

Compatibilization of Natural Rubber–Polyolefin Thermoplastic Elastomeric Blends by Phase Modification

NAMITA ROY CHOUDHURY and ANIL K. BHOWMICK,*
*Rubber Technology Centre, Indian Institute of Technology,
Kharagpur 721302, India*

Synopsis

Natural rubber–polyolefin (70/30) blends have been studied by incorporation of modified rubber and plastic phases with a view to make the heterogeneous phases compatible. The modified rubbers used were epoxidized natural rubber (ENR) and sulfonated ethylene–propylene diene rubber (S-EPDM) at a level of 20 parts. Other rubbers such as chlorinated polyethylene (CPE) and ethylene propylene diene rubbers (EPDM) were also used at a level of 20 parts in the natural rubber–polyethylene (NR/PE) systems. The plastic phase was chemically modified with maleic anhydride (MA) in presence of benzoyl peroxide (BPO) and used at a concentration of 10% of PE, i.e., PEm. The tensile properties such as the modulus, elongation at break, tensile strength, and hysteresis were studied. NR/ENR/PEm/PE shows the greatest improvement in tensile strength (45% over control NR/PE). NR/S-EPDM/PEm/PE also shows similar improvement, although the hysteresis loss decreases. The change in these properties could be related to the adhesive strength. This was found to be improved by the incorporation of modified rubber and modified plastic phases. The best adhesion values have been obtained with NR/ENR/PEm/PE and NR/S-EPDM/PEm/PE. Thus, a correlation between tensile and adhesive strength was obtained for all the systems. The increase in adhesive strength is due to chemical reactions between the various phases. Probable chemical reactions have been suggested. Morphological observations show that the phases are interpenetrating, and this is consistent with the increased tensile strength. The natural rubber–polypropylene (NR/PP) systems do not offer good strength properties with the modified PP and modified rubbers. The adhesive strength also decreases with the incorporation of the modified system. The hysteresis properties show some improvement.

INTRODUCTION

In recent years, elastomeric rubber–plastic blends have become technologically important for use as thermoplastic elastomers. Although a large number of blends has been proposed for commercial purposes,¹ all of them do not have the required mechanical properties due mainly to their incompatibility. This arises because of the absence of specific interaction between the two phases. It has been observed that better tensile properties are obtained when the rubber and plastic have some similarity in chain structure and are compatible, e.g., EPDM and polypropylene blends.² The interaction between the component phases may, however, be brought about either by addition of agent which interacts with both phases and renders them mutually compatible or by specific reactions between the two phases. It is now generally accepted that a

*To whom correspondence should be addressed.

block copolymer can make a mixture of the parent homopolymers compatible by acting as macromolecular surfactant.¹ Reports on technological compatibilization through rubber and plastic reactions are few. Dimethylol phenolic compound has been found to be useful to technologically compatibilize a mixture of polyolefin- and amine-terminated nitrile rubber.³ The formation of polymer-polymer grafts can also be accomplished by using maleic-modified polypropylene to form a block-polymeric compatibilizing agent between amine-terminated NBR and PP.

Natural rubber producing countries have commercialized natural rubber-polyolefin thermoplastic elastomers. The problems of technological compatibilization do exist in these systems which are not highlighted so far. In our earlier communication,⁴ we have been able to improve the technical properties of NR-polyolefin thermoplastic blends by using a third amorphous component which has some similarity in chain structure with the plastic phase. It has been observed that EPDM and chlorinated polyethylene are useful third component for NR-PE systems. The present investigation deals with the chemical modification of the plastic phase, which is either polyethylene or polypropylene, and then using the modified plastic in definite proportion to form NR-polyolefin intercopolymers *in situ* during melt mixing. Their effects on the technical properties and adhesion between the components have been studied. Modified rubbers are also added in a few compositions in order to promote interaction between rubber-plastic components.

EXPERIMENTAL

Materials Used

Natural rubber (NR). ISNR 5 was supplied by Rubber Board, Kottayam, India. Molecular weight $MW = 780,000$; intrinsic viscosity (benzene, 30°C , dL/g) $[\eta] = 4.45$; Wallace plasticity $\rho_0 = 59.0$.

Polyethylene (PE). Indothene 16 MA 400 was supplied by IPCL, Baroda. Density (g/cm^3) = 0.916; melt flow index (MFI) ($\text{g}/10 \text{ min}$) = 40.

Polypropylene (PP). Koylene M0030 was supplied by IPCL, Baroda. Molecular weight $MW = 530,000$; density (g/cm^3) = 0.910; melt flow index (230°C and 2.16 kg) (MFI) = 10.

Chlorinated Polyethylene (CPE) (chlorine 36%) was supplied by Dow Chemicals. Specific gravity = 1.16; Mooney viscosity $ML_{(1+4)} (121^\circ\text{C}) = 80$.

Ethylene Propylene Diene Rubber (EPDM). Keltan 520 was supplied by DSM, The Netherlands, through SBM Chemicals, India. Specific gravity = 0.86; Mooney viscosity $ML_{(1+4)} (125^\circ\text{C}) = 46$.

Epoxydized Natural Rubber (ENR). ENR 25 was supplied by MRPRA, Malaysia. Density (g/cm^3) = 0.97; epoxydation level = 25 mol %; Mooney viscosity $ML_{(1+4)} (100^\circ\text{C}) = 110$.

Sulfonated EPDM (S-EPDM). Ionomer 2590 was supplied by Uniroyal Chemical Co. Density (g/cm^3) = 1.12; Mooney viscosity $ML_{(1+4)} (100^\circ\text{C}) = 45-50$; average number of SO_3^- groups/molecules = 13; % by weight ionic group = 2.7%.

Dicumyl Peroxide (DCP) was supplied by Hercules Inc., Wilmington, DE. **Benzoyl Peroxide (BPO)** and **Maleic Anhydride (MA)** were also used.

TABLE I
Composition of the Mixes (NR/PE)

Blend component	A	A'	B	B'	C	C'	D	D'	E	E'
NR	70	70	70	70	70	70	70	70	70	70
CPE	—	—	20	20	—	—	—	—	—	—
EPDM	—	—	—	—	20	20	—	—	—	—
S-EPDM	—	—	—	—	—	—	20	20	—	—
ENR	—	—	—	—	—	—	—	—	20	20
PE	30	27	30	27	30	27	30	27	30	27
PEm	—	3	—	3	—	3	—	3	—	3

Modification of Polyolefins

The modification of polyolefins was carried out by melt mixing 100 parts of polyolefin with 5 parts of maleic anhydride at 150°C for LDPE and 180°C for PP in a Brabender plasticorder (Model PLE 330) at 60 rpm. After they were well mixed, 0.82 part of benzoyl peroxide was added and mixing continued until the decreasing mixing torque leveled off. This indicated the completion of the reaction. The procedure is similar to that used by Coran and Patel.³ The functionalized polypropylene was brittle because of the lower molecular weight. However, the same was not observed with polyethylene. Infrared spectroscopic analysis and differential scanning calorimetry studies were carried out to characterize the modified polymers. The maleic modified polymers are designated as MA-mod PE (PEm) and MA-mod PP (PPm), respectively. Multiple additions of a mixture of MAH and BPO were also carried out for polyethylene.

The MAH content of MAH-PP and MAH-PE is about 40 and 25% respectively, using the same procedure described by Coran and Patel³ and Gaylord et al.⁵

Blend Preparation

The compositions of various thermoplastic NR-polyolefin blends are given in Tables I-III. Two types of blends were prepared (a) blends containing unmodified polyolefin and (b) blends containing modified polyolefin. Coran¹ reported that 10% of the functionalized polyolefin is needed to obtain substantial improvement in the properties of the blend. The composition was 70/30

TABLE II
Composition of the Dynamically Vulcanized Mixes (NR/PE)

Blend component	F	F'	G	G'	H	H'
NR	70	70	70	70	70	70
CPE	—	—	20	20	—	—
EPDM	—	—	—	—	20	40
DCP	0.5	0.5	0.5	0.5	0.5	0.5
PE	30	27	30	27	30	27
PEm	—	3	—	3	—	3

TABLE III
Composition of the Mixes (NR/PP)

Blend component	I	I'	J	J'	L	L'	M	M'
NR	70	70	70	70	70	70	70	70
CPE	—	—	20	20	—	—	—	—
EPDM	—	—	—	—	20	20	—	—
ENR	—	—	—	—	—	—	20	20
PP	30	27	30	27	30	27	30	27
PPm	—	3	—	3	—	3	—	3

for binary rubber-plastic blends and 70/20/30 for the ternary rubber-plastic blends.

Compositions were prepared in a Brabender plasticorder by melt mixing the plastic and rubber at 150°C for PE and 180°C for PP containing blends. Mixing was performed at 60 rpm with cam-type rotor for about 5–6 min during which the plastic melted and formed a blend with the rubber. Curative (DCP) was added as required and mixing continued until the torque increased by 3–4 units. The hot mass was pressed into a sheet of 3 mm thickness from which test slabs of 2 mm thickness were prepared by compression molding using a hydraulic press at temperatures of 150 and 180°C for PE and PP blends, respectively. A pressure of 1/4 tons/in.² for 3 min was used. The slabs were subsequently plunged in cold water.

Preparation of Samples for Adhesion

Fabric-backed rubber sheets of 2 mm thickness were prepared by a molding technique using a gentle pressure at 100°C. The plastic sheets of 1 mm thickness both unmodified and modified were prepared by compression molding at 150°C for PE and 180°C for PP. The plastic sheet was placed over the fabric-backed rubber sheet in between which a cellophane paper was introduced partially to get the parting line. The assembly was then heated for 10 min at 100°C followed by 15 min at 150°C for PE and 180°C for PP under light pressure.

Mechanical Testing

Dumbbell shaped specimens (BS-E type) were cut with a hollow punch from the test slabs. Tensile tests were performed at room temperature on Zwick UTM (Model 1445) at a crosshead speed of 200 mm/min. With these dumbbell specimens, hysteresis tests were also performed at a rate of 50 mm/min, for one cycle between two selected force intervals (0.001–15 N for PE and 0.001–40 N for PP). The hysteresis loss (W_2) during the complete cycle was calculated.

Measurement of Adhesive Strength

In order to measure the adhesive strength, 180° peel test was performed on the specimen (Fig. 1) and the strength was calculated using the formula

$$G_a = 2F/w,$$

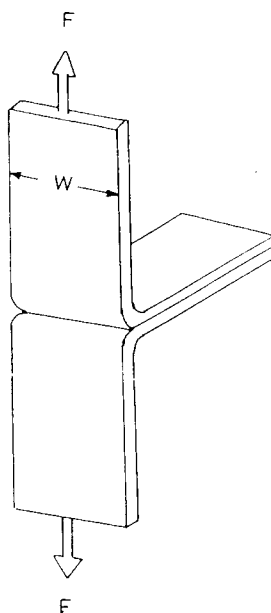


Fig. 1. 180° peel test geometry.

where G_a = adhesive strength, F = peeling force, and w = width of the specimen. All the adhesion tests were carried out at room temperature and at 200 mm/min rate.

Determination of Rubber Pickup by the Plastic after Peeling

The peeled plastic surface containing some amount of rubber was put in *n*-hexane for 48 h at room temperature to dissolve the rubber. The plastic was dried; the weight before and after treatment gave an estimate of the rubber pickup.

Electron Microscopy Studies

The blends were characterized with the help of a scanning electron microscope (Philips 500 Model). The morphology of the samples was examined after solvent extraction for 2 days at room temperature using *n*-hexane to extract the rubber removed from the blend. The samples were then finally dried. The vulcanized samples were etched with nitric acid for 2 days, washed with water, and then dried. All the samples were sputter-coated with gold and examined within 24 h of preparation.

RESULTS AND DISCUSSION

Mechanical Properties of the NR / PE Blends

The properties of the (NR/PE) compositions containing both modified and unmodified polyolefins are given in Tables IV and V (various methods of addition of MAH-BPO for modification give similar results). The effect of

TABLE IV
 Mechanical Properties of the Mixes (NR/PE)

Mix no.	20% modulus (MPa)	Tensile strength, σ_b (MPa)	Elongation at break (%)	σ_b/σ_H^a	Hysteresis loss W_2 ($\times 10^2$ N m)
A	0.54	3.6	560	0.395	141
A'	0.90	3.94	485	0.46	90
B	0.42	4.61	490	0.51	107
B'	0.74	4.73	666	0.58	101
C	0.64	3.4	600	0.37	^b
C'	1.01	4.42	684	0.52	15
D	1.02	3.77	577	0.41	79
D'	1.08	4.12	634	0.50	75
E	0.86	3.86	627	0.42	86
E'	2.68	5.21	470	0.64	2

^a σ_H = tensile strength of the hard phase.

^bSample failed under testing condition.

incorporation of the modified polymer is best understood by comparing their properties with that of the control samples. The control samples used were NR/PE, NR/CPE/PE, NR/EPDM/PE, NR/S-EPDM/PE, and NR/ENR/PE. In the modified samples, 10 parts of the functionalized polyolefin were used. Coran¹ noted that an improvement in properties could be obtained when as little as 0.16% of the rubber was grafted onto polyolefin. We have also made similar observation in NR-PE system in the present study. In fact, the system containing fully modified PE/NR shows deterioration in tensile properties. It is observed from Table IV that the introduction of 10 parts of functionalized PE gives rise to improved tensile strength (9.4%) and a reduction in elongation at break (13.4%) over the control NR/PE system. This may be due to better interaction between the two phases in the presence of a small amount of modified PE as well as due to the presence of crosslinked PE resulting from attempted reaction with MAH-BPO. A similar observation has been made by Coran using modified PP in the amine-terminated NBR-PP system.¹ This will be considered later.

The system NR/CPE/PE/PEm also shows an increased strength as well as elongation at break. This may be attributed to some sort of interlinking

 TABLE V
 Mechanical properties of the Dynamically Vulcanized Mixes (NR/PE)

Mix no.	20% modulus (MPa)	Tensile strength σ_b (MPa)	Elongation at break (%)	Hysteresis loss W_2 ($\times 10^2$ N m)
F	0.73	7.92	480	32.3
F'	1.45	5.29	312	6.0
G	0.48	9.2	457	22.1
G'	0.98	5.92	440	17.0
H	0.48	8.24	384	17.4
H'	0.94	4.22	357	13.0

between the rubber matrix and the plastic phase through the functionalized PE segment which acts as a stress transfer media. In other words, higher σ_b values are due to the fact that the functionalized PE is preferentially located between the matrix and dispersed phase, acting as an interfacial agent. This is further confirmed from the study of morphology.

The same trend is observed for the NR/EPDM/PE/PEm system. But the improvement in tensile strength is substantial (30% greater than the control sample) whereas the elongation at break value increases by 14% only. In the case of blend consisting of NR/S-EPDM/PE/PEm, the enhancement in strength property is only 9%, elongation at break value increases by 10%, and there is a marginal improvement in 20% modulus value. It must be pointed out that the modified LDPE increases the brittleness of the matrix as observed from the modulus and the decrease in elongation at break associated with the increase in modulus.

The highest values for the strength were obtained with the NR/ENR/PEm/PE system. The tensile strength increases by 35% and was accompanied by a reduction in elongation at break value by 25% over NR/ENR/PE system. This can be explained since the functionalized PE containing pendant succinic anhydride groups interacts with the epoxy group of the ENR to give a $-\text{COO}-$ linkage between the ENR and functionalized PE by a ring opening reaction, the details of which are given in later section. It must be emphasized that the use of 10 parts functionalized PE and modified rubber has improved the strength by 45% over that of the NR/PE. In all these cases, the modifiers have enhanced the properties of the control.

In each case there is an increase induced in the matrix by the addition of modified polymer (by as much as fivefold). The 20% modulus values, in all the above cases, show a similar trend to that of the tensile strength. All the above results indicate the effectiveness of blending maleic modified polyethylene with different thermoplastic elastomeric compositions.

Dynamic vulcanization is commonly used to improve the failure properties by crosslinking the rubber phase during mixing. The dynamically vulcanized NR-PE systems in the present investigation displayed somewhat different results (Table V). All the blends exhibit a drop in strength value as well as in elongation at break value. It was observed that with pure NR/PE the strength could be improved either by crosslinking the rubber phase (NR/DCP/PE) or with the incorporation of a small amount of modified polyolefin (NR/PEm/PE). The low value of the tensile strength corresponds to the fact that one process is suppressing the other. Thus, the NR/PE system in the presence of both DCP and modified PE shows a drop in tensile strength. This indicates that resultant technological compatibility of the NR/PE system is inhibited in the presence of both DCP and MA-mod PE. Hence, dynamic vulcanization in the presence of DCP is dependent on the components of the system.

Mechanical Properties of the NR / PP Blends

The properties are reported in Table VI. All the NR/PP blends display a decrease in the tensile strength with the introduction of functionalized PP, whereas the elongation at break values show a regular increase. The percent

TABLE VI
Mechanical Properties of the Mixes (NR/PP)

Mix no.	20% modulus (MPa)	Tensile strength σ_b (MPa)	Elongation at break (%)	Hysteresis loss W_2 ($\times 10^2$ N m)
I	12.84	13.72	25	2.2
I'	6.2	7.2	32	20
J	10.63	16	36	3.9
J'	3.97	6.72	127	^a
L	8.56	10.47	28	6.4
L'	2.59	6.43	209	^a
M	8.89	10.62	30	3.0
M'	4.68	6.47	80	^a

^aSample failed under testing condition.

reduction in the strength in all the blends is supported by the fact that the spherulitic growth of PP crystals is highly disturbed in presence of other additive.⁶ The modulus at 20% elongation also reveals the same trend. The crystallinity of PP is reduced to some extent by its modification and further incorporation of the rubbers leads to a drastic drop in crystallinity (50% reduction from DSC) and hence a decrease in strength. The DSC results of NR/PE/10% PEm do not show such a trend. On dynamic vulcanization, in the presence of DCP, the whole mass becomes brittle. A similar observation was made earlier.⁷ Hence, further study is limited on this line.

Hysteresis Properties of the Blends

The hysteresis property of various blends is reported in Tables IV–VI. The hysteresis loss W_2 have been calculated for one cycle at forces between 0.001 and 15 N for the NR/PE blends and at forces between 0.001 and 40 N for NR/PP blends. In NR/PE blends the hysteresis values show a regular trend. The unmodified blends display a higher hysteresis value than the modified blends. This may be attributed to higher adhesion/interaction in the case of modified blends. The technological compatibilization improves the failure properties, but reduces the hysteresis loss. The same relation between hysteresis property and strength is observed also for NR/PP blend, but in the NR/PP blend modification enhances the hysteresis loss and lowers the strength.

Adhesive Strength

In order to understand the interaction behavior between the components, adhesive strengths were measured for all the systems. The results are reported in Table VII.

The peel adhesion of NR–PE is 140 J/m². While strength increases on addition of modified polyethylene, a drop in adhesive strength is observed for the NR/EPDM/PE/PEm system. NR/CPE/PE, NR/ENR/PE, and NR/S-EPDM/PE systems show, however, improved adhesive strength on addition of 10 parts of modified polyethylene. The improvement is sometimes

TABLE VII
Adhesive Strength

Sample ref.	Adhesive strength (J/m ²)	Pickup (g/cm ²)
NR/PE	140	—
NR/PEm ^a /PE	175	—
NR/CPE ^b /PE	150	—
NR/CPE ^b /PEm ^a /PE	250	—
NR/EPDM ^b /PE	3190	—
NR/EPDM ^b /PEm ^a /PE	700	—
NR/S-EPDM ^b /PE	175	—
NR/S-EPDM ^b /PEm ^a /PE	450	—
NR/ENR ^b /PE	170	—
NR/ENR ^b /PEm ^a /PE	430	—
NR/CEP ^b /DCP/PE	250	—
NR/CPE ^b /DCP/PEm ^a /PE	600	—
NR/EPDM ^b /DCP/PE	560	—
NR/EPDM ^b /DCP/PEm ^a /PE	1400	—

^aPEm was used at a concentration of 10% of PE.

^bTwenty parts of the rubber were added to NR.

150% over the control as in the case of NR/S-EPDM/PE/PEm. This is certainly due to the interfacial chemical reaction as described in the later section. It is interesting to note that improved adhesion gives rise to improved tensile properties. Dynamically vulcanized systems also show similar increase in adhesive strength, provided that there are chemical reactions at the interface. However, the tensile properties of the dynamically vulcanized system are not in accord with adhesion values. A typical plastic surface after peeling is shown in Figure 2. The voids in the surface indicate that rubbers are mostly fractured.

In the case of NR/PP systems (Table VIII), addition of modified PP decreases the adhesion. In NR/CPE/PP and NR/EPDM/PP systems, the rubber is stuck to the plastic surface and a true value of interfacial strength is not measured. The rubber pickup is more for the EPDM system because of

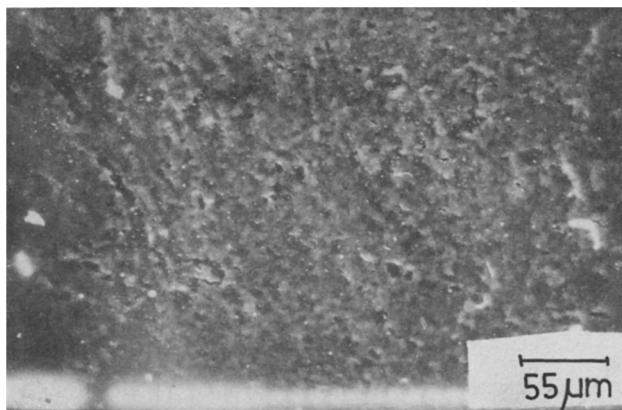


Fig. 2. SEM photograph of peeled plastic surface.

TABLE VIII
Adhesive Strength

Sample ref.	Adhesive strength (J/m ²)	Pickup (g/cm ²)
NR/PP	500	—
NR/PPm ^a /PP	150	—
NR/CPE ^b /PP	1000	—
NR/CPE ^b /PPm ^a /PP	—	0.014
NR/EPDM ^b /PP	600	—
NR/EPDM ^b /PPm ^a /PP	—	0.021

^aPPm was used at a concentration of 10% of PP.

^bTwenty parts of the rubber were added to NR.

better interaction of EPDM with PP due to some similarity in chain structure.

A correlation between adhesive strength and the properties of the composite has been attempted. Coran and Patel⁸ found a correlation between crystallinity, surface energy mismatch, and critical entanglement spacing. The failure of composite involves a large amount of viscoelastic losses. Hence, we have plotted G_a vs. σ_b/σ_H (Fig. 3). It is clear from the figure that the tensile properties increase with the increase in adhesion for a particular system.

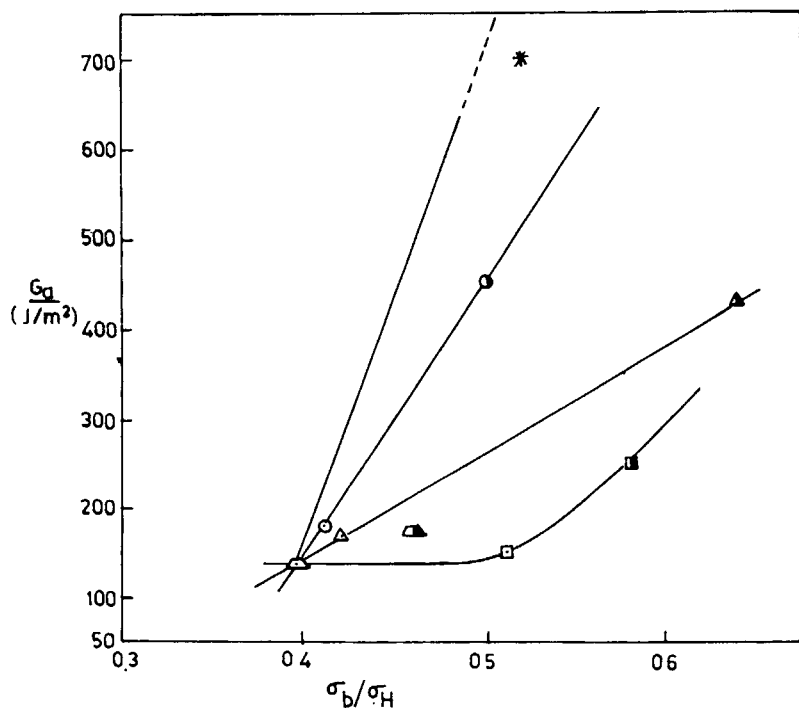


Fig. 3. Plot of adhesion strength (G_a) (J/m²) vs. σ_b/σ_H : (\square) NR/PE; (\blacktriangle) NR/PEm/PE; (\triangle) NR/ENR/PE; (\blacktriangle) NR/ENR/PEm/PE; (\square) NR/CPE/PE; (\blacksquare) NR/CPE/PEm/PE; (\circ) NR/S-EPDM/PE; (\bullet) NR/S-EPDM/PEm/PE; ($*$) NR/EPDM/PE.

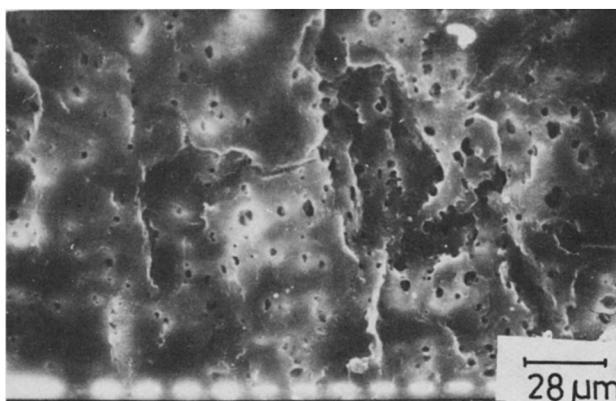


Fig. 4. SEM photograph of extracted surface of NR/PEm/PE.

S-EPDM, EPDM, and ENR systems show a steep slope in the above plot. However, CPE system shows an exponential increase. The various systems, however, could not be fitted on the same straight line. The correlation indicates that the failure in the composite goes through a peeling mechanism.

Morphology Study

The morphology of the blends as measured under SEM is shown in Figures 4–15. In these micrographs the dark phases are the voids left by the extracted rubber. As is evident from the micrographs, the morphology of the different systems varies over a wide range, depending on the characteristics of the individual polymer present in the TPO blends. The NR/PE/PEm system (Fig. 4) reveals the same morphology as that of the NR/PE system with the exception of regular and homogeneous distribution of dispersed phase. The size of the hole is about $2.5 \mu\text{m}$. The NR/PEm/PE/DCP (Fig. 5) also shows the same feature as the control sample. However, the systems NR/CPE/PEm/PE and NR/EPDM/PEm/PE (Figs. 6 and 7) exhibit an interpenetrating structure where both the phases are continuous. On the introduction of

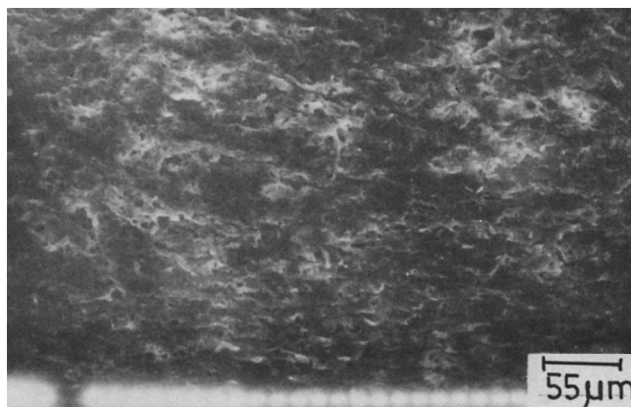


Fig. 5. SEM photograph of extracted surface of NR/PEm/PE/DCP.

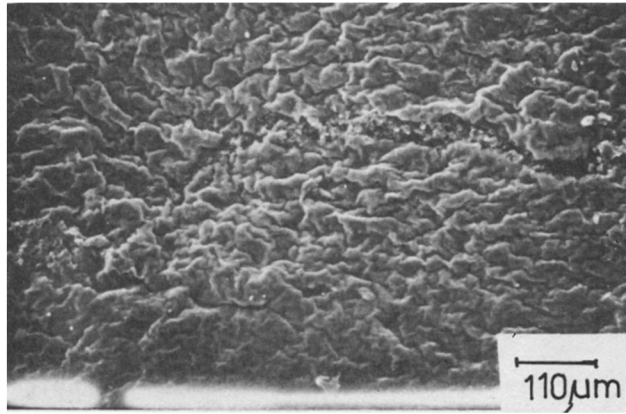


Fig. 6. SEM photograph of extracted surface of NR/CPE/PEm/PE.

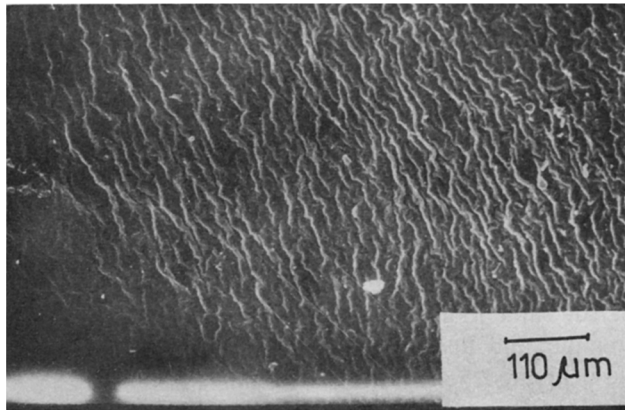


Fig. 7. SEM photograph of extracted surface of NR/EPDM/PEm/PE.

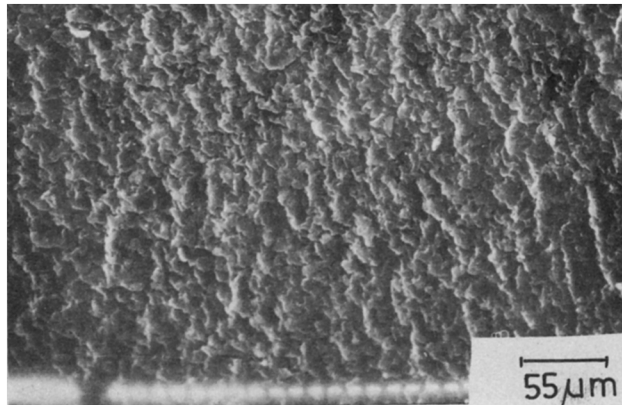


Fig. 8. SEM photograph of extracted surface of NR/S-EPDM/PE.

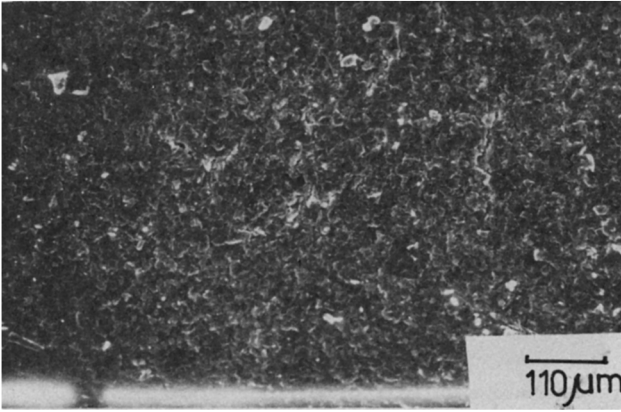


Fig. 9. SEM photograph of extracted surface of NR/S-EPDM/PEm/PE.

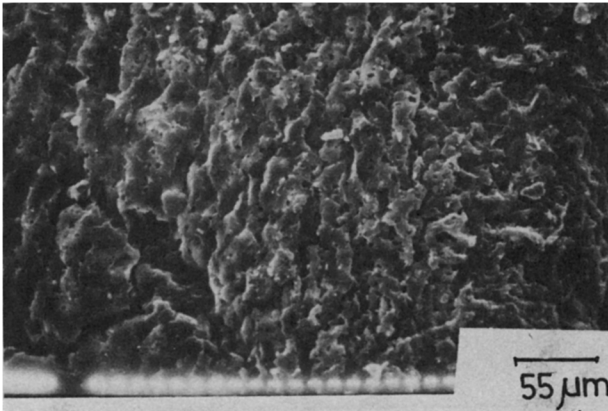


Fig. 10. SEM photograph of extracted surface of NR/ENR/PE.

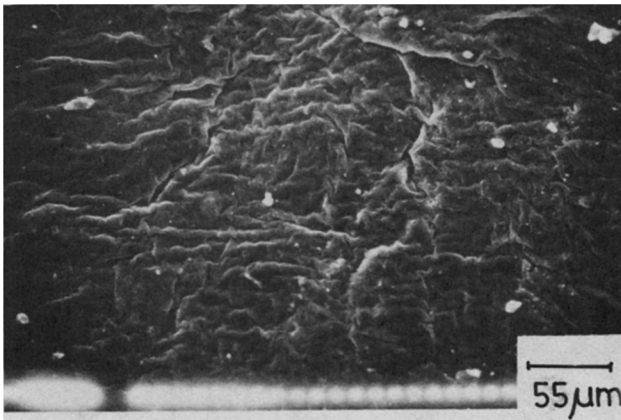


Fig. 11. SEM photograph of extracted surface of NR/ENR/PEm/PE.

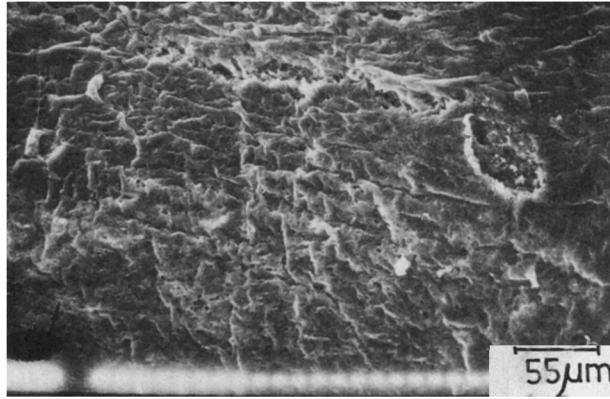


Fig. 12. SEM photograph of extracted surface of NR/CPE/PEm/PE/DCP.

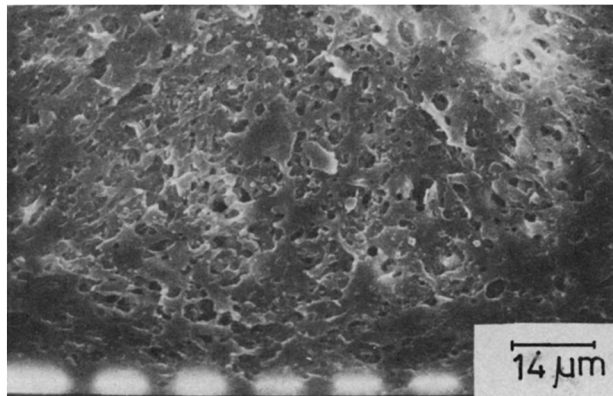


Fig. 13. SEM photograph of extracted surface of NR/PPm/PP.

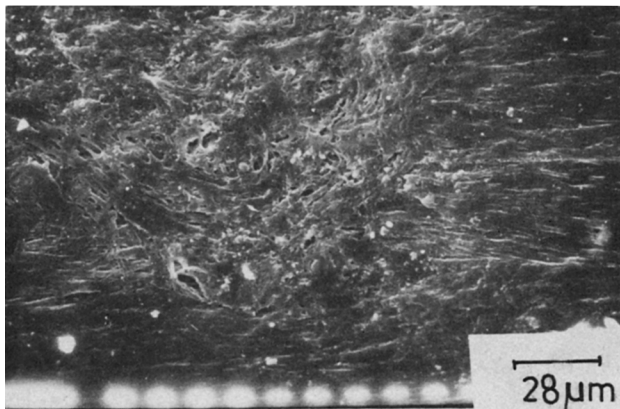


Fig. 14. SEM photograph of extracted surface of NR/ENR/PP.

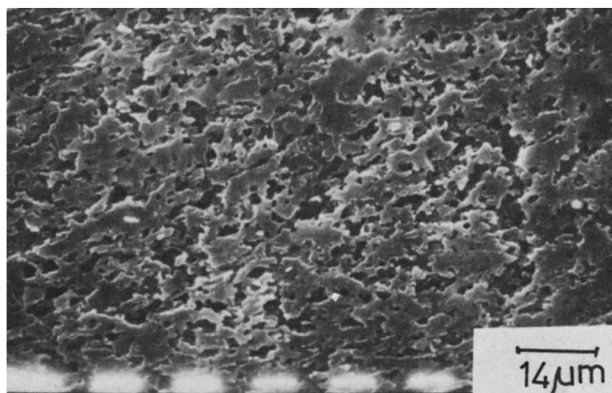


Fig. 15. SEM photograph of extracted surface of NR/CPE/PPm/PP.

sulfonated EPDM or ENR in NR/PE system, the same interpenetrating network is observed (Figs. 8 and 10). Incorporation of modified polyethylene does not change this structure (Figs. 9 and 11). Figure 12 represents the dynamically vulcanized NR/CPE/PEm/PE system. All these morphological observations are in accord with the tensile strength of these blends. The systems which have improved mechanical strength have a better cocontinuous nature of the phases permitting direct-load transfer of the components. The stress transfer area is also higher because of the cocontinuity. The cocontinuity of the matrix in the case of modified system is a result of improved adhesion. A similar result has been reported by Barlow and Paul.⁹

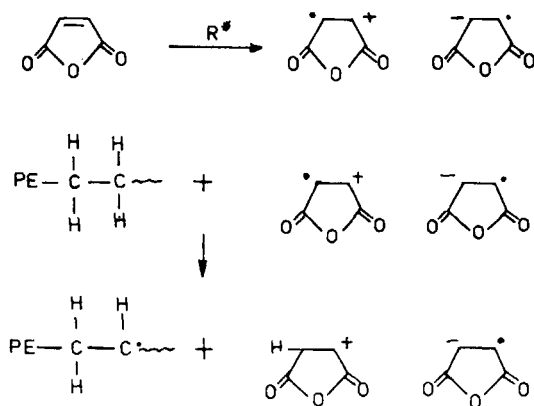
The NR/PP blend with ENR displays the voids of the extracted rubber (Fig. 14) while the micrograph of NR/CPE/PPm/PP blend resembles an open cell type foam (Fig. 15). This type of structure could only be the result of the rubber phase present as a continuous phase and interconnected with the plastic phase before its extraction for microscopy. It must be mentioned here that the morphology of NR/PP changes on introduction of modified polypropylene from a layered structure¹⁰ to these observed in Figures 13 and 15. The properties of the control and modified systems could not be compared on an equal basis because of the change in the morphology of the whole system. The degree of orientation also affects the strength property in these blends. For, though the cocontinuous nature of the matrix allows the load to be shared, yet PP orientation is a pronounced factor which will impart the ultimate strength to these blends. And there is some evidence that PP orientation is greatly disturbed in the presence of the other compound.⁶ Hence, all these PP blends exhibit poor mechanical property in spite of the presence of a continuous network of both the phases.

Probable Mechanism for Interfacial Reaction

It is clear that the adhesion/technical properties improvement in the system discussed before is due to surface chemical reactions. The probable reactions are summarized below.

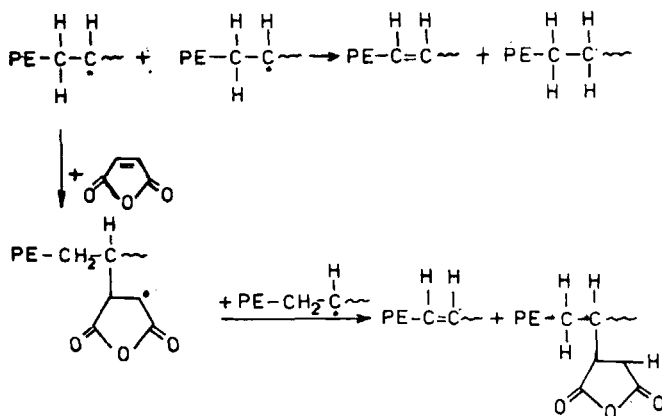
Scheme 1 shows the modification of polyethylene by maleic anhydride similar to the proposition by Gaylord et al.⁵ In the presence of benzoyl

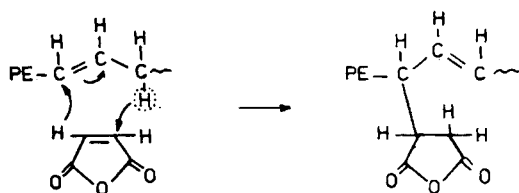
REACTION SCHEME FOR MODIFICATION OF POLYETHYLENE



peroxide, excited charge transfer complex or excimer is formed, which then abstracts hydrogen from polyethylene to generate a polyethylene radical. This may undergo coupling reactions through a mechanism of electron transfer. The formation of MAH containing PE in the presence of BPO is shown in Scheme 2. The PE radical may append MAH by addition across the double bond to form PE-MAH radical, which may terminate either by hydrogen abstraction reactions or disproportionation.

The formation of pendant individual MAH units to PE chain may also occur via the "ene" reaction with unsaturated PE which results from disproportionation between PE radicals and PE-MAH radicals. The "ene" reaction occurs through a concerted electron shift and a transposition of the double bond, without radical intermediates. Although the "ene" reaction is a viable alternative, the overall reaction scheme is more likely at higher temperatures



ENE REACTION

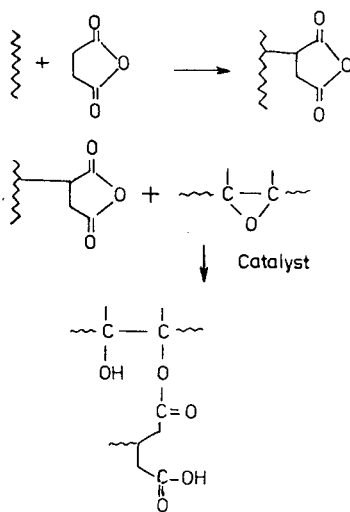
Scheme 3.

(probably suited for polypropylene mixed at 180°C) because of temperature dependence of the rate of the "ene" reaction.⁵ This is shown in Scheme 3.

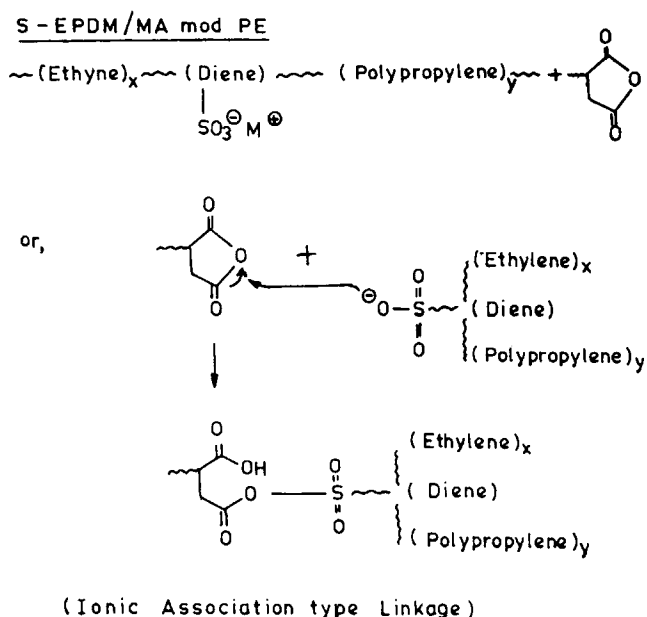
The modified PE thus formed may react with natural rubber through free radicals generated under shear at high temperature. However, when rubbers containing polar groups (ENR, S-EPDM, and CPE) are added in the mixture, the possibilities of chemical reaction between rubber and plastic could be visualized as shown in Schemes 4 and 5.

The above chemical reactions will introduce chemical crosslinking at the interface, thus improving the adhesion between the dissimilar substrates and the technical properties of the composite. However, with EPDM, the mechanism of interaction is mainly physical. EPDM has partial structural similarity with PE and is amorphous. Hence, it will distribute itself between two phases

REACTIONS OF FUNCTIONALISED POLYETHYLENE
WITH DIFFERENT RUBBERS

ENR/MA-mod. PE

Scheme 4.



Scheme 5.

and adheres better to each of the blend components than the major components adhere to each other.

CONCLUSION

The following conclusions can be drawn from the results:

1. Improvement in tensile properties can be obtained through phase modification with the use of either modified plastic phase or the use of modified rubber or both in the case of NR/PE systems.
2. The highest tensile strength can be achieved whenever both the modified phases chemically interact with each other, for example, in the case of ENR and MA-mod PE combinations in NR/PE systems. However, the hysteresis loss is found to be reduced in all the systems through phase modification.
3. Higher adhesive strength is obtained in the systems involving chemical reactions.
4. A correlation between the adhesive strength and the strength of the composite (after correction for hard phase) is found out for all systems. Thus, the phase modifiers which adhere well improve the blend property better than the control.
5. Morphological observations carried out on all the samples show the continuity of both the phases which is responsible for higher strength property.
6. The NR/PP systems do not offer good strength property through phase modification due to the disturbance in the crystal growth of PP. The hysteresis property, however, is improved. The adhesive strength is lowered through phase modification.

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