Electrical and Mechanical Properties of Polyethylene–Rubber Blends

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ABSTRACT: A systematic electrical and mechanical study was carried out on styrene butadiene rubber (SBR), as a nonpolar rubber, and nitrile rubber (NBR), as a polar one blended with pure and waste polyethylene (PE), low and high density. The compatibility investigations, which were carried out by the dielectric method and confirmed by the calculated heat of mixing, indicate that SBR–PE blends (either low or high density) are compatible, while NBR–PE blends are incompatible. From the electrical and mechanical results, it is found that the addition of waste PE to either polar or nonpolar rubber leads to better electrical and mechanical properties when compared with those for the blends having pure PE. The values of permittivity ε' are found to increase pronouncely, while the values of dielectric loss ε'' slightly decrease. Shore hardness was also measured for all the investigated systems and found to vary linearly with the permittivity ε'. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 775–783, 1998

INTRODUCTION

The use of recycled polymers becomes one of the most important aspects of industry to overcome the problem of environmental pollution as such waste is not biodegradable. Recycled plastic is considered to be a source for new material with an economic impact.

Waste polyethylene recovered from wire jackets and cable sheets was blended with an ethylene vinyl acetate copolymer containing >25% vinyl acetate to give a product with high environmental stress, cracking resistance, and good low-temperature resistance.[1,2] On the other hand, waste polyethylene when blended with lignin is used in the manufacture of shipping containers.[3]

The compatibility of polymer–polymer blends was studied by many authors[4–8] with different methods. The theoretical calculation of heat of mixing can be considered as one of these methods.[4]

The aim of the present investigation is to study the electrical and mechanical properties of pure low- and high-density polyethylene blended with two different types of rubber, nitrile rubber (NBR) and styrene butadiene rubber SBR, which are polar and nonpolar, respectively. It is also aimed to carry out the same investigation to find out the possibility of using waste PE in the blend instead of pure.

EXPERIMENTAL

Materials

The virgin low-density polyethylene (LDPE) used in the study was supplied by Dow, while the high-density polyethylene (HDPE) was supplied by Hoechst. The materials had the following characteristics.

Property	LDPE	HDPE
Density at 23°C (g/cm^3)	0.94	0.95
Melt flow index 190/2.16 (g/10 min)	3.20	8.00
Vicat softening point (VST/B/50°C)	117.00	123.00
Hardness (Shore C)	79.00	94.00

The waste PE was obtained from the National Plastics Company and had the following characteristics.

Property	LDPE	HDPE
Density at 23°C (g/cm^3)	0.94	0.95
Melt flow index 190/2.16 (g/10 min)	6.20	6.80
Vicat softening point (VST/B/50°C)	123.00	129.00
Hardness (Shore C)	79.50	90.30

The two types of rubber used are nitrile rubber (butadiene acrylonitrile copolymer with 32% acrylonitrile) and styrene butadiene rubber (butadiene styrene copolymer with a styrene content of 23.5%). Peroxide (1,3-bis(isopropyl)butyl benzene peroxide) on calcium carbonate; trade name Perkadox 14/40; molecular weight 338) was used in this work.

Blend Preparation

The melt 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 the peroxide was added to the mix on a laboratory two-roll mill (470 mm diameter; 300 mm working distance). The speed of the slow roll was 24 rev/min with a gear ratio of 1 : 1.4. The compounded blends were left overnight before vulcanization.

Vulcanization

ASTM standards were followed for the determination of rheometric characteristics, maximum torque M_H, minimum torque M_L, scorch time t_{s2}, and optimum cure time t_{c90}; and the cure rate index (CRI) was done using a Monsanto Oscillating Disc Rheometer 100.

The vulcanization was carried out in a heated platen press under pressure of about 40 kg/cm^2 and a temperature of 172 $\pm$ 1°C.

Techniques

The Shore hardness test was determined by a Shore C durometer from CEAST (ASTM, C 2240 CEAST 1983) Wolpert (DIN 51220 Klass 10) using averaged multiple readings for each specimen.

The mechanical properties were measured at room temperature on a tensile testing machine (ASTM D 412–661, 1967; Zwick 1101).

Vicat softening temperature was determined by using 1-cm^3 samples according to the DIN 53460 method.

An LCR meter-type AG-4311B Ando electric LTD was used to measure the capacitance and loss tangent (tan δ) at the frequency range between 100 Hz up to 50 kHz. These parameters were obtained directly from the bridge from which the permittivity ε' and ε'' were calculated. The cell was calibrated using standard samples with known permittivity according to the method discussed before.[9]

RESULTS AND DISCUSSION

Styrene Butadiene Rubber–Polyethylene Blends

Table I summarizes the rheometric characteristics and the physicomechanical properties of the SRF–LDPE pure and waste blends. One can see clearly that minimum torque (M_L) and maximum torque (M_H) for SBR–LDPE blend decrease as the LDPE (pure or waste) content increases, while optimum cure time (t_{c90}) and scorch time (t_{s2}) increases with increasing LDPE content. This result is in good agreement with modulus data and tensile strength. This could be attributed to the LDPE behaving as the fiber-forming phase while SBR behaves as the matrix.[10] It is observed also from Table I that the addition of LDPE waste to SBR causes a significant improvement when compared with the pure LDPE.

The rheometric characteristics and the mechanical properties of the SBR–HDPE blends are given in Table II. From this table, it is clear that M_H and M_L decrease by increasing HDPE content in the blend, but in the case of HDPE waste, M_H and M_L have higher values. This is in good agreement with modulus at 100% elongation and tensile strength.

Figure 1 shows the frequency dependence of permittivity ε' and dielectric loss ε'' at room temperature 25°C for 5 different blends of SBR with either pure or waste, low- and high-density PE. From this figure, it is clear that ε' is decreased by increasing the applied frequency showing

Table I   Rheometric Characteristics and Mechanical Properties of SRF–LDPE Pure and Waste Blends

Ingredients	Sample No.								
	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9
Formulation									
SBR	100	75	50	25	—	75	50	25	—
LDPE (pure)	—	25	50	75	100	—	—	—	—
LDPE (waste)	—	—	—	—	—	25	50	75	100
Peroxide	4	4	4	4	4	4	4	4	4
Rheometric characteristics at 172 ± 1°C									
M_L (dN m)	9.0	4.0	3.0	1.3	2.0	4.5	3.0	3.8	2.0
M_H (dN m)	86.0	34.0	35.0	16.0	13.0	50.5	37.8	34.0	46.8
t_{s2} (min)	1.0	2.0	2.0	4.0	4.5	1.5	2.8	1.2	2.0
t_{cgo} (min)	11.5	16.0	19.0	19.5	14.5	16.0	21.0	18.5	20.0
CRI (min^{-1})	9.5	7.1	5.9	6.5	10.0	6.9	5.5	5.8	5.6
Mechanical properties									
M-100 MPa	0.7	2.3	5.6	5.8	—	4.3	—	9.4	13.9
T-S. MPa	0.7	4.3	7.2	8.4	11.8	6.9	13.9	14.9	18.7
Elongation (%)	100	200	160	180	50	200	80	250	280
Hardness (Shore C)	16	46	60	71	79	48	63	73	80
VST	81	89	97	109	117	95	105	117	123

anomalous dispersion. It is also noticed that the values of ε' increase by increasing the polymer content regardless of whether it is high or low density. Also, it is of great interest to notice that the values of ε' of waste PE–SBR blends are higher than those containing pure PE–SBR blends. This increase may be due to the oxidation of polyethylene. Such oxidation, which is deter-
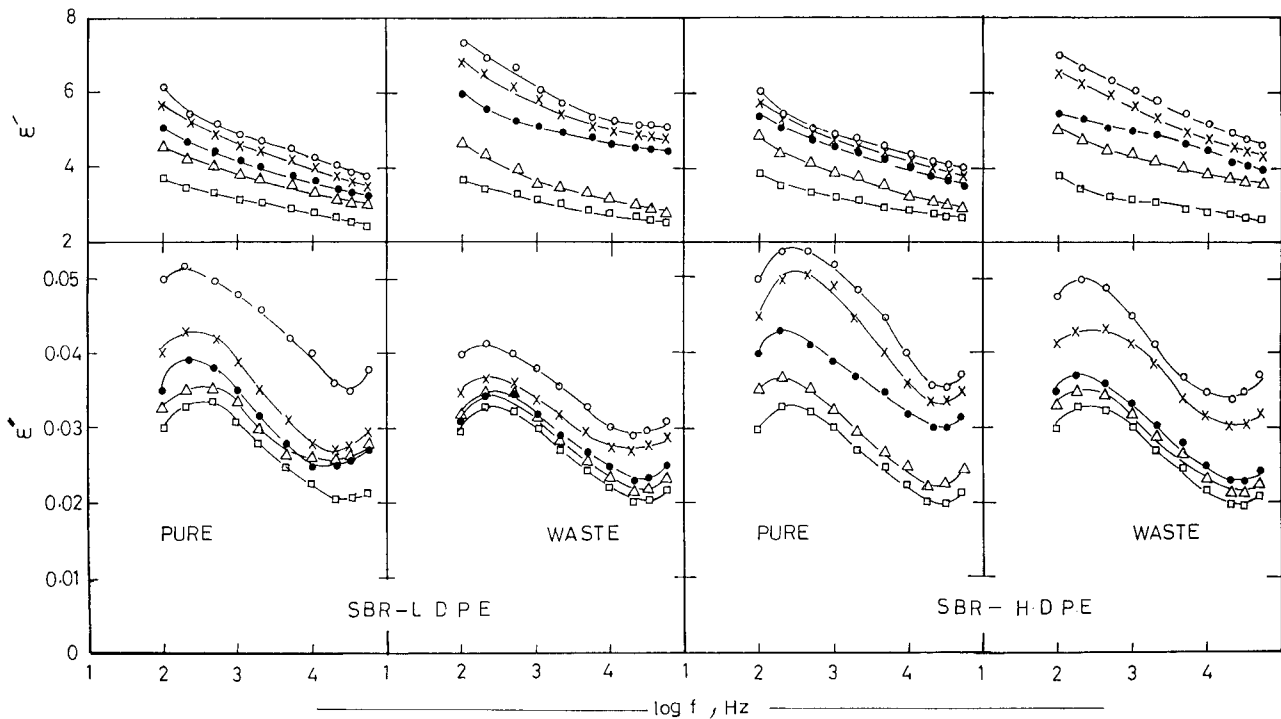

Figure 1 The permittivity ε' and dielectric loss ε'' versus frequency for SBR–PE blends: (○) 100 PE, (×) 75 PE, (●) 50 PE, (△) 25 PE, and (□) 0 PE.

mined by carbonyl groups, was studied by Reddish and Barrie[11] on the basis of comparison of dielectric data with infrared spectroscopic measurements by oxidative degradation. The increase in ε' is found to be slightly higher in the case of HDPE (either pure or waste) than that of LDPE. This increase may be due to the increase in the degree of crystallinity, which was found to be 87% for HDPE and 60% for LDPE.[11]

The absorption curves relating ε'' and log f shown in Figure 1 indicate several relaxation mechanisms. The Maxwell Wagner effect, which is expected to be at the lower frequency range at about 500 Hz, is considered to be one of these mechanisms. This effect is ascribed to the multi constituents of the investigated systems having different permittivities and conductivities. This region is found to be independent of the rubber content in the rubber–PE blend. The other undetected relaxation mechanisms may be due to the main chain and its related motions. From Figure 1, it is clear that the values of ε'' are lower in the case of waste PE–rubber blends than those for pure PE–rubber blends. Also, it is clear that the values of ε'' are higher in case of HDPE–SBR blends than those for LDPE–SBR blends.

From the above investigation it is seen that the values of the permittivity ε' increase while the dielectric loss values ε'' decrease by the addition of waste polymer. So, it could be concluded that when SBR is blended with the waste PE, it gives much more promising insulating properties than that containing the pure PE. Also it is found that the HDPE–SBR blends give better dielectric properties than the LDPE–SBR blends.

In order to test the compatibility between SBR and PE, the permittivity ε' is plotted graphically, as shown in Figure 2, versus the content of rubber in the blend at 1 kHz frequency. From this figure, it is clear that the values of ε' for SBR–PE, whatever the type of PE, are found to coincide with the line connecting SBR and PE, with fluctuation not exceeding 2%. This linearity indicates that the SBR–PE blends are compatible through the whole investigated range of concentrations. This presumption may be justified through the calculated heat of mixing. It is clear from Figure 3 that these systems are expected to be thermodynamically compatible as the calculated heats of mixing at all compositions are found to be lower than the upper limit of compatibility.[4]

Shore hardness was also measured for all the investigated blends using either pure or waste PE, and the obtained data are given in Tables I and II. From these tables, it is clear that hardness increases by increasing the PE for all the types of PE. It is also clear from this table that the hardness is slightly higher for the HDPE blends than for LDPE blends. Also, the values of hardness for the waste PE–rubber blend are found to be higher than those for pure ones.

Figure 4 represents the variation of ε' with hardness at two different frequencies 1 and 50 kHz. From this figure, it is clear that this relation is represented by a straight line with correlation factor not less than 0.99 for all the investigated blends. Any deviation was found to be within the experimental error, which was not more than 2.5%.

Vicat Softening Points (VST) were also measured for all investigated blends and are listed in Tables I and II to find out the temperature below which the product can be used.

Nitrile Rubber–Polyethylene Blends

The blends of NBR and LDPE (pure and waste) were prepared. The formulations of these blends are given in Table III. From the rheometric characteristics of these blends, it is seen that M_L and M_H decrease as the content of LDPE increases in the blend. On the other hand, t_{s2} and t_{c90} increase by increasing LDPE in the blend. This may be attributed to the nature of LDPE, which is considered to be an elastomer with a very low unsaturation content. Also, one can see that both modulus at 100% elongation and tensile strength increase with the increase of LDPE content. This means that these properties are improved by the replacement of NBR by about 25% LDPE.

The rheometric characteristics of the NBR–HDPE blends are given in Table IV. The data show that M_L and M_H decrease as the HDPE content in the blend increase. This is in good agreement with cure rate index (CRI) data. Table IV also shows that t_{c90} increases with an increasing HDPE content.

The mechanical properties of the investigated blends are given in Table IV. From this table, it is noticed that tensile strength and modulus at 100% elongation are increased by increasing the HDPE content in the blend. On the other hand, it is noticed that the tensile strength for the blend that contains waste HDPE is higher than that containing pure PE. This means that the presence of waste PE in the blend improves its mechanical properties.

Five different concentrations of NBR blended with pure or waste PE of low and high density were prepared. The same dielectric measurements were carried out, and the obtained data are
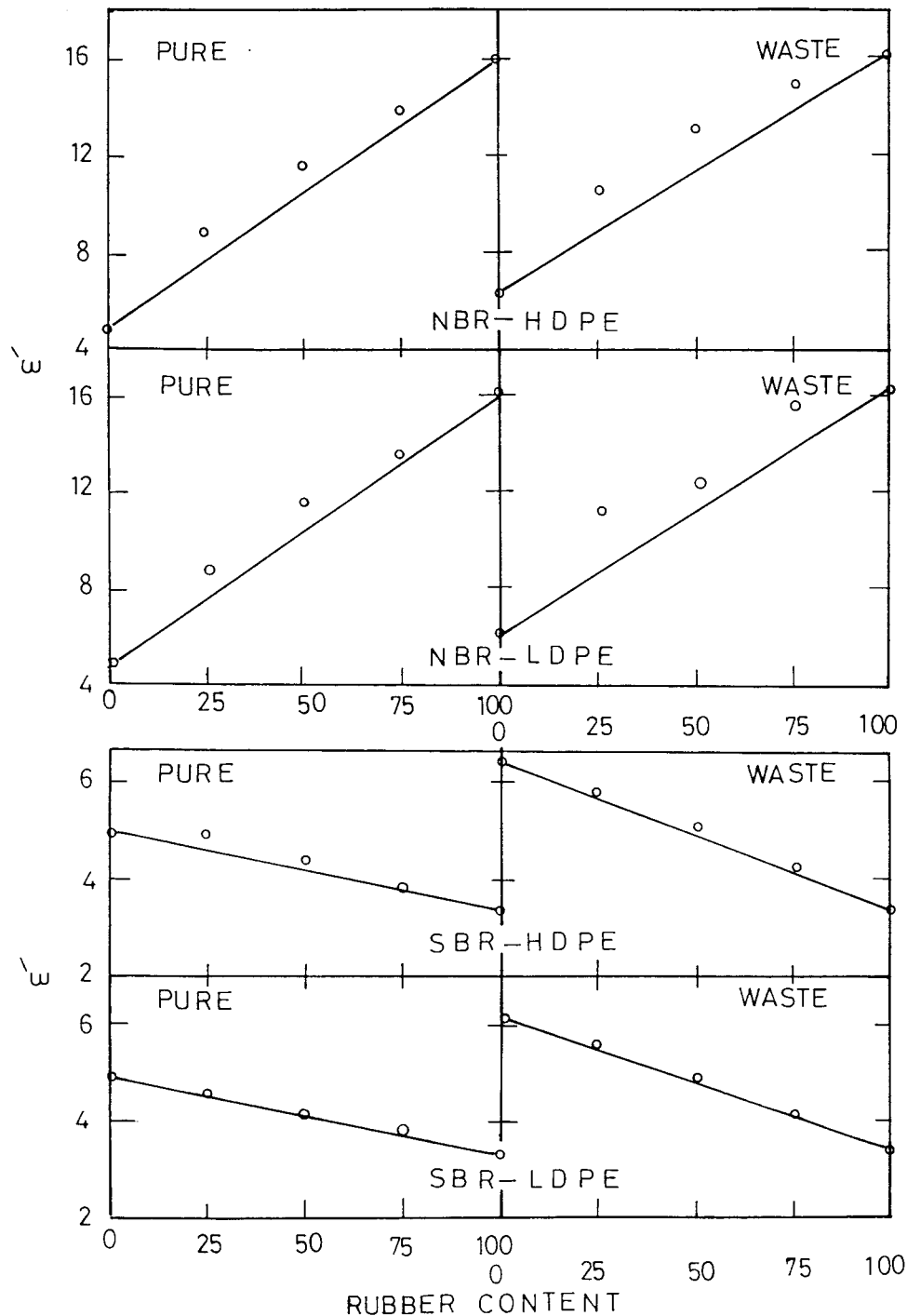
Figure 2 Relation between the permittivity ε' at 1 kHz and the rubber content.

illustrated graphically in Figure 5. The values of ε' for NBR are found to be much higher than those for polyethylene, so it is clear from Figure 5 that ε' decreases by increasing the PE content for all the investigated systems. From this figure, it is also clear that the values of ε' for HDPE–NBR blends is slightly higher than those of LDPE–

NBR blends either for pure or waste systems. This may be due to the higher degree of crystallinity of HDPE, which is responsible for the higher values of ε', as mentioned before.

On the other hand, it is found that ε' values of waste PE–NBR blends are found to be higher than those of pure ones. This behavior, which is
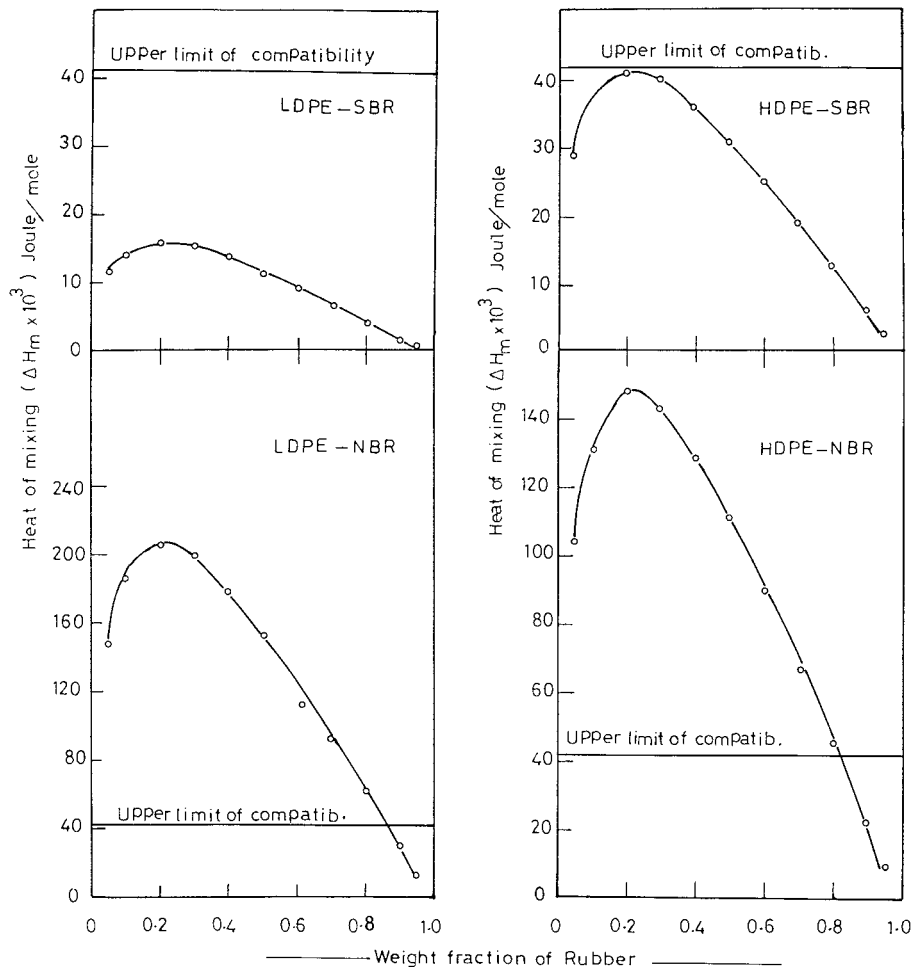
Figure 3 Relation between the heat of mixing and the weight fraction of rubber.

similar to that noticed in the case of the SBR–PE blend, may be due to the presence of carbonyl groups formed by oxidation of PE.[11]

From Figure 5, which represents the variation of ε'' with the applied frequency, it is clear that the values of ε'' decrease by increasing the PE content in the blend. This decrease is found to be higher in the case of HDPE than that of LDPE, which is contrary to that found for the nonpolar rubber SBR. On the other hand, it is also clear that the values of ε'' for waste PE–NBR blend are found to be lower than those for the pure PE one, which gives the same trend found in the case of SBR.

From Figure 5, it is found that the waste HDPE–NBR blends possess the highest values of permittivity ε' and the lowest dielectric loss ε''. This result leads to a conclusion that this type of blend is promising for electrical insulating purposes.

To check up the compatibility between NBR and both pure and waste PE, the permittivity ε' is plotted graphically in Figure 2 versus the content of rubber in the blend at a frequency of 1 kHz. From this figure, it is clear that the deviation of ε' of the blends from the line connecting the values of both NBR and PE (pure or waste) ranges from 20 to 25%. This nonlinearity indicates that NBR–PE blends, either for low- or high-density PE, are incompatible. This result is supported by the calculation of the heat of mixing, as given in Figure 3. From this figure it is clear that the calculated values of heat of mixing for NBR–LDPE and NBR–HDPE blends are found to lie in the upper limit of compatibility. Therefore, these blends are considered to be technologically and thermodynamically incompatible blends.

Shore hardness was measured for the investigated NBR–PE pure and waste blends. The obtained data are given in Tables III and IV. Comparing these tables with Tables I and II, it is clear that same trend as for SBR is obtained.

Table II   Rheometric Characteristics and Mechanical Properties of SBR–HDPE Pure and Waste Blends

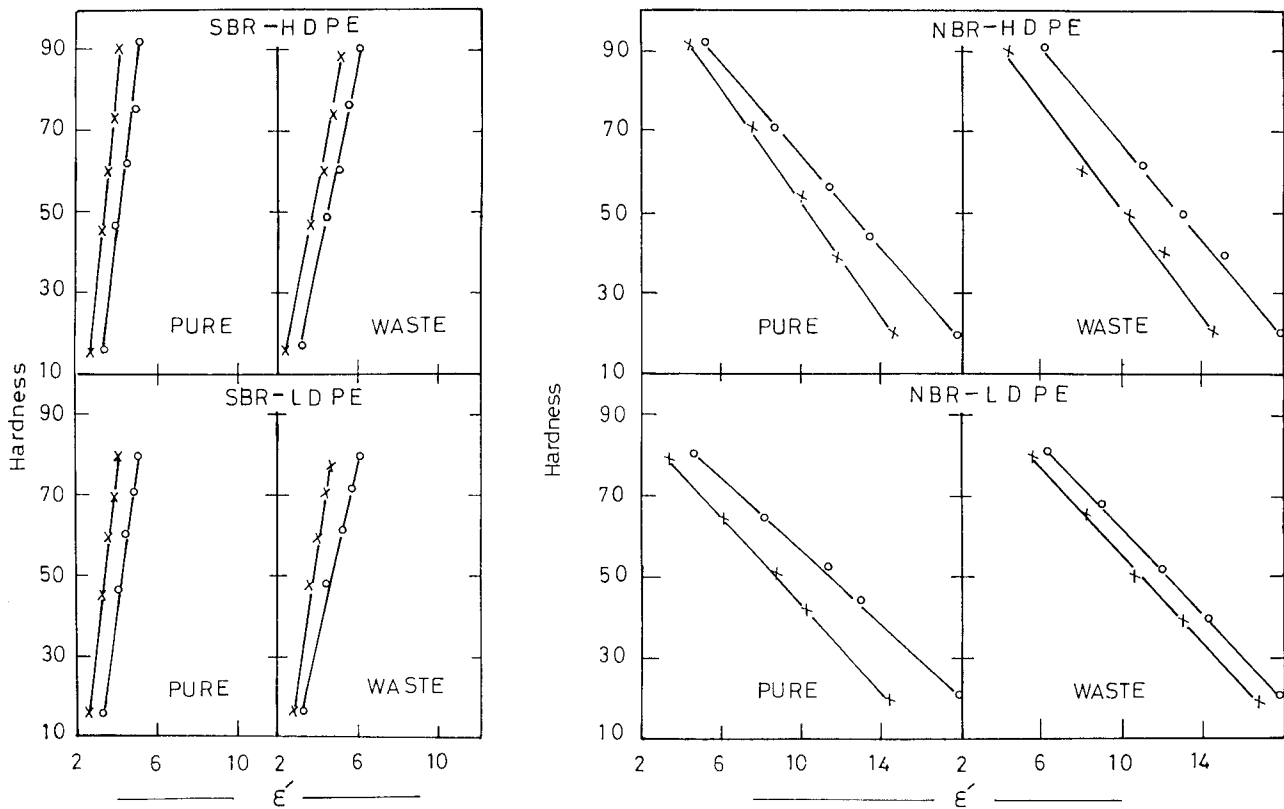|	Sample No.								
Ingredients	A_1	B_2	B_3	B_4	B_5	B_6	B_7	B_8	B_9
Formulation									
SBR	100	75	50	25	—	75	50	25	—
HDPE (pure)	—	25	50	75	100	—	—	—	—
HDPE (waste)	—	—	—	—	—	25	50	75	100
Peroxide	4	4	4	4	4	4	4	4	4
Rheometric characteristics at 172 ± 1°C									
M_L (dN m)	9.0	6.0	2.5	2.0	2.3	6.5	5.0	2.0	4.5
M_H (dN m)	86.0	39.0	27.0	24.5	13.0	46.0	44.0	28.0	16.0
t_{s2} (min)	1.0	2.0	3.0	3.0	4.0	1.8	2.0	3.0	3.5
t_{cgo} (min)	11.5	16.5	18.5	22.5	14.5	17.5	21.0	19.0	16.0
CRI (min^{-1})	9.5	6.9	6.5	5.1	9.50	6.3	5.3	6.3	8.0
Mechanical properties									
M-100 (MPa)	0.7	3.7	8.3	13.85	—	6.1	10.4	14.8	—
T-S (MPa)	0.7	5.9	11.3	16.3	14.9	8.8	14.4	16.0	18.8
Elongation (%)	100	225	200	150	50	200	200	200	70
Hardness (Shore C)	16	48	62	76	94	49	67	77	90
VST	81	97	107	115	123	97	108	119	129

Figure 4   Relation between the permittivity ε' at (○) 1 kHz and (×) 50 kHz and the hardness.

Table III   Rheometric Characteristics and Mechanical Properties of NBR–LDPE Pure and Waste Blends

Ingredients	Sample No.								
	C_1	C_2	C_3	C_4	A_5	C_5	C_6	C_7	A_9
Formulation									
NBR	100	75	50	25	—	75	50	25	—
LDPE (pure)	—	25	50	75	100	—	—	—	—
LDPE (waste)	—	—	—	—	—	25	50	75	100
Peroxide	4	4	4	4	4	4	4	4	4
Rheometric characteristics at 172 ± 1°C									
M_L (dN m)	5.5	3.0	2.0	1.3	2.0	5.5	3.8	2.5	2.0
M_H (dN m)	80.0	30.0	29.0	18.0	13.0	50.0	29.0	40.5	46.8
t_{s2} (min)	1.8	2.3	2.5	4.5	4.5	1.5	2.0	2.3	2.0
t_{cgo} (min)	10.0	15.0	18.0	18.5	14.5	19.5	17.0	21.5	20.0
CRI (min^{-1})	12.1	7.8	6.5	7.1	10.0	5.5	6.7	5.2	5.6
Mechanical properties									
M-100 (MPa)	0.5	2.3	3.8	7.1	—	5.9	10.0	14.4	13.9
T-S (MPa)	1.5	5.2	7.9	8.6	11.8	11.0	16.0	15.6	18.7
Elongation (%)	225	355	340	230	50	250	250	216	280
Hardness (Shore C)	20	43	53	67	79	44	54	76	80
VST	87	93	97	113	117	92	96	112	123

The relationship between the hardness and ε' is illustrated graphically in Figure 4. From this figure, it is found that ε' varies linearly with the hardness for all investigated blends with a deviation not exceeding 2.5%, which is the same relation obtained for the compatible SBR–PE blends.

From this result it could be concluded that ε' varies linearly with hardness for the two types of rubber–PE blends. This linearity seems to be independent of the compatibility of the blend.

Vicat softening points (VST) were also measured for all investigated blends and are listed in Tables III and IV to find out the temperature below which the product can be used.

Table IV   Rheometric Characteristics and Mechanical Properties of NBR–HDPE Pure and Waste Blends

| Ingredients	Sample No.								
	C_1	D_2	D_3	D_4	B_5	D_5	D_6	D_7	B_9
Formulation									
NBR	100	75	50	25	—	75	50	25	—
HDPE (pure)	—	25	50	75	100	—	—	—	—
HDPE (waste)	—	—	—	—	—	25	50	75	100
Peroxide	4	4	4	4	4	4	4	4	4
Rheometric characteristics at 172 ± 1°C									
M_L (dN m)	5.5	2.8	1.0	1.5	2.3	7.8	3.5	2.5	4.5
M_H (dN m)	80.0	31.0	17.0	25.5	13.0	58.0	33.0	28.5	16.0
t_{s2} (min)	1.8	2.3	3.0	2.3	4.0	2.0	2.5	2.8	3.5
t_{cgo} (min)	10.0	15.0	17.0	18.0	14.5	16.5	21.0	23.0	16.0
CRI (min^{-1})	12.1	7.8	7.1	6.3	9.5	6.9	5.4	4.9	8.0
Mechanical properties									
M-100 (MPa)	0.5	4.4	9.0	9.9	—	4.6	10.5	14.3	—
T-S (MPa)	1.5	7.2	13.8	13.0	14.9	8.5	15.9	16.2	18.8
Elongation (%)	225	255	485	400	50	250	215	225	70
Hardness (Shore C)	20	44	56	72	94	46	54	63	90
VST	87	94	98	115	123	96	103	114	129
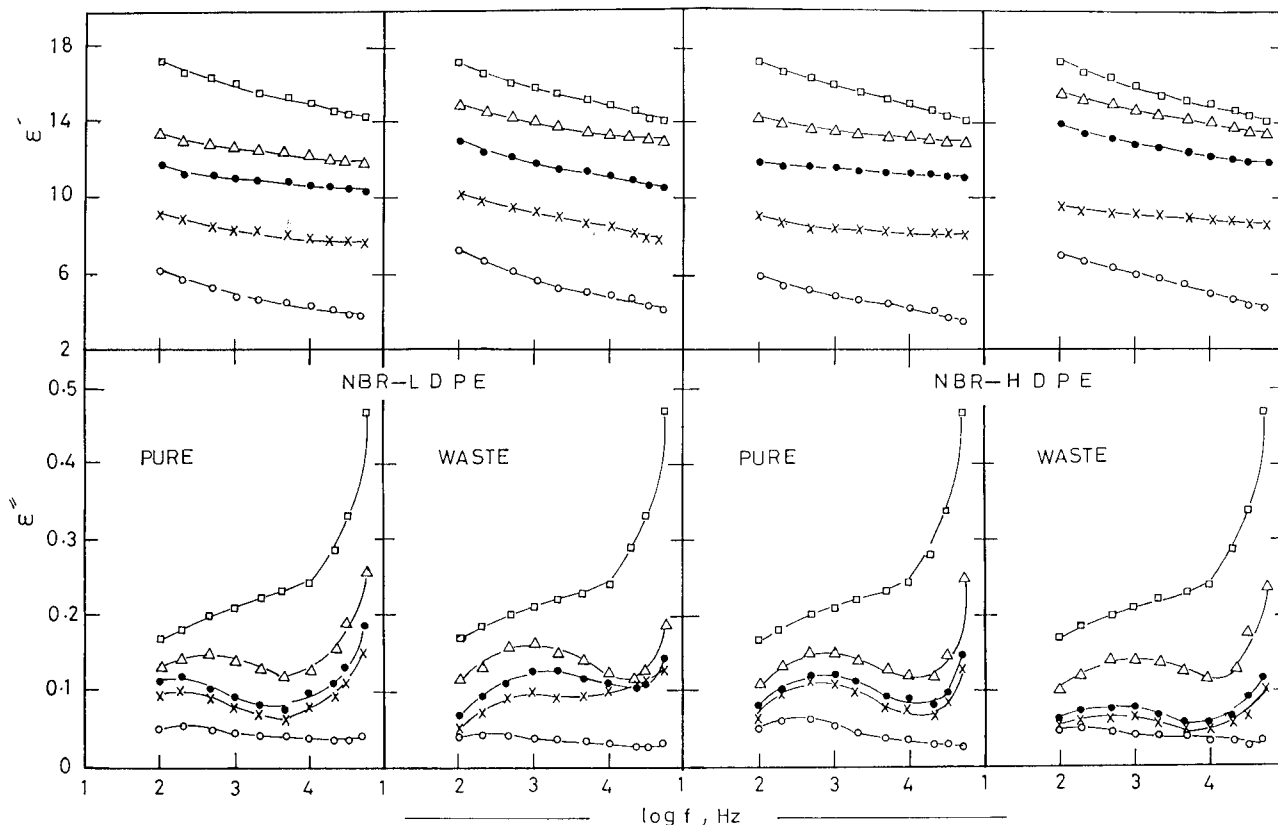
Figure 5 The permittivity ε' and dielectric loss ε'' versus frequency for NBR–PE blends: (○) 100 PE, (×) 75 PE, (●) 50 PE, (△) 25 PE, and (□) 0 PE.

From the above investigations it could be concluded that the addition of waste PE to either polar or nonpolar rubber provides preferable insulating properties than those containing pure ones. So waste polyethylene, which contributes a high risk of environmental pollution, can be consumed by blending it with rubber to form new industrial products that possess promising electrical, as well as mechanical, properties.

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