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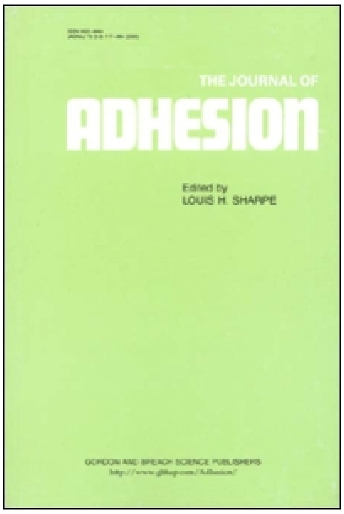

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Studies on Adhesion Between Natural Rubber and Polyethylene and the Role of Adhesion Promoters

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Studies on adhesion between natural rubber (NR) and polyethylene (PE) with different levels of interaction (physical and chemical) have been carried out. Ethylene propylene diene rubber (EPDM) and chlorinated polyethylene (CPE) were used as physical promoters and epoxidised natural rubber/modified polyethylene (ENR/PEm) and sulfonated ethylene propylene diene rubber/modified polyethylene (S-EPDM/PEm) were used as chemical adhesion promoters. The failure surfaces were examined with the help of scanning electron microscopy (SEM), optical photography and electron spectroscopy for chemical analysis (ESCA) techniques.

The peel strength between natural rubber and polyethylene as measured in this study is 140 J/m^2. With the incorporation of physical promoters such as EPDM, the peel strength increases twenty fold because of structural similarity of EPDM with PE and the rubbery nature of EPDM. Similarly, the other promoters show significant improvement in peel strength. At high temperature and low rate of peeling, the nature of failure is mainly "stick-slip" for joints with interaction promoters. The average peel strength increases with increase in test rate and decrease in test temperature for most of the joints. All the data could be shifted onto a master curve indicating that the increase in strength is a result of viscoelastic dissipation. NR/EPDM/PE and NR/CPE/PE systems, however, behave in a different way probably because they alter the nature of crack propagation at or near the interface. ESCA results of the peeled PE surface show a chemical shift of C_{1S} peak. SEM photographs also indicate interaction at the interface when modifiers are used. An increase in crystallinity of PE from 30% to 64% and modulus increase the peel strength of NR/PE joints by a factor of four. The results of peel strength measurement at 90° are lower than those at 180°. Lap shear results are in line with peel strength.

KEY WORDS Adhesion; adhesion promoters; EPDM; natural rubber; polyethylene.

INTRODUCTION

The mutual adhesion between component phases is expected to monitor ultimate properties of polymer blends. It is well known that the phenomenon of adhesion plays a major role in determining the performance of composites.[1,2] Generally, the main factors are the nature of substrate, method of joint assembly and

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conditions of testing, *e.g.* the rate and temperature of testing.[3] All these variables act in a complex manner in determining the strength of the joint. The stress distribution in each component, the interaction forces at the interface and the rheological behavior of the components are also influenced to different extents by these variables. Though rubber-to-rubber adhesion[4,5] and plastic-to-plastic adhesion[6] have been reported earlier, very limited studies on rubber-to-plastic adhesion have been carried out. These studies are important in view of the recently commercialized thermoplastic elastomers from rubber-plastic blends.[7–10] Bhowmick *et al.*[11,12] reported preparation of thermoplastic natural rubber and their preliminary results on adhesion between natural rubber (NR) and polyethylene (PE) and natural rubber and polypropylene (PP). The present investigation deals with the detailed studies on adhesion between natural rubber and polyethylene used for the preparation of thermoplastic natural rubber. The variables taken up for the present study are as follows:

1) Effect of adhesion promoters
2) Effect of testing rate and temperature
3) Studies on failure surfaces by ESCA and SEM
4) Effect of crystallinity/modulus of plastic
5) Effect of different modes of testing.

EXPERIMENTAL

Materials used

Natural Rubber (NR)—ISNR 5 was supplied by the Rubber Board, Kottayam, India. Molecular weight M_w – 7,80,000. Intrinsic visocisty (Benzene, 30°C, dl/g) (η) – 4.45, Wallace plasticity ρ_0 – 59.0.

Polyethylene (PE)—Indothene 16 MA 400, was supplied by IPCL, Baroda. Density (g/cm^3)—0.916. Melt Flow Index, MFI, (g/10 min)—40.

High Density Polyethylene (HDPE)—Hostalen GA 7260, was supplied by IPCL, Baroda. Density (g/cm^3)—0.960. Melt Flow Index, MFI, (g/10 min)—16.

PEm—Polyethylene modified by benzoyl peroxide and maleic anhydride.[13]

Chlorinated polyethylene (CPE)—36% chlorine, was supplied by Dow Chemicals, USA. Specific gravity—1.16. Mooney viscosity $ML_{(1+4)}$121°C—80.

Ethylene propylene diene rubber (EPDM)—Keltan 520, was supplied by DSM, Holland, through SBM Chemicals, India. Specific gravity—0.86. Mooney viscosity $ML_{(1+4)}$125°C—46.

Sulfonated EPDM (S-EPDM)—Ionomer 2590, was supplied by Uniroyal Chemical Co., USA. Density (g/cm^3)—1.12. Mooney viscosity $ML_{(1+4)}$100°C—45–50. percent by weight ionic group—2.7.

Epoxidised natural rubber (ENR)—ENR 25, was supplied by MRPRA, UK. Density (g/cm^3)—0.97. Epoxidation level 25 mol%. Mooney viscosity $ML_{(1+4)}$100°C–110.

Preparation of the samples

Natural rubber was masticated in an open mill for 2 mins and was sheeted out to a thickness of 2 mm in a hydraulic press at 100°C. For the preparation of the rubber-plastic joints, in which two rubbery components are present, the modified rubber was incorporated into the NR phase at a level of 20 parts (in 70 parts rubber) and the same procedure was followed. The sheet was fabric backed on one side and had aluminium foil on the other side. This assembly was then kept for 15 min at room temperature to allow for shrinkage. The plastic was also sheeted out to 1 mm thickness at 150°C. The modified plastic (PEm) was mixed with PE at a concentration of 10% by wt. of PE in a Brabender Plasticorder and was sheeted out. Then the plastic sheet was put over the fabric-backed rubber sheet in between which cellophane paper was partially introduced to get a demarcation line for gripping during testing. The assembly was heated for 10 min at 100°C followed by 15 min at 150°C and was then cooled to ambient temperature over a period of 30 min.

Measurement of strength of adhesion

The test pieces were punched out from the molded sheet at a width of 20 mm by a hollow punch. Peel testing at 180° and 90° was done in a Zwick UTM (1445 model) at different rates and temperatures. Single lap shear test was also conducted using specimens 4 inch by 1 inch with a 1-inch square overlap. Figure 1 shows the different geometries of the adhesion samples. The lap specimens were tested at a crosshead speed of 200 mm/min at room temperature and the force at break was recorded.

The peel strength for 180° and 90° peel was calculated using the following

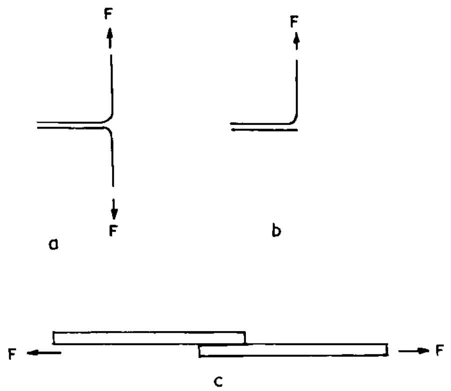

FIGURE 1 Different geometry of the adhesion samples. a) 180° peel test, b) 90° peel test, c) single lap shear.

TABLE I
Peel strength data

System	Rate (mm/min)	Peel strength in J/m^2				Observation
		Room Temp. (25°C)	50°C	75°C	100°C	
1	2	3	4	5	6	7
NR/PE	50	100	80	45	Rupture from plastic surface takes place.	Sharp interface at all temperatures and rates
	200	140	100	50		
	500	140	110	55		
	750	150	110	60		
NR/CPE/PE	50	145	75	Rubber sticking onto plastic surface & rupture from plastic phase.	—	Stick-slip failure at low rates and high temperature
	200	155	80			
	500	200	100	160	—	
	750	250	100	140		
NR/EPDM/PE	50	3000	2500	900 (after 40 mm adhesive failure)	—	Rubber sticking onto plastic surface at low rate & high temp. at normal rate & temp. the 2 surfaces separated through fibrillar linkages.
	200	3190	2600	1500	—	
	500	3200	2700	1600	—	
	750	3250	2800	1800 (rupture from plastic surface)		

NR/S-EPDM/PE	50	150	140	Rupture from fabric rubber interface	—	Stick-slip failure at low rates & high temperature
	200	175	160	100	—	
	500	180	170	100	—	
	750	210	200	120	—	
NR/S-EPDM/PEm/PE	50	180	165	120	—	Stick-slip failure at low rates & high temperature
	200	210	210	160	—	
	500	300	250	170	—	
	750	320	250	180	—	
NR/ENR/PE	50	130	120	60	—	Smooth failure at all rates & low temperatures but at higher temperature it changes to stick-slip failure
	200	160	140	70	—	
	500	170	142	75	—	
	750	180	150	80	—	
NR/ENR/PEm/PE	50	350	250	200	—	Stick-slip failure at low rates and high temperature.
	200	430	265	230	—	
	500	500	280	250	—	
	750	520	300	260	—	

relations

$$\mathrm{Ga}_1 = \frac{2F}{w} \quad \text{(for 180° peel)} \tag{1}$$

$$\mathrm{Ga}_2 = \frac{F}{w} \quad \text{(for 90° peel)} \tag{2}$$

where F = load in newtons required to separate the layers and w = width of the specimen. All the joints were tested within two days after preparation.

Surface analysis

ESCA Failure surfaces generated by peel tests were studied by electron spectroscopy for chemical analysis (ESCA) using a Model ESCA LAB MK II electron spectrometer, with MgKα radiation as the source of excitation and with a sample chamber pressure of 2×10^{-8} m Bar.

SEM studies To study the morphology of the peeled surfaces a few fractured samples were examined in the scanning electron microscope within 24 hrs. of testing.

Optical photography Optical photographs of a few failed samples were taken with a Rolleiflex camera.

RESULTS AND DISCUSSION

The peel strength between various components over a range of rates and temperatures is given in Table I. In general, the adhesion promoters either physical (EPDM or CPE) or chemical (ENR/PEm or S-EPDM/PEm) increase the peel strength between natural rubber and polyethylene. The increase is sometimes thirty-fold depending on composition, temperature and rate. It is also important to note that all the joints do not show similar failure behavior as observed on the force charts (Figure 2). The NR/EPDM/PE and the NR/CPE/PE show wider variation of force with continuous failure initiation and arrest than does the control NR/PE system. In the case of NR/CPE/PE, the rate of crack propagation may be faster than the test rate resulting in periodic failure. Some investigators[14] have reported that such failure is associated with a well-defined maximum and minimum and the distance between them does not depend on test rate.

Effect of testing rate

Whatever the nature of failure may be, the average strength increases with increase in the test rate at all temperatures for all the joints. This is due to the viscoelastic effects at the interface as described earlier.[15] The NR/EPDM/PE

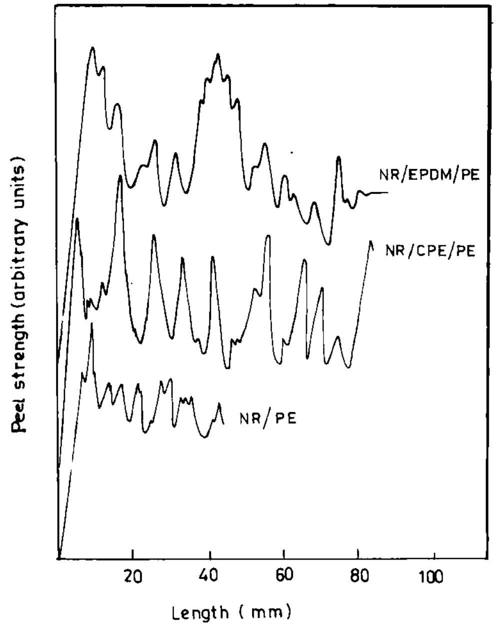

FIGURE 2 Failure curves of different joints tested at a rate of 750 mm/min and room temperature.

joint shows the maximum peel strength because of some structural similarity of EPDM with PE and interaction with NR. The detachment changes from a "stick-slip" mode, with peel force oscillating between high and low values (due to tearing in the rubbery phase) at low rates, to comparatively smooth failure at high test rates.

Effect of test temperature

The effect of testing temperature on the peel strength is also reported in Table I. As the temperature is increased (from room temperature to 50°C) the joint strength decreases for almost all the systems. At higher temperature (75°C) the rubber sticks onto the plastic phase and complete "stick-slip" failure occurs. In some cases (NR/S-EPDM/PE) rupture from the fabric-rubber interface also takes place at 75°C and at the 50 mm/min rate. At still higher temperature (100°C) the plastic starts to soften and in most cases the plastic phase undergoes rupture. Practically, it was impossible to conduct the test at that temperature. At 50°C NR/ENR/PE and NR/PE show "smooth" failure at all rates, whereas NR/EPDM/PE, NR/CPE/PE, NR/ENR/PEm/PE and NR/S-EPDM/PEm/PE show 'stick-slip' failure at very low rates, 'smooth' failure at medium rates but at high rates they show mixed "stick-slip" and "smooth" failure. At still higher temperature (75°C) "smooth" failure changes to "stick-slip" failure. For testing uncrosslinked rubbery adhesives by the peel geometry the same sort of transition from "smooth" to "stick-slip" failure with the increase in temperature was reported by some authors.[16] Such behavior, according to them, is due to a change from an elastic response (interfacial failure) to a viscous flow response (cohesive failure) and is valid only for uncross-linked elastomers. It is interesting to note that there is some analogy between high temperature and low rate of testing. Both induce stick-slip failure. Moreover, not only will the interface be influenced by temperature but also the ultimate strength and rheological properties of the constituent polymers.

Master curves

All the data at various rates and temperatures are now converted into equivalent rates at room temperature by using the standard shifting technique[17] as shown in Figure 3. It must be mentioned that not all of the data obtained for various systems are shiftable. For example, master curves could not be obtained for NR/EPDM/PE or NR/CPE/PE joints whereas those for NR/PE, NR/S-EPDM/PE, NR/S-EPDM/PEm/PE, NR/ENR/PE and NR/ENR/PEm/PE are shown in Figure 3. Thus the variation in the peel strength with the rates and temperatures for the latter systems clearly arises from a viscoelastic energy loss mechanism. In NR/EPDM/PE or NR/CPE/PE joints, the nature of crack propagation seems to play a more important role than the viscoelastic losses at the interface (or the interfacial region) so as to make the data deviate from the master curves, especially at higher temperatures.

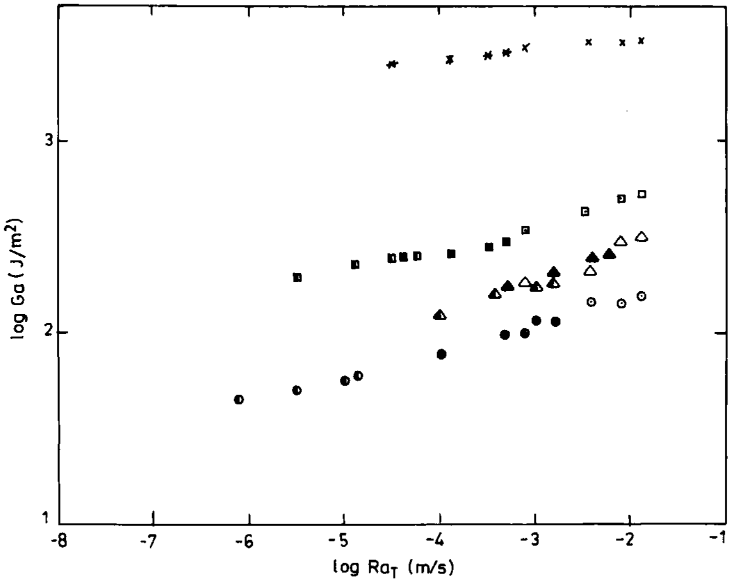

FIGURE 3 Master curve for various joints. ○, ●, ◐ NR/PE (25°, 50° and 75°C), △, ▲, ◭ NR/S-EPDM/PEm/PE (25°, 50° and 75°C), □, ■, ◧ NR/ENR/PEm/PE (25°, 50° and 75°C), X, • NR/EPDM/PE (25°, 50°C).

TABLE II
ESCA of the failed surface of plastic in rubber/plastic joints (tested at room temperature and 200 mm/min rate)

	Sample Ref. NR/PE		Sample Ref. NR/EPDM/PE	Sample Ref. NR/CPE/PE	Sample Ref. NR/ENR/PEm/PE
	NR side	PE side	PE side	PE side	PEm/PE side
		Binding energy (eV)			
O_{1S}	535.0	532.2	535.0	537.5	532.5
C_{1S}	—	283.4	283.5	284.0	283.9
	284.25 (along with two satellite peaks at 263.8 and 275.6)	285.6 (occurrence of double peak)	284.5 (occurrence of double peak)	—	—

STUDIES ON FAILURE SURFACES

ESCA

A systematic study of the failure surfaces was carried out with the help of ESCA, the results of which are shown in Table II. The O_{1S} and C_{1S} peaks are detected on the polyethylene side of the failure surfaces. The shift of the C_{1S} main peak, shown in Figure 4, with different kinds of modification clearly reflects the increasing adhesion as described below. For the control, NR/PE, the C_{1S} peak is

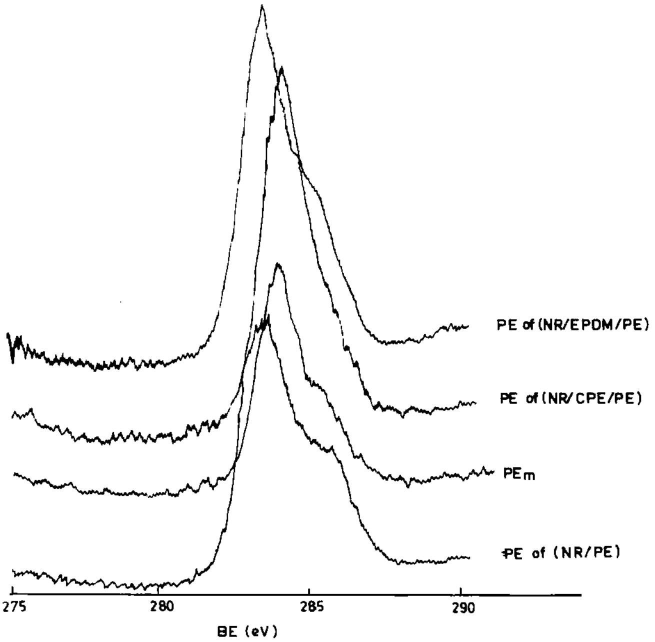

FIGURE 4 ESCA spectrum of the failure surface of different NR/PE joints.

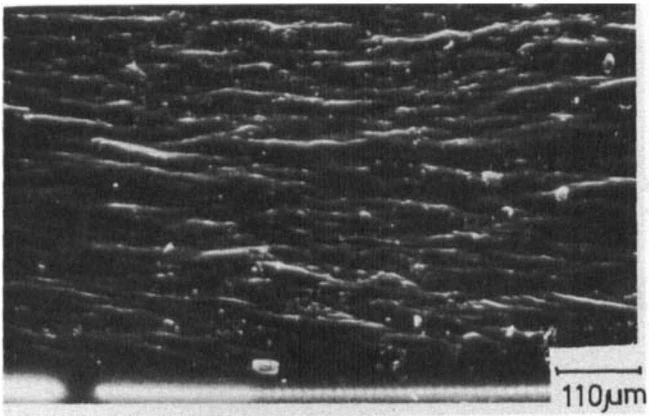

FIGURE 5 SEM photograph of peeled NR surface of NR/PE joints.

detected at 283.4 ev whereas with modifiers like EPDM and CPE the shift in C_{1S} peak is 0.1 and 0.6 ev, respectively. For the CPE system the shift is higher because halogen induces a shift to a higher binding energy.[18] This result clearly indicates that bonding between rubber (NR/EPDM or NR/CPE) with polyethylene is *via* the EPDM or CPE phase. Again, for the chemically-modified system (ENR/PEm) the shift is 0.5 ev. This is also the result of bond formation between NR and PE through ENR and PEm. Xiang *et al.*[19] also reported this kind of shift of binding energy for the aluminium-polyethylene interface. According to them, such a shift is the result of formation of a new primary bond and we are giving it the same interpretation. A physical model for NR/Modifiers/PP system was proposed in our earlier communication.[12]

SEM and photographs

The morphology of peeled surface from adhesion tests was studied with the help of scanning electron microscopy (SEM) and optical photography. SEM photo-

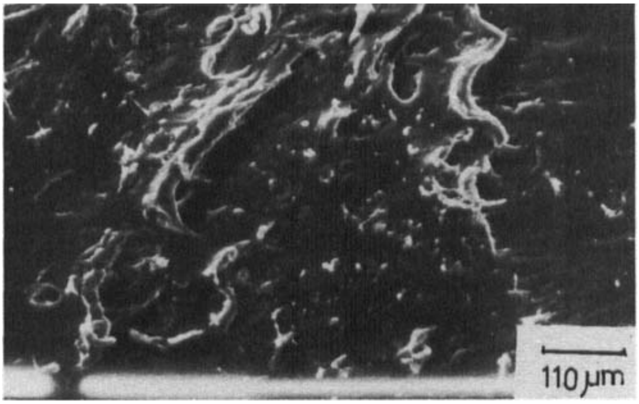

FIGURE 6 SEM photograph of peeled rubber surface (NR/EPDM) of NR/EPDM/PE joint.

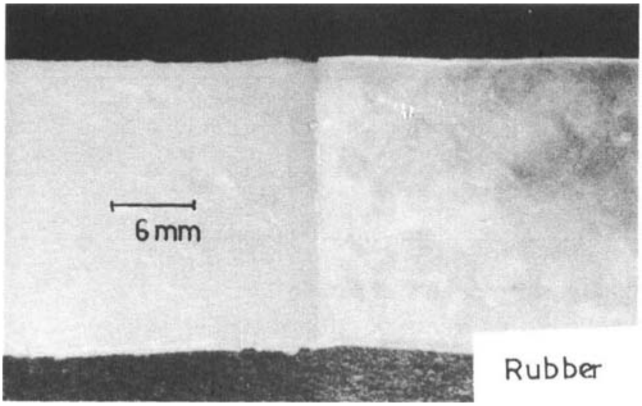

FIGURE 7 Optical photograph of NR/ENR/PE joint tested at room temperature.

graphs of the peeled rubber surface of NR/PE and NR/EPDM/PE (room temperature and 50 mm/min rate) are shown in Figures 5 and 6. The NR/EPDM surface from the NR/EPDM/PE joint shows a very rough surface with cavities all over (Figure 6) whereas the NR surface in NR/PE shows a ridge-like structure (Figure 5) clearly indicating the different nature of the failure response of the two samples. EPDM, having a structural similarity with PE, has been taken out of the NR/EPDM surface by the plastic phase creating the cavities on the surface. To show the interface during failure optical photographs of the NR/ENR/PE joint tested at different temperatures are given in Figures 7 and 8. It is interesting that the sample tested at room temperature shows smooth failure (Figure 7) whereas the same sample tested at high temperature (75°C) shows tearing from rubber surface (Figure 8).

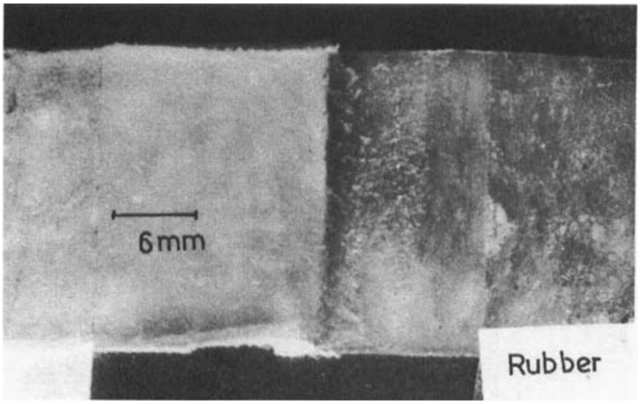

FIGURE 8 Optical photograph of NR/ENR/PE joint tested at higher temperature.

TABLE III
Effect of crystallinity of polyethylene on peel strength (tested at a rate of 200 mm/min and room temperature)

System	Crystallinity of polyethylene (%)	Modulus of PE at 10% MPa	Peel strength (J/m)
1. NR/LDPE	30	4.5	140
2. NR/HDPE	64	20.0	550

Effect of crystallinity and modulus of plastic

The peel strength data for joints of natural rubber and polyethylene of varied crystallinity are reported in Table III. It is interesting to note that as the crystallinity and modulus of PE increase the increase in joint strength is nearly four-fold (tested at 200 mm/min and room temperature). This may be due to the fact that as crystallinity increases, the modulus of the substrate also increases and the joint strength increases. Thus, not only the extent of intermolecular interaction at the interface is responsible for good peel strength, but also the mechanical response of the two materials is equally important. Kammer *et al.*[20] made a similar observation. It is also well known that the largest part of the energy of peeling arises from mechanical deformation of the peeled adherends, *i.e.* plastic yielding, in addition to that expended for adhesive separation.

Effect of different modes of testing

We have also carried out studies in order to understand the effect of modes of testing (180° peel, 90° peel and lap shear) on joint strength for the various NR/PE

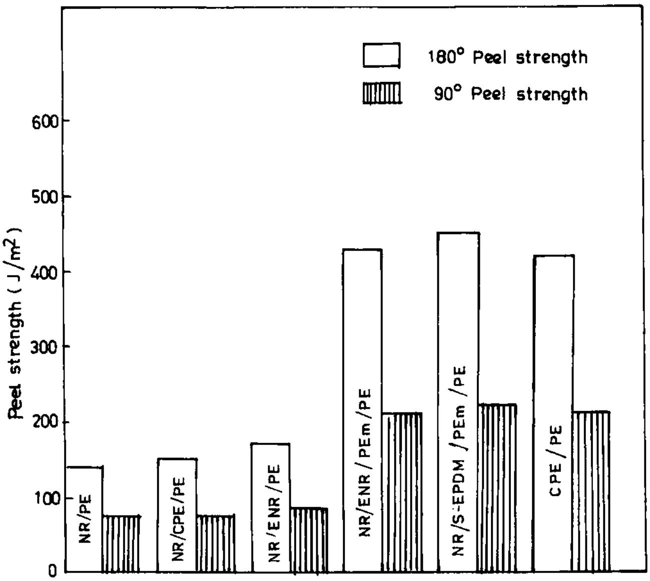

FIGURE 9 Effect of peel angle on peel strength.

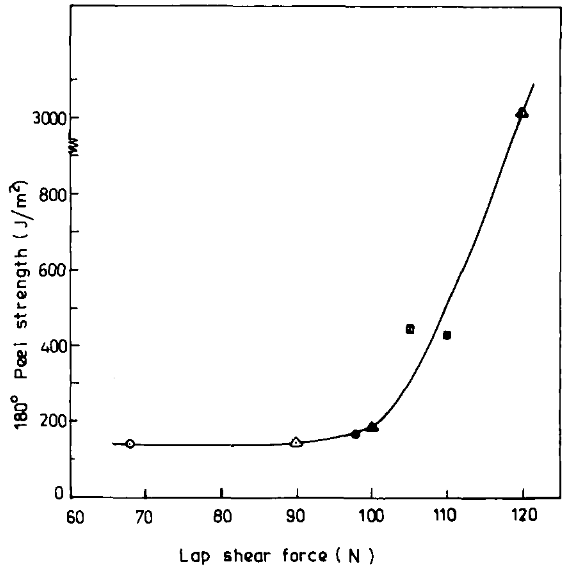

FIGURE 10 Plot of 180° peel strength *vs.* lap shear force. ○—NR/PE, △—NR/CPE/PE, ●—NR/ENR/PE, ▲—NR/S-EPDM/PE, ⊡—NR/S-EPDM/PEm/PE, ■—NR/ENR/PEm/PE, ◭—NR/EPDM/PE.

joints. The results are reported in Figures 9 and 10. It is observed that the 180° peel strength values are approximately double than those measured at 90° (Figure 9). This is true for all the joints. Gardon[3] reported on the effect of variation of peel angle on the strength of a joint consisting of cellophane/pressure-sensitive adhesive/aluminium foil and found that the joint strength varied irregularly with the peel angle. Gent *et al.*,[21] however, reported results similar to the present investigation for testing of Mylar film adhering to thermoplastic elastomer. They ascribed this to plastic yielding occurring at the interface. This is different at different peel angles. However, the trend in joint strength with material variables is the same for both 180° and 90° joints.

The results of the lap shear tests are reported in Figure 10. The lap shear force between NR and PE is the lowest and that between NR/EPDM/PE is the highest. These are in line with the peel strength values. With the incorporation of physical or chemical modifiers the lap shear strength of the interface increases. Barlow and Paul[6] reported variation of lap shear strength with the variation of interfacial interaction in plastic-to-plastic joints.

Figure 10 shows that after a certain lap shear force (~100N) there is a substantial increase in the peel strength value. This may be due to the fact that above this region the energy dissipative processes for peeling became more prominent.

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