Schneider equation.[14] The calculation done by Sidkey and coworkers[11] leads to the values of heat of mixing above the upper limit of compatibility, as shown in Figure 5, indicating that the EPDM–CR blends are incompatible.

To overcome the problem of phase separation between EPDM and CR, PVC was chosen to act as a compatibilizer and 10 phr was added to the above investigated blends. ε' and ε'' were again measured in the same way discussed above and the obtained data are illustrated graphically in Figure 1. It is clear that the addition of PVC increases slightly the value of ε' for EPDM and for all the investigated blends except that of CR, which was found to be slightly decreased. This decrease may be due to the lower value of ε' for PVC (5.0 at $f = 1$ kHz)[15] when compared with CR (6.3 at $f = 1$ kHz). There was no pronounced change in ε'' after the addition of PVC, as shown in Figure 1, when compared with those before the addition of PVC, as is also clear from the figure. To check the compatibility after the addition of PVC, Figure 4 shows the variation of ε' with the content of EPDM in the blend. From this figure, it is of great interest to find that the values of ε' coincide with the line connecting the values of ε' for both EPDM and CR. So, it could be concluded

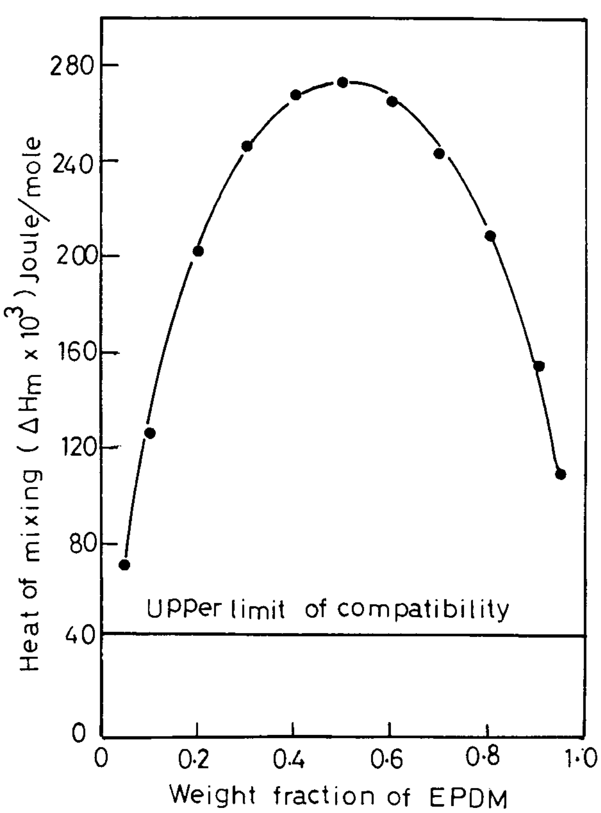

Figure 5 Relation between heat of mixing and weight fraction of rubber.

that the addition of PVC with a concentration 10 phr to the EPDM–CR blend may improve to some extent its compatibility.

The authors wish to express their deep gratitude to Dr. Samia Mokhtar, Assistant Professor of Chemistry, Faculty College for Girls, Ain Shams University, for her suggesting PVC as a compatibilizer.

REFERENCES

1. A. Abou-Bakr, M.Sc. Thesis, Cairo University, 1971.
2. F. F. Hanna, A. A. Yehia, and A. Abou Bakr, *Ind. J. Phys.,* **44,** 514 (1970).
3. A. Y. Coran, *Rubb. Chem. Technol.,* **61,** 281 (1988).
4. R. C. Nmita and K. B. Anil, *J. Adhes.,* **32,** 1 (1990).
5. P. K. Pal and S. De, *J. Appl. Polym. Sci.,* **28,** 3333 (1983).
6. F. L. Washougb, *Rubber World,* Oct. 27 (1987).
7. A. F. Younan, A. M. Gohneim, A. A. A. Tawfik, and K. N. Abd-EL-Nour, *Polym. Deg. Stab.,* **49,** 251 (1995).
8. W. C. Schneider, W. C. Carter, M. Magat, and C. P. Smyth, *J. Am. Chem. Soc.,* **67,** 959 (1945).
9. F. F. Hanna, K. N. Abd-EL-Nour, and S. L. Abd-EL-Messieh, *Polym. Deg. Stabil.,* **35,** 49 (1992).
10. A. M. Ashraf, S. El Sabbagh, and A. Y. Abbas, in *2nd Arab International Conference on Advances in Mechanical Science & Engineering (Polymeric Materials),* Cairo, 1993.
11. A. A. Sidkey, A. A. Yehia, N. S. Abd-El-Aal, and A. M. Eid, in *2nd Arab International Conference on Advances in Mechanical Science & Engineering (Polymeric Materials),* Cairo, 1993.
12. S. L. Abd-EL-Messieh, M.Sc. Thesis, Cairo University, 1989.
13. A. L. G. Saad, M.Sc. Thesis, Cairo University, 1980.
14. B. Schneider, *J. Appl. Polym. Sci.,* **17,** 3175 (1973).
15. A. M. Bishai, F. A. Gamil, F. A. Wani, and El-Khayat, *J. Appl. Polym. Sci.,* **30,** 2009 (1985).