JOURNAL OF MATERIALS SCIENCE 25 (1990) 5237–5247

Promotion of adhesion of low-density polyethylene by polymer blending

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LDPE blends of variable composition are prepared with several polymer additives, which include chromic acid-etched LDPE, polyhydroxyetherimide (PHEI), butylated silica and LDPE oxidized with phase-transferred permanganate. The strength of adhesion measured as the force required to peel off the laminated aluminium foil by 180° is found to be a function of time of etching, blend composition and the effective amount of polar groups on polymer–metal interface. LDPE-based additives, e.g. chromic acid oxidised LDPE and LDPE oxidised under phase transfer catalysis in benzene, promote practical adhesion by factors of 8 and 16, respectively. In the case of the silane additive there is virtually no enhancement of the peel load despite a large number of polar groups present in the blend. The results can be interpreted in terms of cohesive failure.

1. Introduction

Many of the applications of polyethylene (PE) require good adhesion and problems arise in a number of different situations such as adhesive bonding, printing, extrusion coating or heat sealing. If good adhesion between PE and another material is needed, it is customary either to pretreat the polymer or to modify the other surface. Effective pretreatments for PE have been available commercially for several decades, for example corona discharge [1], flame treatments [2], and chemical etching [3, 4] etc. If PE is considered the adherate, the adherend can be PE or another polymer, paper or cellulose and a smooth surface including metals and alloys. In the case of autohesion of PE, aqueous $KClO_3$ has been used by Baszkin and Saraga [5] to introduce carbonyl groups on the polymer surface and this resulted in a two-fold increase in the peel strength. In other studies of adhesion of polyethylene [6] epoxy-based adhesives are interposed. In the case of bonding to aluminium, the metal surface is often pretreated by corona treatment [7], alkali etching [8, 9] or chromic acid oxidation [10]. Invariably the strength of adhesion is enhanced more in such cases compared to the situations where PE, and not the metal, is pretreated oxidatively or otherwise. The largest increase occurs when an oriented monolayer of aliphatic carboxylic acid is deposited on the surface of aluminium [8, 9]. According to Yamakawa [11] the mutual irradiation process of PE in methyl acrylate vapour and subsequent hydrolysis treatment, gives much higher peel strength of PE–epoxy joints than oxidative treatments which, however, give higher peel strength than helium plasma treatment. Of late, the surface modification of PE has been carried out by graft polymerization of acrylic acid [12], acrylamide [13], or even ethylene-α-olefin copolymer containing acrylic acid or maleic anhydride [14]. In the latter case, the peel strength is reported to have increased considerably ($235\,N\,m^{-1}$).

In order to find an easier method to introduce polar groups onto the low-density polyethylene (LDPE) surface, and thereby improve its adhesive property, recourse has been taken to polymer blending. LDPE is blended with four polymers each containing different polar groups, with the expectation that these polar groups will be oriented on the surface, thus facilitating interactions between LDPE and a smooth substrate, such as aluminium. The effects of blending have been characterized by scanning electron microscopy, infrared and peel strength measurements. The influence of composition on the peel strength of the blends has also been studied. An attempt was made to compare the contribution of polar groups containing oxygen with that of the nitrogen-containing groups towards the improved adhesion of LDPE.

2. Experimental procedure

2.1. Materials

"Alkathene WNC-71" is a low-density polyethylene with a melt flow index of 7 and is obtained from I.C.I.(P) Ltd, India, in the form of beads. It contains a standard amount of unspecified commercial antioxidant. All other chemicals employed are of analytical grade and used without further purification.

2.2. Preparation of oxidized LDPE

2.2.1. Heterogeneous oxidation

LDPE was oxidized using chromic acid as the oxidizing agent. The chromic acid was prepared by dissolving 35 g $K_2Cr_2O_7$ in 416.5 ml concentrated. H_2SO_4 and

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60 ml distilled water in the ratio 7 : 150 : 12 by weight [15].

For oxidation, 60 g powdered LDPE was added to 200 ml chromic acid mixture. The mixture was heated with continuous stirring using a glass stirrer in an oil-bath at 60 to 70° C for variable periods of time, from 6 to 12 h. After the completion of the reaction, the mixture was poured into distilled water and thoroughly washed to eliminate traces of free acid present. Oxidized LDPE was filtered and completely dried under vacuum.

2.2.2. Oxidation under phase transfer catalytic conditions

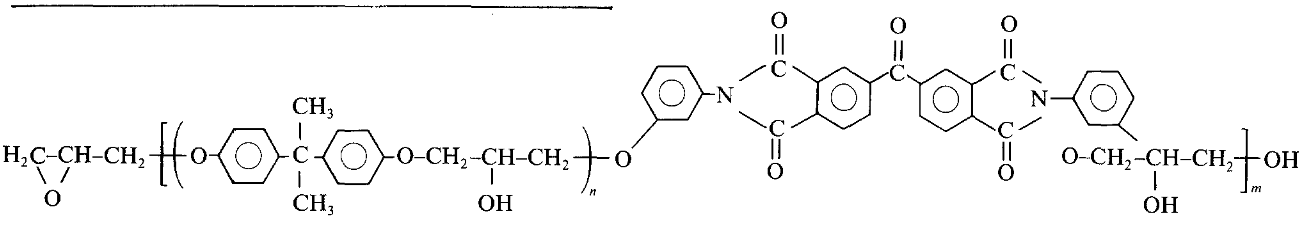
The phase transfer catalyst used was tetrabutyl ammonium bromide (TBAB, Kodak Chemicals Ltd). The oxidant was potassium permanganate transferred from an aqueous phase saturated with NaCl into benzene with the help of TBAB as the phase transfer agent. LDPE was dissolved in benzene and refluxed in the presence of phase transferred permanganate from 6 to 12 h. The detailed procedure was described in a previous communication [16].

2.3. Preparation of polyhydroxy-ether imide (PHEI)

The synthesis of this polymer [17] was carried out in two stages

Stage 1. Synthesis of the monomer: 26.94 g benzophenone tricarboxylic dianhydride was dissolved in an optimum quantity of *N*,*N*-dimethyl formamide (DMF) in a two-necked round-bottomed flask and to this 18.24 g *m*-aminophenol was added. The mixture was refluxed at 140 to 150° C for 3 h. After refluxing, the mixture was poured into distilled water and bis-imidodiphenol was precipitated out. This bis-imidodiphenol was used as the monomer in the next stage of synthesis.

Stage 2. 17.85 g diglycidyl ether of bisphenol A was taken in a round-bottomed flask and to that 5.25 g bisphenol A was added. The mixture was slowly heated in an oil-bath up to 100° C with constant stirring by using a teflon stirrer. As the temperature reached 100° C, benzyltrimethylammonium hydroxide was added as the catalyst and the temperature was slowly raised to 180 to 200° C and then kept constant at about 200° C for an hour. To the above mixture, 11.58 g monomer was added. As the viscosity of the reaction mixture was very high, stirring became difficult. In order to fluidize it, *N*-methyl-2-pyrrolidone was added as the solvent and the reaction was carried out for 8 h at 180 to 200° C. Thereafter the aprotic solvent, DMF was added in excess. The entire mass was poured into distilled water with constant stirring to precipitate the polymer out. This was filtered, dried and further purified by dissolving in THF and reprecipitating from distilled water. The purified polymer was filtered and dried thoroughly. The structure of the polymer is shown below.



Poly-hydroxy ether-imide

2.4. Preparation of butylated silica [18]

About 200 ml *n*-butanol was made completely water-free by azeotropic distillation. 50 g silica and 150 ml anhydrous *n*-BuOH were refluxed together at 115 to 120° C for 5 h under atmospheric pressure. After the reaction was over, the reation mixture was cooled to room temperature and excess *n*-BuOH was removed by washing with acetone. Butylated silica was dried under vacuum at 110 to 120° C. Butylated silica is represented as $-S_i-O-C_4H_9$.

2.5. Characterization of additives

The various additives (oxidized LDPEs, PHEI and butylated silica) were characterized using the following techniques.

2.5.1. Infrared spectroscopy

The transmission infrared spectrum of oxidized LDPE film was recorded using a Perkin–Elmer 298 IR spectrophotometer in the range 4000 to 200 cm^{-1}. The film was prepared from hot toluene solution.

PHEI powder was pellitized with KBr and the infrared spectrum was recorded as above.

For butylated silica the spectrum was taken in nujol mull.

2.5.2. Non-aqueous titration

Oxidized LDPE was also characterised by a chemical method (non-aqueous acid–base titration) to determine the bulk acidity in the sample. For this determination, 0.2 g sample was dissolved in 15 ml toluene at 70° C in a water bath. As soon as a clear viscous solution was obtained, 15 ml ethyl alcohol was added to convert it into a colloidal solution. The mixture was cooled and titrated with standardized ethanolic NaOH using phenolphthalein indicator.

2.6. Preparation of LDPE blends with various additives

Separate blends of various compositions containing different additives were prepared by mixing them in a "Brabender Plasticorder" with LDPE as the matrix. The mixing was performed at 160° C. In each case, LDPE was first introduced into the brabender and melted for 2 min. Then the additive was added and the mixing continued for another 4 min at a rotor speed of 60 rpm. The material was taken out immediately and was milled in the hot condition to obtain a crepe sheet of almost uniform thickness.

2.7. Characterization of blends

Various techniques were used for the characterization of the blends.

2.7.1. *Infrared spectroscopy*

The infrared spectra of the blends were taken in Perkin-Elmer 298 IR spectrophotometer in the form of film. Films were prepared from a 15% hot toluene solution of each blend.

2.7.2. *Non-aqueous titration*

This method was used to determine the bulk acidity of the oxidized LDPE blends. The procedure is exactly the same as that used for oxidized LDPE except that pieces of blended crepe sheets were used instead of powdered sample.

2.7.3. *Scanning electron microscopy*

ISI 60 scanning electron microscope was used to determine the blend miscibility. The sample surfaces were sputter-coated with gold and taken for SEM observations.

2.8. Peel test measurements

To inspect and determine the quality of the adhesive-bonded joints, peel test measurements were used. The experiment was carried out in three steps.

1. The compression-moulded sheets for each blend composition were prepared in a Losca press. The moulding parameters were moulding temperature 150° C, heating time 15 min, cooling time 10 min, pressure 10.16 g cm^{-2} and sheet thickness 0.052 cm.
2. The laminated sheets were prepared from the compression-moulded sheets using pure aluminium foil as the substrate at a moulding temperature of 150° C.
3. The laminated sheets were then conditioned for variable periods of time at 25° C, and test panels having the dimensions 14 cm × 2.5 cm were cut from the laminated sheets and each of these was shaped in the form of "T" (see Fig. 1).

The peel test was performed on a modified tensile testing machine at the I.C.I. laboratory at Rishra, India. The ends of a laminated sheet were clamped and then the sample was peeled at the rate of 30.5 cm min^{-1}. Four specimens of each blend were tested three times each and the recorded value is the mean of twelve readings.

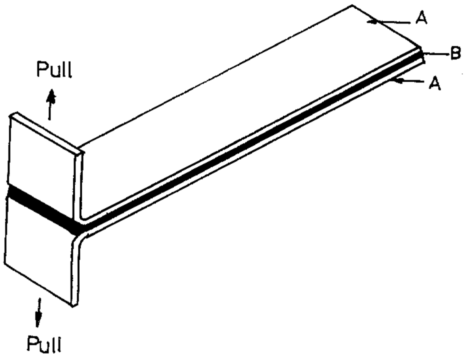


Figure 1 Test panel (14 cm × 2.5 cm) for T-peel testing; A = aluminium foil, B = polymer.

3. Results

When LDPE is blended with various additives containing considerable amounts of several functional groups with the idea of increasing its adhesion, the polar groups of the additives are anticipated to be occupying the surface sites [7, 19]. Infrared spectroscopic analysis was utilized to characterize the functional groups present in the additives and the blends.

3.1. Infrared observations

Figs 2 to 4 represent the infrared spectra of LDPE, different polymeric additives and their blends.

The transmission infrared spectrum of LDPE film (Fig. 2) shows a strong band at 2940 to 2840 cm^{-1} due to CH_2 stretching vibrations. The band for CH_2 bend appears at 1460 cm^{-1}, while the bands for twisting and rocking vibrations are obtained at 1305 and 730, 720 cm^{-1}, respectively. The appearance of a strong peak at 1375 cm^{-1} confirms the presence of a considerable amount of branching in it [20].

The spectral profile of oxidized LDPE is found to be almost the same as that of LDPE with some new signals at 3350, 1720, 1115 and 1015 cm^{-1}. While -OH stretching frequency is seen at 3350 cm^{-1}, the 1720 cm^{-1} peak is assigned to carbonyl stretching and the two lower energy bands to the $-SO_3H$ and $-COO^-$ stretching vibrations.

Comparing the major peaks of LDPE and the blend of LDPE with oxidized LDPE (Fig. 2) it is evident that a new peak at 1070 cm^{-1} appears in addition to all the peaks observed in oxidized LDPE. The new peak is assigned to the coupled $-SO_3H$ and $-COO^-$ stretching vibrations. The two vibrations of $-SO_3H$ found in oxidized LDPE do not show up separately in the blend. The surface orientation may cause them to come closer and overlap into a single broad band. The hydroxyl and the carbonyl stretching frequencies which are observed in oxidized LDPE are also found in the blend. In contrast to chromic acid-etched LDPE, the major functional groups generated during phase transfer catalytic oxidation are carbonyl, carboxyl, epoxy and hydroperoxo [21]. The blends of this oxidized LDPE with LDPE also exhibit the characteristic infrared peaks. It is noteworthy that these blends contain C–O–C and –O–OH groups which are also reported in the X-ray photoelectron spectroscopy studies of the flame-treated LDPE surfaces [2].

The strong absorption of the imide group at 1790 cm^{-1} and that of the coupled vibration of $>$CO and -NH at 1740 to 1690 cm^{-1} in polyhydroxy ether imide (Fig. 3) confirm the presence of these groups in the molecule. Similarly, absorption at 1385 to 1360 cm^{-1} confirms the presence of gem dimethyl group in the polymer repeating unit. The broad peak in the region 3500 to 3200 cm^{-1} is ascribed to the presence of hydroxyl groups.

The absorption at 2960 to 2940 cm^{-1} as well as 2870 to 2860 cm^{-1} in PHEI are due to $-C-CH_2-C$ symmetric and asymmetric stretching vibrations, whereas

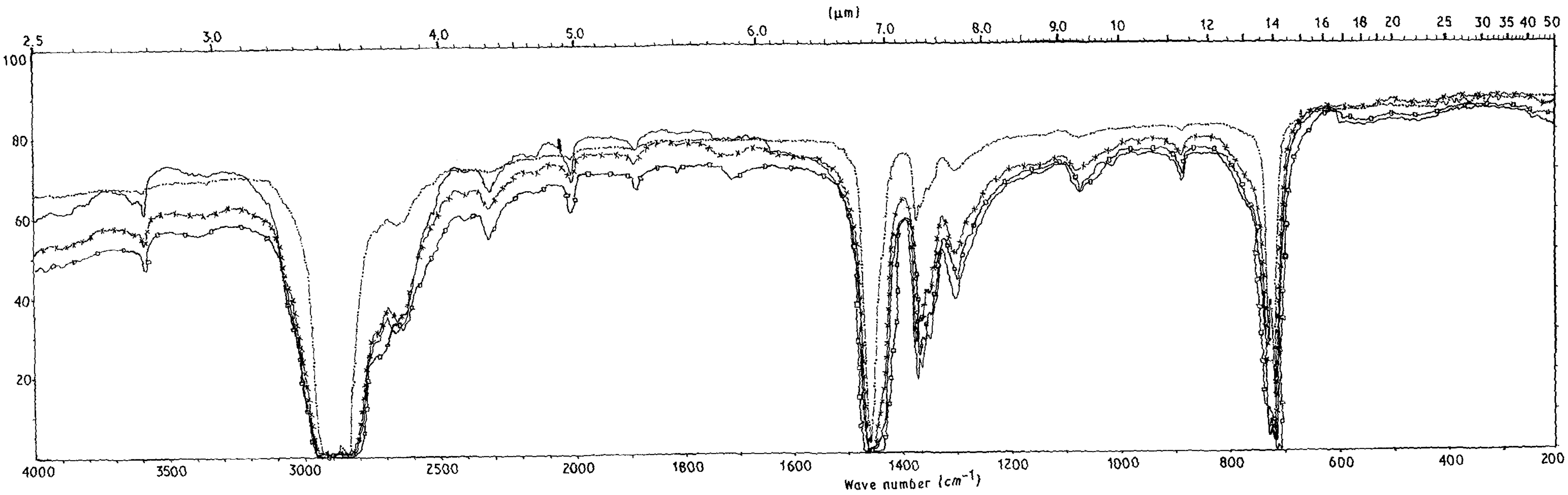


Figure 2 Infrared spectrum of (–··–) LDPE, (——) 5% blend of ox-LDPE, (——×——) 10% blend of ox-LDPE, (-□-) 15% blend of ox-LDPE.

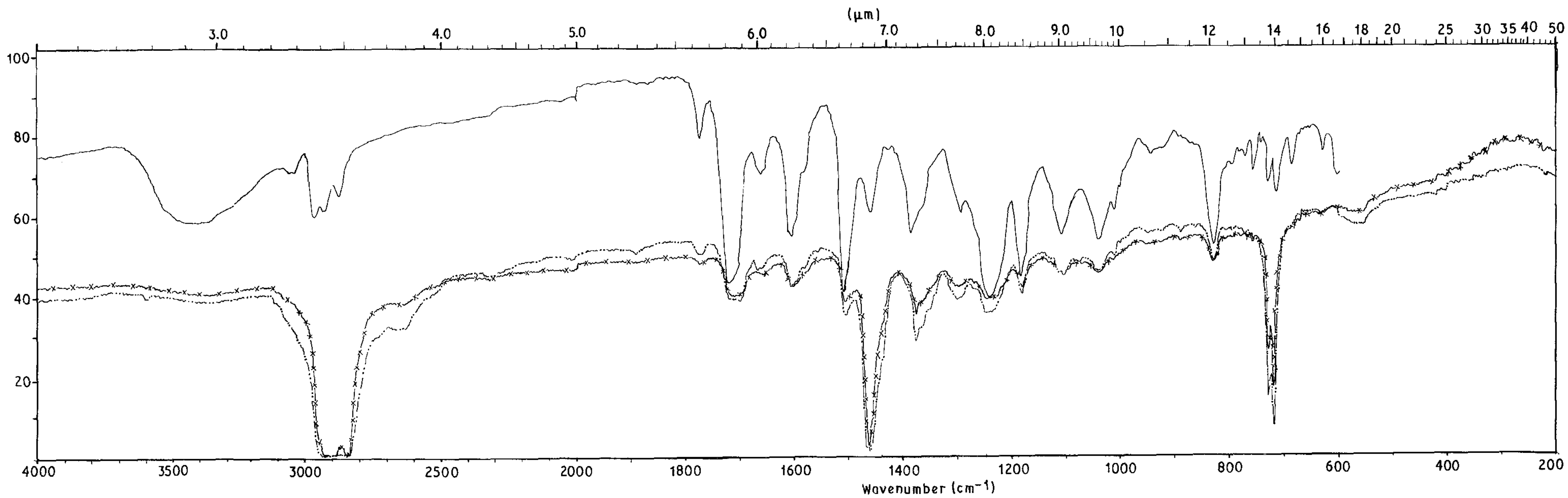


Figure 3 Infrared spectrum of (——) PHEI, (——×——) 5% blend of PHEI, (—··—) 10% blend of PHEI.

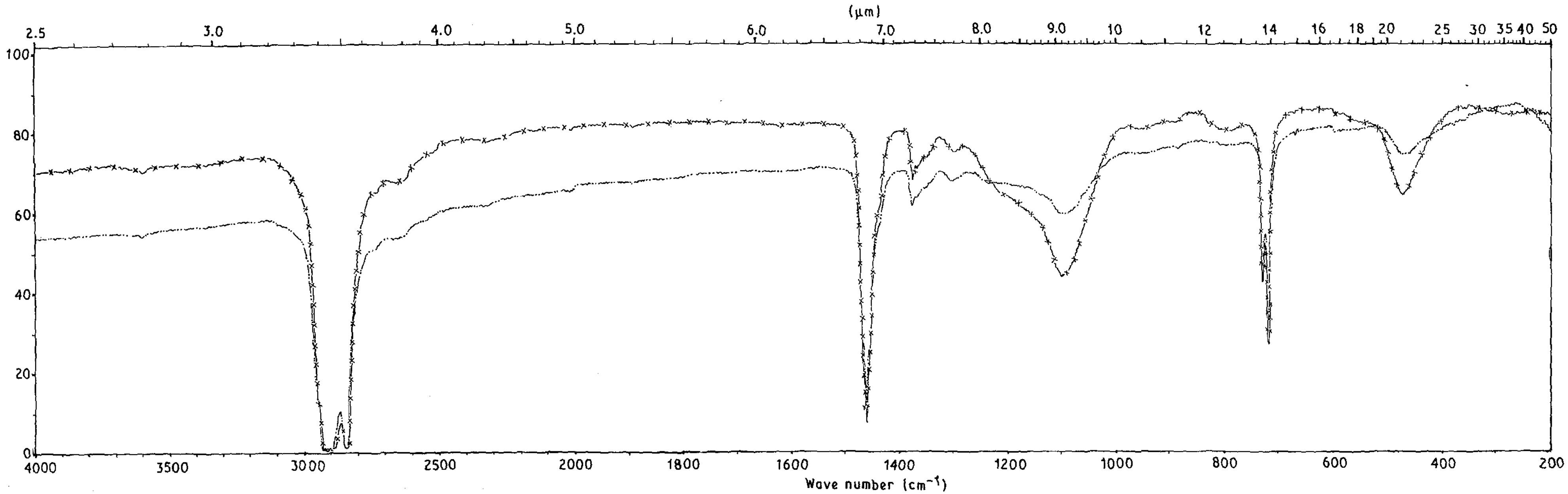


Figure 4 Infrared spectrum of (—··—) 5% blend of butylated silica, (——×——) 10% blend of butylated silica.

the absorption at 1250 to 1230 cm^{-1} is due to asymmetric stretching vibration of aryl alkyl ether oxygen. The absorption at 1100 cm^{-1} indicates the presence of secondary alcoholic -OH groups in the polymer. The absorption peaks at 1610, 1500 and 1450 cm^{-1} may be attributed to the aromatic C–C stretching vibration within the ring.

A number of absorption bands of variable intensity appear in the 1000 to 670 cm^{-1} region which are due to C–H bending vibrations as well as substitution in the benzene ring. The absorption peaks at 830 to 810 cm^{-1} and at 790 to 740 cm^{-1} are due to C–H out-of-plane bending while the bands at 1085, 1025 and 695 to 685 cm^{-1} are due to C–H in-plane bending.

In addition to the usual peaks of the two components, the blend in the form of a film shows the following peaks (Fig. 3) at 3500 to 3200 cm^{-1} (due to -OH); 1780 cm^{-1} (due to imide), 1720 to 1685 cm^{-1} (due to imide–carbonyl coupled vibration) and 1260 to 1220 cm^{-1} (due to aryl C–O–alkylene C).

The infrared spectral profile of butylated silica was taken in nujol mull because the nujol peaks do not interfere with the pattern, and pelletization with KBr powder is not easy to carry out in this instance. The Si–O bond produces bands due to bending vibration at 500 to 400 cm^{-1} and stretching vibration at 1000 to 800 cm^{-1} which is also assigned to the Si–OH bond. The band at 790 cm^{-1} is due to the overlapping of silanol and siloxane groups occurring in the complicated structures formed by connecting the silica tetrahedra [22]. The band at 1080 cm^{-1} is due to Si–O–Si stretching vibration and the band at 3400 cm^{-1} is caused by water hydroxyl groups.

The most prominent features in the spectral profile of the film of the butylated silica blend (Fig. 4) are two broad and strong bands at 1100 and 470 cm^{-1}. Because they refer to the Si–O–Si stretching and Si–O bending vibrations, respectively, it is evident that the above groups must have accumulated in the surface and the subsurface layers during the formation of the blend.

By taking the peak at 1460 cm^{-1} of $-\mathrm{CH_2}$ bending vibration as the internal standard, the relative peak intensities for different functional groups introduced in the different blends have been calculated (see Table I) for quantitative determination of these groups. The maximum amount of polar functional groups is present in the LDPE blend of butylated silica, followed by the PHEI blend. The blend with chromic acid-etched LDPE shows the least relative proportion of the polar functionalities.

TABLE II Acidity of oxidized LDPE at various oxidation times

Time of oxidation (h)	Bulk acidity (%)
6	13.86
9	14.03
12	14.32

3.2. Non-aqueous titration results

Non-aqueous acid-base titration helps us to determine the amount of acid groups present in oxidized LDPE (see Table II). It is evident that with the increase in the amount of oxidized LDPE in the blend as well as with the increase in the duration of oxidation of LDPE with chromic acid, the total acidity of the oxidized LDPE is increased (see Tables III and IV). The theoretical and experimental acidity values are within the limits of experimental error which may have occurred in carrying out the measurements in a heterogeneous medium. Some errors will also arise from the improper mixing of the polar additive (oxidized LDPE) with non-poplar LDPE. In addition, the higher melting point of oxidized LDPE (T_m = 210 to 220° C) may also have hindered the uniform mixing because the blending of LDPE with this additive was carried out at a temperature below its melting temperature.

3.3. SEM observations

During mixing in the brabender, the additive is likely to occupy random position in the LDPE matrix. But the polar $>$CO, $-$ $\mathrm{COO^-}$, -OOH or $-\mathrm{SO_3H}$ groups in the oxidized LDPEs, the ether, the imide and the hydroxyl groups in PHEI, and Si–O, Si–OH, and Si –O–R groups of the butylated silica can be accommodated in the bulk of LDPE only at a high energy cost. The scanning electron (Figs 5b and c) show that intrinsically the additives are compatible with LDPE, although some indication of domain formation is visible. This may be attributed to (i) non-uniform mixing, and (ii) surface aggregation of polar components. There is no indication of demixing even at the microscopic level.

Fig. 5a shows the morphology of untreated LDPE. The scratches and irregularities are evident on the surface. Fig. 5b shows the blend of chemically etched LDPE with LDPE. It is seen that the distribution of polar groups is not homogeneous. Domain formations are visible; they are found to be distributed in a random manner.

TABLE I Peak area ratio relative to $-\mathrm{CH_2}$ band at 1460 cm^{-1}

Substance	Group			
10% blend of	-OH	$>$C=O		$-\mathrm{S(O_2)OH}$ + $-\mathrm{COO^-}$
oxidized LDPE	0.0602	0.0745		0.0802
10% blend of PTC	-O-OH	$>$C = O	C-O-C	$-\mathrm{COO^-}$
Oxidized LDPE	0.3481	0.3762	0.2169	0.0872
10% blend of	imide	imide + $>$C=O	-OH	aryl C-O-alkylenic C
PHEI	0.1487	0.4948	0.1972	0.2664
10% blend of	Si-O-Si	-Si-O + Si-OH		Si-O
Butylated silica	2.483	0.5881		0.2720

PTC = phase transfer catalyst.

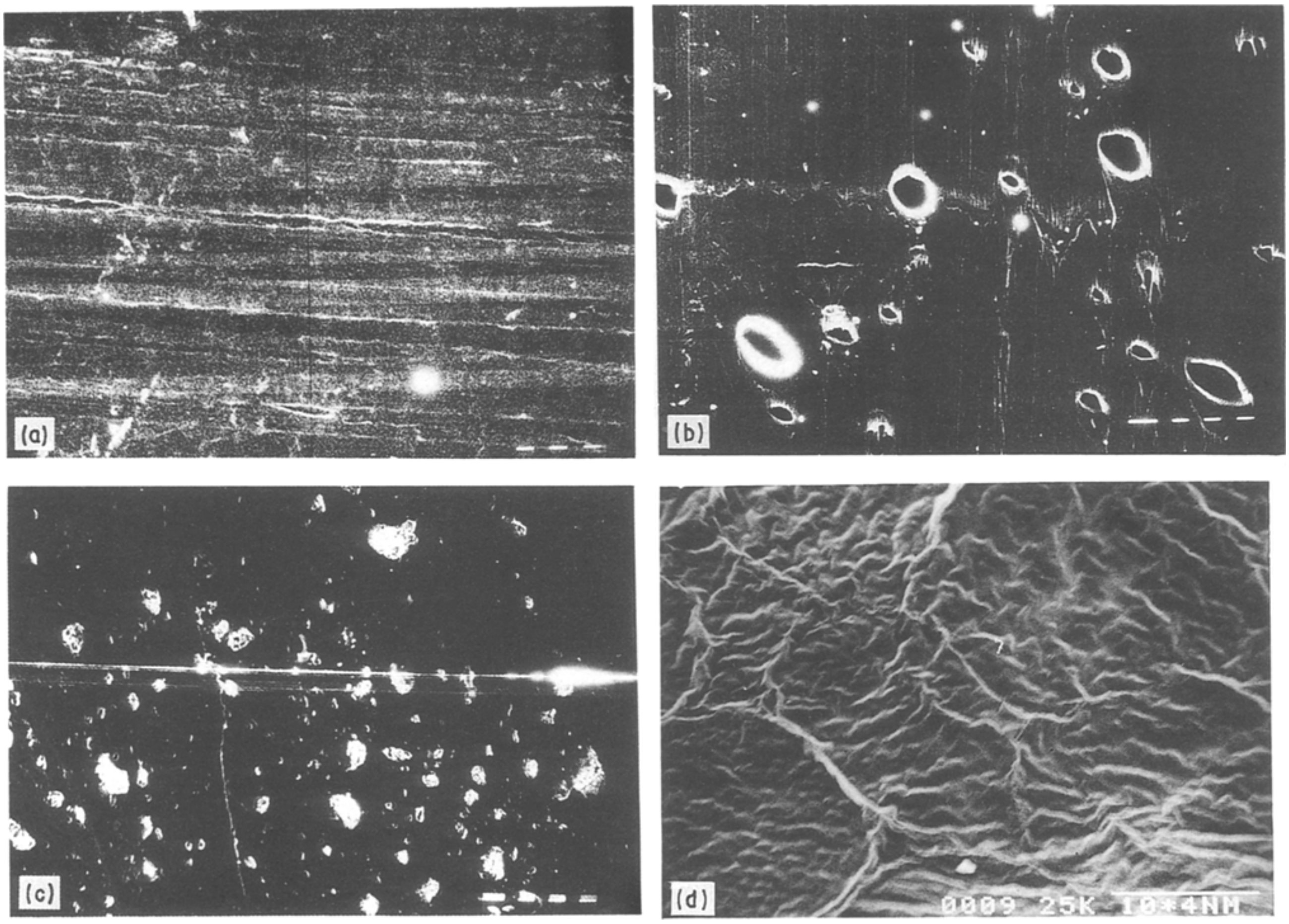


Figure 5 Scanning electron micrographs of (a) LDPE, (b) oxidized LDPE blend, (c) butylated silica blend and (d) PTC oxidized LDPE blend. × 500.

The micrograph of PHEI blend closely resembles that of the oxidized LDPE blend but the distribution of polar groups is quiet uniform here. The micrograph of LDPE blend with butylated silica (Fig. 5c) depicts slightly more surface roughness with several larger domains.

Fig. 5d, where a criss-cross of pittings and scratches emerges at a magnification of × 500, shows the 10% blend with LDPE oxidized in benzene medium by phase transferred permanganate using $Bu_4N\,Br$ as the phase transfer agent [23].

None of the blends show such extensive surface roughness with extended chains. Evidently this polymer blend has a higher surface energy and hence should exhibit better adhesion properties than the blends mentioned earlier.

3.4. Peel strength measurements

Comparing the peel strength values at 1% blend composition of various additives (Table V), it is observed that the blend containing LDPE (oxidized with phase transferred permanganate) has the highest value and that with butylated silica the lowest. The peel strength values obtained for different higher blend compositions of butylated silica were very low (Table VI) even at 10% composition, compared to other polymer additives.

Peel strength values for chromic acid-etched LDPE at higher blend compositions show an interesting result. A change in additive concentration is the blend from 1% to 20% initially increases peel strength, which more or less remains constant beyond 10% composition (Fig. 6). Ageing of the samples does not alter the above trend but shows slightly higher peel strength. Increasing the time of oxidation during the preparation of oxidized LDPE and its subsequent blends with LDPE indicated an increase in the peel strength values (Fig 7). Ageing of such samples gives rise to even higher peel strength. The same behaviour pattern is obtained in the case of LDPE oxidized by phase transferred permanganate.

Another interesting feature of Table V is the variation of the range of peel strength (i.e. the difference between the maximum and the minimum force peaks)

TABLE III Acidity of oxidized LDPE blends at different blend compositions

Percentage composition of blends	Bulk acidity (%)	
	Experimental	Calculated
1	0.16	0.14
5	0.62	0.69
10	1.23	1.39
15	1.87	2.08
20	2.58	2.76

TABLE IV Acidity of 10% oxidized LDPE blends at different oxidation times

Time of oxidation of LDPE (h)	Bulk acidity (%)
6	1.23
9	1.28
12	1.32

TABLE V Peel strength of LDPE blends with different additivies at 1% blend composition

Additive used	Peel strength (N m^{-1})		
	Maximum force peak	Minimum for peak	Average force peak
None	18.50 ± 2.0	12.30 ± 1.3	15.40 ± 1.6
Oxidized LDPE	136.92 ± 15.1	92.80 ± 10.2	115.54 ± 12.2
PHEI	91.58 ± 11.7	70.50 ± 6.3	81.02 ± 8.1
Butylated silica	25.01 ± 3.3	18.30 ± 2.5	20.80 ± 2.3
PTC oxidized LDPE	358.20 ± 32.0	137.00 + 11.0	252.60 ± 20.0

with the nature of the blending partner. With butylated silica blend the range is virtually the same as in unmixed LDPE. Even the two kinds of oxidized LDPE blends differ from one another in the values of the range of peeling load: 44 for chromic acid-oxidized LDPE blend and 221 for phase transferred permanganate-oxidized LDPE blend. These differences probably reflect the overall variability of the surface composition.

4. Discussion

The literature data for chromic acid-etched polyethylene [3, 24] indicate that the depth of oxidation is much greater than for flame or electrical discharge treatment and it is possible to relate the degree of oxidation with the adhesion levels [25]. However, all these studies deal with aluminium-epoxide adhesive-pretreated PE systems. The results are usually interpreted to support the theory of the formation of weak surface layers in weak adhesive bonds.

In the present study the polymer blend is directly laminated to aluminium foil. So the adhesive bond forms between Al/Al_2O_3 and the polar groups on the surface layers of the polymer blends. In a previous paper [26], in which the influence of functionality and phase transfer catalyst on the adhesion characteristics of LDPE was discussed, we have shown that the peel strength linearly increases with increasing proportions of keto, carboxyl, the sum of the two and also of the total oxo groups. It also increases with the time of oxidation but levels off to a constant value beyond 6 h. This non-linear variation of peel strength with the time of oxidation indicates cohesive failure deeper within the polyethylene samples. Longer chromic acid attack can also give rise to such effects as shown in Fig. 7. The level-off in peel loads beyond 9 h with LDPE-etched LDPE blends must largely reflect the progressive increase in the PE–Al surface adhesive bond strength. This, in turn, will affect the uniformly cohesive interior of the film. The surface topography changes dramatically from unetched to etched LDPE showing a larger degree of surface roughness. One might then postulate that the enhanced strength of adhesion in the case of the blends with the two oxidized LDPEs is brought about not only by the chemical interactions of the polar groups on the PE surface with Al/Al_2O_3 but also by the mechanical interlocking. The large paractical adhesion shown by the phase transferred permanganate-oxidized LDPE blend should be ascribed to the bonding of aluminium to peroxo and carboxyl groups [26].

TABLE VI Peel strength of butylated silica blend at different blend compositions

Composition of the blend (%)	Peel strength (N m^{-1})		
	Maximum for peak	Minimum force peak	Average force peak
1	25.01 ± 3.3	18.30 ± 2.5	20.82 ± 2.3
2	33.59 + 4.1	22.01 ± 3.3	27.80 ± 3.5
5	48.11 ± 7.4	37.00 ± 4.9	40.15 ± 5.0
10	66.05 ± 8.1	49.07 ± 6.0	55.62 ± 6.2

Contrary to expectation, the peel adhesion does not increase with increasing amount of polar groups (Fig. 8a). The butylated silica–LDPE blend gives hardly any enhancement of the peeling load over plain LDPE. However, the surface morphology (Fig. 5c) implies segregation of certain regions on the surface which may have resulted from association between the surface polar groups. The polymer–polymer miscibility in a blend is generally predicted on the basis of the solubility parameter, δ. By analogy to several $(\mathrm{R\ MeSiO})_n$ polymers [27] and functional polysiloxanes [28], the butylated silica can be assigned a δ value of 7 to 8 which closely resembles the solubility parameter (7.7 to 8.4) of LDPE [19]. Despite expected compatibility of the two polymers, the adhesion level is quite low. Assuming that the silane at the metal–polymer interface is polysiloxane network with some free Si–OH groups [29], it is possible that the silanol groups are hydrogen-bonded to Si–O–Si as also to Si–OH groups on the surface. Hence the large extent of domain formation results, leaving only the siloxane groups free for adhesive bonding to aluminium. Similarly, in PHEI blends, the majority of keto oxygen and

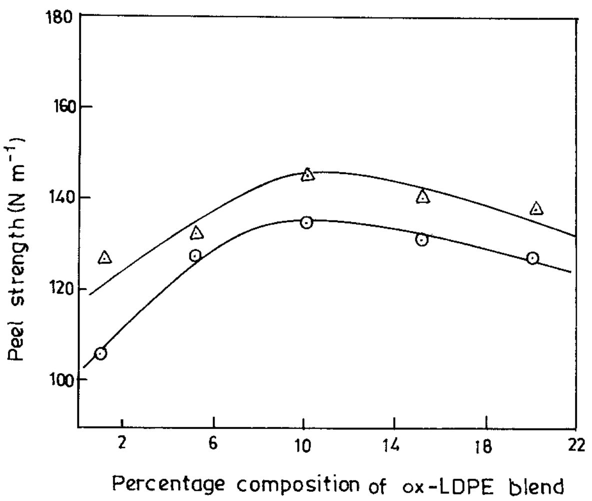


Figure 6 Peel strength of oxidized to LDPE blend at various compositions after ageing for (⊙) 24 h, (△) 7 d.

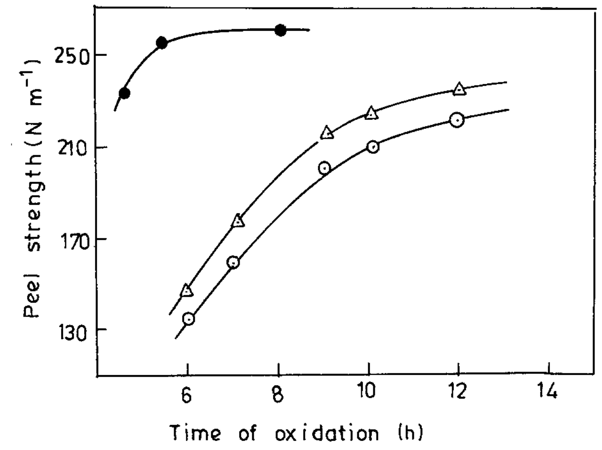


Figure 7 Peel strength of 10% oxidized LDPE blends at various oxidation times, aged for ⊙ 24 h. (△) 7 d. PTC oxidized LDPE blends, aged for ● 24 h.

hydroxyl hydrogen will associate to produce the domains. Thus the imide nitrogen will possibly be the only anchoring sites. When the peel strength is plotted against the proportion of the "effective" polar sites (Fig. 8b), a strong correlation is obtained.

The oxidized surfaces retain or even increase the bondability after 7 d. Should the adhesion of oxidatively treated PE have been due to the presence of mechanically weak surface layer consisting of oxidative-degradation products of PE alone, the adhesive bondability would have been lost on ageing. Because of the isomorphism of the polymeric chains, the two LDPE matrices (oxidized LDPE and untreated LDPE) are truly miscible, and the chemical interactions extend beyond the subsurface layers and progress gradually with time. If the maximum in peel strength is considered to be a measure of the adherent failure, the greater this quantity, the stronger is the role of cohesive failure in practical adhesion. Interpenetration of one molecular species into and beyond the interface would also be expected to yield improved mechanical compatibility.

PHEI and butylated silica are blendable with LDPE without subsequent "sweat-out", but they differ widely in molecular forces. The limited practical adhesion of these blends is due to the surface layer of excessive polar groups which is mechanically weak. Because peel adhesion has a well-established viscoelastic basis [30], the surface chemical or energetic criteria are a necessary condition, but not a sufficient condition for maximum practical adhesion.

5. Conclusions

1. A severe chromic acid treatment of LDPE causes a level of oxidation lower than oxidation with phase transferred permanganate in benzene.

2. LDPE blends with oxidized LDPEs give higher peel strengths than the blends with polyhydroxyetherimide and butylated silica.

3. With oxidized LDPE blends, the peel strength increases with ageing, levels off beyond a critical oxidation time and passes through a maximum at 10% blend composition.

4. The practical adhesion does not correlate well with the total number of polar groups in the polymer blend.

Acknowledgements

The authors thank Dr M. Chakraborty for experimental assistance with the SEM studies, Dr B. B. Patra for permission to use the facilities for T-peel measurements at the Rishra factory, Indian Explosives (P) Ltd, and Dr A. K. Banthia for useful discussions.

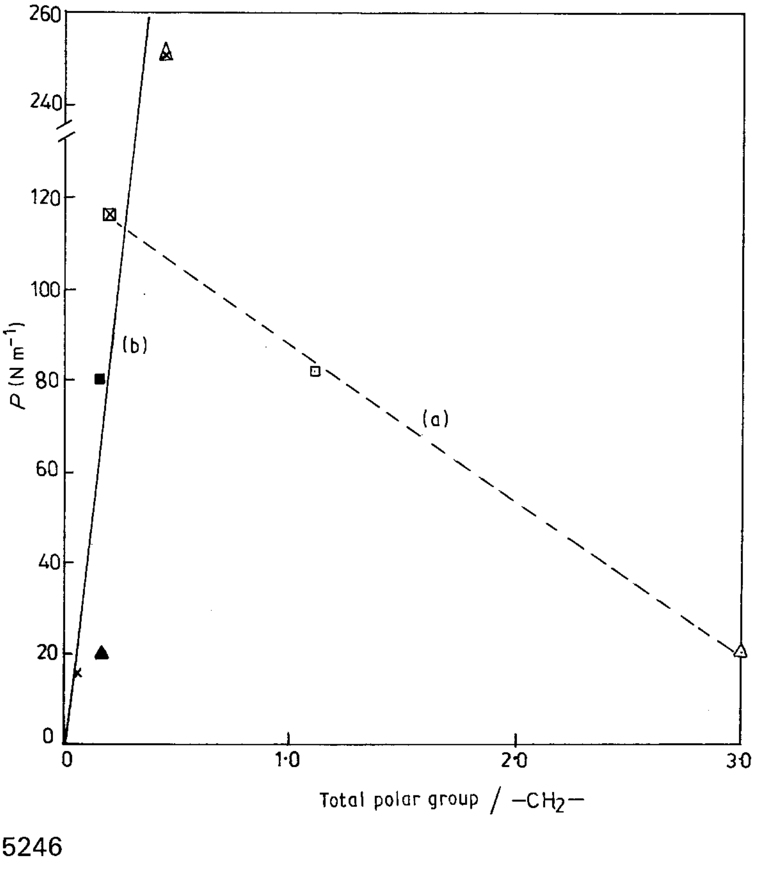


Figure 8 Variation of peel strength with the total amount of polar groups relative to CH$_2$ group. (×) LDPE alone; (⊠) blend of LDPE and OX-LDPE; (◬) blend of LDPE and PTC OX-LDPE; (□) blend of LDPE and PHEI; (■) as (□) but only imide group considered; (△) blend of LDPE and butylated silica; (▲) as (△) but only siloxane group considered.

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Received 23 May 1989
and accepted 1 February 1990