

Mechanical properties and surface energies of low density polyethylene–poly(vinyl chloride) blends

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A series of blends of poly(vinyl chloride) (PVC) and low density polyethylene (LDPE) are prepared and examined. Plasma treatment is applied to one of the components (LDPE) in order to affect the degree of compatibility. For this purpose, different monomers, such as carbon tetrachloride and vinyl chloride, are used. Tensile test results for all the blend samples, with and without plasma-treated LDPE, are compared. The surface energy results of blends prepared from untreated and treated LDPE–PVC showed considerable differences, with appreciable increases for the latter, indicating an increase in the work of adhesion as a result of the plasma surface modifications applied. The tensile test results and the measured surface energies are found to show a similar parallel behaviour. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: LDPE–PVC blends; plasma surface modification; surface energy)

INTRODUCTION

The modification of the interfacial and interphase properties of a polymer blend is mainly carried out in order to achieve a certain degree of compatibilization in the system. For this, appreciable atomic/molecular interactions (adhesive forces) must be present between the different phases constituting the polymer blend. The magnitude of this interaction can be determined from equilibrium and quasi-equilibrium measurements, and contact angle determination of liquids on solids is a widely used experimental technique for this purpose. Although a clear understanding of polymer–polymer adhesion is of great technological importance, there have been few studies accomplished, mainly due to the fact that the adhesive strengths involved are quite low in magnitude and hence difficult to measure with enough precision^{1–6}.

Polymer surfaces can be modified by use of a number of different methods, each with certain advantages and disadvantages. During surface modification by a plasma, a thin surface layer of the polymer can be altered appropriately to create chemical groups capable of interacting with each other (termed plasma treatment), and/or plasma homo/graft polymers can be formed with certain characteristics, which can act as a modifier directly (plasma polymerization). Both of these can give rise to controlled changes in the chemical composition of the polymer surfaces where modifications can be achieved without altering the bulk properties of the polymers involved. Both techniques are clean, environmentally safe, and effective.

Polymer surfaces and surface properties are important for many of the properties of a material, and they are expected to be directly related to properties of the bulk in solid polymer solutions, as is the case for liquid solutions. Hence,

any surface property, *i.e.* surface energy, is expected to be influenced by changes in the bulk, including an increase/decrease of the extent of phase separation and the degree of compatibility; these are known to be reflected strongly in various mechanical properties as well. In fact, the dynamic behaviour of polymer surfaces and the environmental dependence of polymer surface properties are already recognized^{7,8}.

In this study, the existence of a correlation between the mechanical properties and the surface interaction is sought on phenomenological grounds. Blends prepared from two plasma-treated and untreated immiscible polymers, low density polyethylene (LDPE) and poly(vinyl chloride) (PVC), are studied.

THEORETICAL BACKGROUND TO SURFACE ENERGIES

The total surface energy (γ) of a given non-metallic material (i) can be considered as being composed of two parts, namely, the Lifshitz–van der Waals (γ_i^{LW}) component and the acid–base (γ_i^{AB}) component (equation (1))^{9,10}. In equation (2), γ_i^a and γ_i^b are the independent Lewis acid and Lewis base components of the surface free energy.

$$\gamma_i^{TOT} = \gamma_i^{LW} + \gamma_i^{AB} \quad (1)$$

$$\gamma_i^{AB} = 2(\gamma_i^a \gamma_i^b)^{1/2} \quad (2)$$

A characteristic feature of the Lewis acid and base components is their non-additivity. Hence if phase (i) possesses only γ_i^a or γ_i^b , this component does not participate in the total surface free energy of the phase (i). However it will interact with the complementary component of phase (j).

For a bipolar liquid (L), with surface tension γ_L , acidic (γ_L^a) and basic (γ_L^b) surface parameters, and an apolar surface component γ_L^{LW} , the complete equation to be

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Table 1 Plasma treatment conditions

Sample code	Treated polymer	Monomer used in plasma	Power (W)	Time (min)	Average flow rate (ml min ⁻¹)	Average pressure (mbar)	Treatment type ^a
C1	LDPE	CCl ₄	7	30	55.7	0.4	LW-LQ
C3	LDPE	CCl ₄	7	30	58.2	0.4	HW-LQ
C4	LDPE	CCl ₄	14	30	102.0	0.5	HW-HQ
V2	LDPE	CH ₃ Cl	10	15	47.6	0.5	LW-HQ

^aKey: LW, low wattage; LQ, low flow rate; HW, high wattage; HQ, high flow rate

Table 2 Surface free energies (mN m⁻¹) for the probe liquids used, at 20°C

Liquid	γ^L	γ^{LW}	γ^{AB}	γ^a	γ^b
<i>n</i> -Decane	23.83	23.83	—	—	—
Diiodomethane	50.80	50.80	—	—	—
Formamide	58.00	39.00	19.00	2.30	39.60
Ethylene glycole	48.00	29.00	19.00	3.00	30.10

Table 3 Contact angles and calculated surface energies for the samples measured

Code	θ_{DIM}	θ_{FA}	θ_{EG}	γ^{LW}	γ^{AB}	γ^{TOT}
C1075	63.8	75.9	79.2	26.40	0	26.40
C1100	58.4	73.4	72.9	29.47	0	29.47
C3050	60.6	74.0	72.0	28.48	0	28.48
C3075	62.5	84.4	70.8	27.16	0	27.16
C3100	56.8	78.0	71.7	30.40	0	30.40
C4050	62.3	84.1	77.8	27.28	0	27.28
C4075	68.0	79.0	74.0	24.01	0.49	24.50
C4100	69.8	80.6	74.7	28.67	0	28.67
L0050	55.5	80.1	75.4	31.18	0	31.18
L0075	58.7	74.4	76.1	29.35	0	29.35
L0100	57.4	83.1	73.4	30.09	0	30.09
U0000	33.0	63.3	59.1	42.93	0.02	42.95
U0060	66.2	77.3	73.3	20.48	0	20.48
U0075	75.8	77.9	75.7	19.72	0	19.72
U0090	49.2	74.5	68.5	23.02	0	23.02
U0100	57.4	83.1	73.4	30.08	0	30.08
V2050	56.9	83.1	74.5	30.39	0	30.39
V2075	60.5	78.0	71.8	28.31	0	28.31
V2100	58.5	72.0	69.5	29.46	0.21	29.67

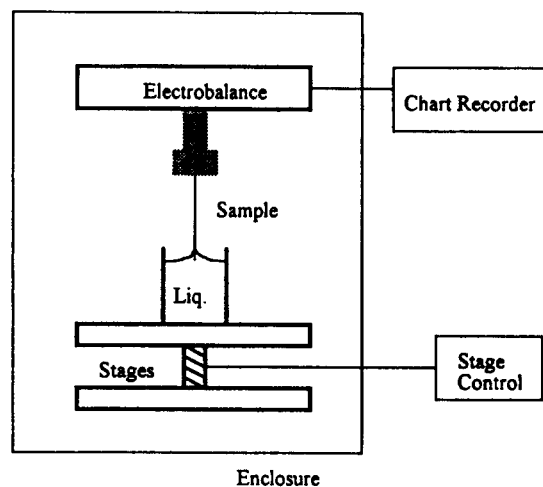
considered is as follows

$$(1 + \cos \theta_L) \gamma_L^{TOT} = 2[(\gamma_L^{LW} \gamma_S^{LW})^{1/2} + (\gamma_L^a \gamma_S^b)^{1/2} + (\gamma_L^b \gamma_S^a)^{1/2}] \quad (3)$$

which can be constructed to form a set of two simultaneous equations, in terms of the parameters of the solid γ_S^a , γ_S^b and two advancing contact angles θ_1 , and θ_2 , which are measured on the solid surface. These two equations can then be simultaneously solved for γ_S^a , and γ_S^b provided that γ_i^a , γ_i^b and γ_L^{LW} for the probe liquids are known.

EXPERIMENTAL

The polymers used in this study, LDPE granules (Petilen type F 2-12, with a melt flow index 2.0 g per 10 min and a density of 0.920 g cm⁻³) and PVC powder (Petvinil type S-23/59, with a *K* value of 54–58 with cyclohexane at 25°C and a relative viscosity of 1.354–1.417 with the same solvent) were both supplied by Petkim Petrochemical Ind. Inc., Turkey. The monomers used in the plasma treatment were carbon tetrachloride (Merck; above 99%) and vinyl chloride (a Petkim product). In addition, a low molecular weight vinyl chloride copolymer (a side-product of a vinyl chloride monomer (VCM) unit of Petkim containing 30%


Figure 1 Contact angle apparatus set-up

Cl) was also used alone in the blend system with composition 0.5 ppm without application of a plasma.

All r.f. plasma treatments were performed in a tubular Pyrex reactor (50 cm in length and 6.2 cm in inner diameter), with use of a 13.56 MHz r.f. generator and external copper electrodes. The plasma was applied to the LDPE granules directly. The plasma conditions used are tabulated in Table 1¹¹, and are selected from those that are known to yield surface modification mainly. Hence, the samples treated in the plasma will be termed 'plasma-modified'.

After plasma surface modification of the LDPE granules, samples with a series of compositions were prepared using PVC powder with the help of the Brabender Plasticorder at 175°C (2 min; 60 rev min⁻¹). After their preparation in the mixer, the samples were premolded in a platen press (for 1 min at the same temperature with 10 000 lb) to first obtain plaques of thick films (thickness about 1 mm), which were then remolded to obtain thinner films (100–250 μm) at 190°C for 1 min with 25 000 lb. The samples were allowed to stand at room temperature for 24 h in order to avoid the effects of the thermal history.

An Instron tensile testing machine, model TM 1102, was used during this study, with a gauge length of 3.5 cm, a thickness within the range 100–250 μm, and a minimum width of 0.285 cm. Tests were performed with a constant cross-head speed of 1.24 cm min⁻¹.

Contact angle measurements were performed by use of an electronic microbalance (Sartorius microbalance model M25 D) and a motor mike (vertical mobile stage; Oriol model 18008). A schematic view of the contact angle apparatus is presented in Figure 1. The linear speed of the vertical stage was kept at 1 μm s⁻¹. Sample sizes tested were typically 5 × 5 × 0.2 mm³.

In the surface energy experiments, diiodomethane (DIM)

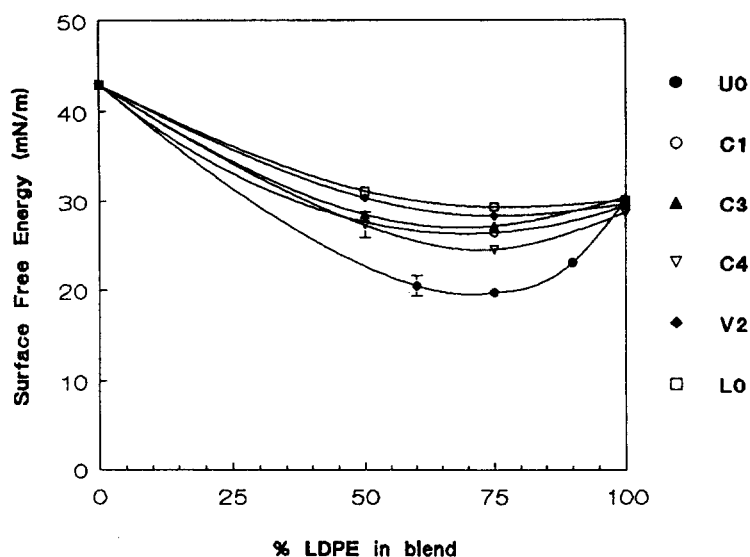


Figure 2 Surface free energies of untreated/treated blends versus blend composition

was used as the probe liquid for the Lifshitz-van der Waals interactions while ethylene glycol (EG), and formamide (FA) were used for the acid-base interactions. In addition, *n*-decane was used as a completely wetting liquid to determine the perimeters of the specimens. The analytical grade liquids were used as supplied. Properties of the probe liquids used are presented in Table 2.

RESULTS AND DISCUSSION

Results of surface energy studies

The results of the surface energy measurements are presented in Table 3, with advancing contact angles of all the samples measured with DIM, FA, and EG, together with the calculated surface energy components. For the coding of the samples, U, C, V, and L were used, corresponding to untreated, carbon tetrachloride plasma-treated, vinyl chloride plasma-treated, and added vinyl chloride copolymer, respectively. The first number following the letter in the first column represents the type of plasma treatment (0, no plasma; 1, plasma applied under low wattage/low monomer flow rate conditions, in short LW-LQ; 2, plasma at HW-LQ; 3, plasma applied at LW-HQ; 4, plasma at HW-HQ). The last three numbers denote the LDPE content of the blends prepared.

Previous reports concerning the surface free energies for pure PE and PVC showed a very satisfactory fit with the data presented in this work (Liston¹²: 31 dyn cm⁻¹ and 39 dyn cm⁻¹, respectively), although considerable differences are expected both in the grades of polymers used as well as in their processing variables during the production of these films, and in the test techniques employed.

The total surface free energies of the prepared samples are presented in Figure 2 as a function of blend composition. As can be seen from the figure, compared to the pure components, the surface free energies decrease non-linearly both for treated and untreated blends. The amount of the decrease is found to be the highest for untreated blends, passing through a minimum at approximately 75% LDPE content. For all plasma-modified and oligomer-added samples, a similar trend in the surface energies is observable; they all showed a similar dependence on the LDPE content, decreasing monotonically

down to the minima at about 75% and then increasing again slightly. For all four different plasma-modified blend sets and one vinyl chloride oligomer-added blend set tested, the surface energies demonstrated different levels of decrease, ranging from C4-type treated samples (showing the largest decrease), up to the oligomer-added samples (showing the smallest decrease), with per cent LDPE. It should be noted that, due to the experimental difficulties involved in the blend and film preparation, blends in PVC (*i.e.* 25% LDPE) could not be prepared and hence there are no data available for them.

Among five differently treated blend samples, the lowest surface energies are obtained for C4 (high-wattage, high-flow rate, CCl₄ plasma-treated). The effects of certain plasma operational parameters on the surface free energies for C4 are also presented in the same figure, which shows that the plasma power used is obviously less effective than the monomer flow rate in altering the surface energies of blends of C4. This is most probably due to fact that the higher the possibility of effective plasma surface treatment, the lower the probability for plasma polymerization, if the power is increased. Surface energies observed for the samples treated at a low plasma wattage are still approximately 30% higher than those for the untreated blend. Both the vinyl chloride plasma-modified and its oligo copolymer-added blends show some 45% and 50% increase in surface energies, respectively, when compared with untreated blends.

Results of mechanical tests

The ultimate mechanical properties, *i.e.* the impact strength, and the stress and strain at break values are known to be the most sensitive to the extent of compatibility. Since LDPE and PVC are known to be mutually immiscible, their blends are expected to exhibit a deterioration in mechanical properties of the system compared with those of the virgin homopolymers alone. Figure 3 represents mechanical test results for the blends prepared with untreated and vinyl plasma-treated LDPE blends, as well as oligomer-added samples, all containing 25% PVC. The latter two modified samples in this group are found to exhibit higher tensile strengths compared with the blend of unmodified polymers. The three curves presented here are for comparison purposes only, and comprehensive results

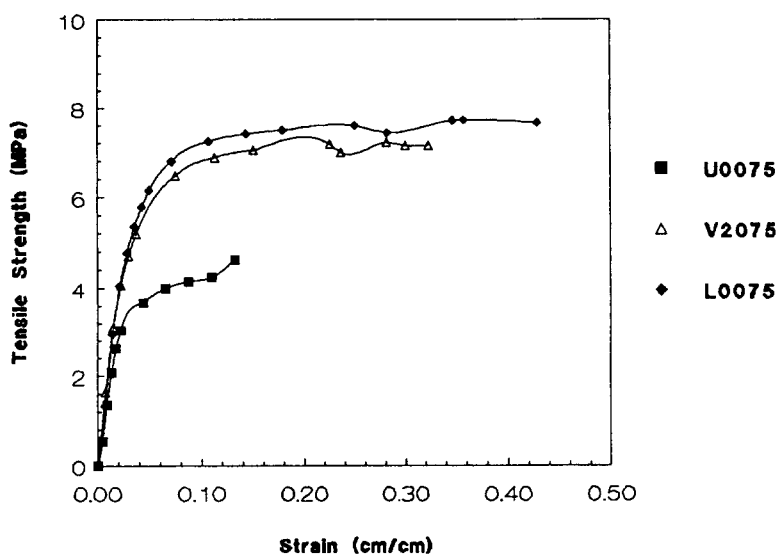


Figure 3 Stress-strain curves for blends with 25% PVC

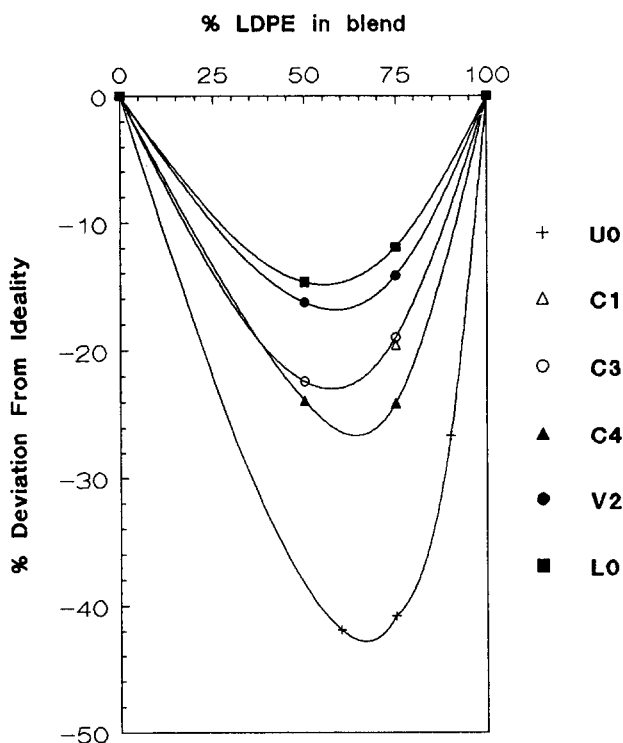


Figure 4 Per cent deviation from additivity as calculated by the linear law, based on contact angle measurements, versus LDPE content (of the LDPE-PVC blends)

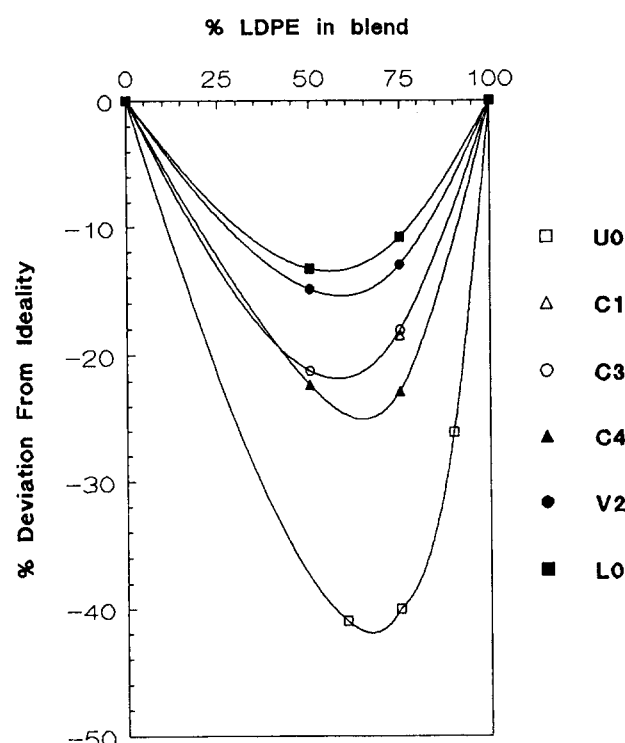


Figure 5 Per cent deviation from additivity as calculated according to the logarithmic law, based on contact angle measurements, versus LDPE content

for the mechanical properties of the series of blends prepared with plasma surface-treated samples are presented in another communication¹³. It is interesting to note that the surface free energies of the first two polymer blend systems mentioned above have also been found to be higher compared to the virgin blend, complementing each other.

In addition to the changes in the measured surface energies presented in the previous section, appreciable changes have also been observed in the bulk properties, both for the treated as well as the oligomer-added blend samples. The results of tensile testing showed that both the vinyl chloride plasma surface treatment of one of the components of the blend or the addition of vinyl chloride oligo copolymer as the compatibilizing agent have positive effects on the tensile strength and tensile strain values

(Figure 3). A similar analysis for the 50% blend, the results of which are not included here, showed exactly the same trend: samples with vinyl chloride plasma-modified and oligomer-treated components showed improved tensile strengths and strains, while blends with carbon tetrachloride plasma-treated components were much poorer mechanically¹³, having comparatively low surface energies. Hence, a correlation between surface energies and the mechanical performances of blend samples exists, at least qualitatively.

Discussion

The change in advancing contact angle (θ_a) can be due to several factors, comprising mainly the chemical heterogeneity¹⁴ or the physical roughness of the surface¹⁸, which tend to increase θ_a . It has been proposed by Israelachvili and

Ge¹⁹ that as the patches of chemical heterogeneity approach the molecular dimensions, the contact angle hysteresis decreases, resulting in a decrease in the measured θ_a . In our system, the LDPE is the continuous phase and the PVC is the discrete phase, most probably as patches on the surface. One can also speculate that the PE content of the surface is greater than its bulk value due to its low surface energy, decreasing the total free energy of the system. The experimental results initially show an increase in θ_a with increase in PVC content, namely an increase in the surface heterogeneity. With PVC contents approaching 50%, the trend is towards higher surface energies in accordance with the higher surface energy of the PVC. With appropriate plasma treatment or copolymer addition, the advancing contact angles decrease, most probably indicating the formation of a less heterogeneous or a more compatible system. This is also supported by the mechanical test results. It can indeed be observed that the large increase in tensile strength for the vinyl chloride copolymer-added LDPE is also matched by the highest surface energies; this may be thought of as an indication of better compatibility compared with other samples.

According to the well-known Cassie–Baxter equation¹⁴, the measured contact angles should fall between that of PVC and that of treated LDPE. The minima in the surface energy curves (Figure 2) can be related to edge effects due to phase-separated islands of PVC. As the compatibility increases, the phase separation most probably acquires a more diffuse form, which dilutes the effects of the edges¹⁵. The apparent contact angles on the phase edges can take a multitude of values in order to satisfy the Young–Dupre and Young–Laplace equations which describe the shape of a liquid surface. A more critical evaluation of the contact angle data is beyond the scope of this study; nevertheless, we observed that a correlation exists between the improvement or deterioration in mechanical properties (which reflects the degree of compatibility) and the surface properties (pseudo-surface free energies). If the straight line between any corresponding value for pure LDPE and pure PVC is taken as the reference corresponding to the ‘ideally compatibilized case’ (in accordance with the ‘rule of additivity’), and if it is compared with the values obtained for treated and untreated blend samples, certainly ‘deviations from the additivity line’ will be obtained for the surface energies as well as for the mechanical properties. In this context, the smallest deviation would mean better compatibility, and the largest deviation, as observed for the unmodified blends, would mean a higher degree of phase separation. This concept can be re-utilized further, as applied by Bernardo *et al.*¹⁶ and Bataille *et al.*¹⁷, to follow the degrees of compatibilities, if the linear and/or logarithmic additivity rules are revisited, equations (4) and (5)

$$P_{av} = x_1 P_1 + x_2 P_2 \quad (4)$$

$$\ln P_{av} = x_1 \ln P_1 + x_2 \ln P_2 \quad (5)$$

where the sum of any property P (or its log) multiplied by fractions of the individual pure components would give the average of that property representing the whole system. Pseudo-surface energy results are presented in Figures 4 and 5, showing per cent deviations according to linear and logarithmic law dependences, respectively. As can be seen, both figures are similar and the deviations exhibit a maximum value for the untreated blends, as expected, while the blends prepared with vinyl chloride plasma-treated LDPE or with added oligo copolymer provide much fewer deviations.

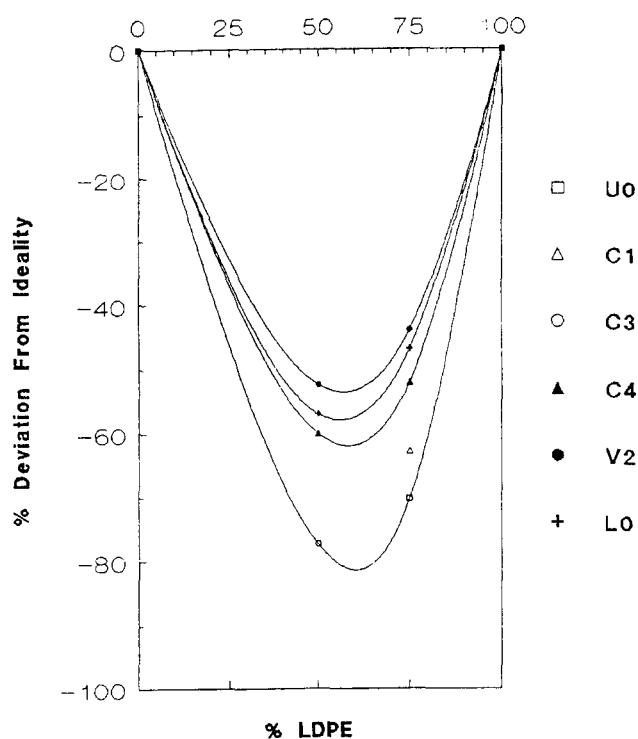


Figure 6 Per cent deviation from additivity according to the linear law, based on stress at break values, versus LDPE content

Similar results were observed from mechanical tests¹³. Per cent deviations from additivity for the stress at break values observed are presented in Figure 6.

CONCLUSIONS

- (1) The degree of compatibility of mutually incompatible LDPE–PVC blends can be improved by the application of the appropriate r.f. plasma to LDPE prior to mixing. This causes an alteration in the interfacial chemical groups with negligible cross-linking, and to a lesser extent the production of new plasma polymers can occur, leading to a compatibilizing action, as in the case of the use of compatibilizers directly.
- (2) There exists a correlation between the extent of the degree of compatibility (as reflected by mechanical performance) and the surface energies.

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