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Surface properties and adhesion mechanisms of graft polypropylenes

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Improvement of the adhesion capacity of polypropylene to aluminium can be obtained by adding a small quantity of maleic anhydride grafted polypropylene to the polymer. With increasing maleic anhydride content, the peel strength of the polymer–aluminium assembly first increases due to migration, orientation and chemical bonding, and then decreases as a result of the formation of a weak boundary layer, made of the low molecular weight grafted polymer chains. This study stresses the importance of two phenomena in adhesion: the restructuring of the polymer at the metal interface and the formation of an interphase.

1. Introduction

Polypropylene exhibits very poor adhesion properties due to its low surface polarity. Numerous methods have been used to modify its surface properties, such as oxidation, flaming, plasma treatment, grafting, etc. [1]. A route which seemed very interesting to us was to modify the properties of polypropylene by adding to the polymer a small quantity of the same polymer grafted with a polar species such as maleic anhydride (MA). The two polymers being compatible, one should obtain a good dispersion of the grafted into the non-grafted polypropylene. This polymer mixture may behave like a bulk grafted polymer and therefore lead to improved adhesive strength towards polar substrates such as aluminium.

It is well known that polymers exhibit surface properties depending on their history and their environment [2–5]. For instance, when in contact with a model polar environment such as water, many polymer surfaces reconstruct themselves due to the polymer chain mobility and the plasticization effect of the water [2–9]. This is true for hydrogels [2, 3] like polyhydroxymethylmethacrylate or gelatin, polar polymers such as polymethylmethacrylate [4], copolymers [9] and polymers grafted either in bulk [5, 8] or at the surface [6]. For a polyethylene grafted with acrylic acid (1% by weight) [5, 7, 8] in contact with water, at ambient temperature, the surface goes from an apolar to a polar state within a few days. This is due to the polymer surface restructuring, the polar acrylic grafted groups being oriented at the polymer–water interface.

Therefore, the surface energy of a polymer must be considered as a "potential surface energy" because the surface is modified when in contact with different environments.

This interesting property can be correlated with the adhesion mechanism on a metal surface like aluminium [5]. When melting the grafted polyethylene on an aluminium surface, adhesion is obtained by chemical reaction between the reoriented acrylic groups and the hydroxyl groups always present on the aluminium oxide layer covering the metal.

Using the same techniques as previously published [5, 7, 8], the surface properties of these mixtures of grafted and non-grafted polypropylenes were examined by wettability measurements as a function of contact time on water, in order to examine the ability of the polymer to restructure in contact with a highly polar medium. These properties were then compared with the adhesive properties to aluminium, as a function of the maleic anhydride content of the polymer.

2. Experimental details

2.1. Materials

Maleic anhydride was grafted either on homopolymer polypropylene or on ethylene–propylene copolymer containing 5% ethylene by a method using a peroxide in order to obtain a grafting ratio of about 2.7% for the homopolymer and 4.4% for the copolymer.

This grafted polymer was then diluted into the virgin polymer by extrusion and led to dilutions ranging from 100 to 5000 p.p.m. maleic anhydride. Polymer plates (2 mm thick) were obtained from these extruded films (100 μm thick) by compression moulding (2.3 MPa, 180° C, 15 min).

2.2. Potential surface energy determination

Because the reconstruction of the polymer surface was done in contact with water, the method for measuring the surface energy components was the two-liquid-phase technique [10] allowing an *in situ* determination.

The method consists of measuring the contact angle, θ, of a drop of alkane on the polymer surface, the surrounding medium being water. By using an *n*-alkane series (from hexane to dodecane), it is possible to determine the dispersive component, γ_S^D, and the

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polar component, γ_S^P, of surface energy according to Equation 1

$$\underbrace{\gamma_H - \gamma_W + \gamma_{HW}\cos\theta}_{Y} = 2(\gamma_S^D)^{1/2} \times \underbrace{[(\gamma_H)^{1/2} - (\gamma_W^D)^{1/2}]}_{X} - 2(\gamma_S^P\gamma_W^P)^{1/2} \qquad (1)$$

The subscripts H and W correspond to the alkane and water, respectively. By plotting the quantity Y against the quantity X for the alkane series, γ_S^D and γ_S^P are readily obtained from the slope and intercept of this straight line. The surface energy components were determined at 23° C as a function of the time of contact on water at the same temperature. However, the kinetics of reorientation of the groups can be accelerated by increasing the temperature of contact up to 80° C.

Doubly distilled water and alkanes of high purity were employed.

2.3. ESCA analysis

Surfaces were also characterized through X-ray electron spectroscopy–electron spectroscopy for chemical analysis (XPS–ESCA). The spectrometer was an ESCA 3 (Vacuum Generators Ltd) equipped with a Mg$K\alpha$ source (1253.6 eV energy). The C_{1s} and O_{1s} peaks were recorded. Calibration on the C–C peak was assigned to 286 eV. The presence of carboxylic groups leads to a component shifted by 4.2 eV [11].

Spectra were collected on polymer samples before and after contact with water, and also after peeling from the aluminium substrate.

2.4. Adhesive strength measurements

The polymer plate was bonded to a 100 μm thick aluminium foil (99.5% purity) by compression under 2.3 MPa at 180° C for 15 min followed by fast cooling to room temperature. The adhesive strength of the assembly was measured using a classical 180° peel test. The energy of separation (or peel energy or energy of adhesion), W, is given by

$$W = 2F/\omega \qquad (2)$$

where F is the applied force and ω the width of the test piece.

Peeling was performed on an Instron 1195 testing machine, the peel rates, R, ranging from 0.5 to 500 mm min^{-1}. The peeling experiments were done not only in air but also in ethanol in order to determine the respective contribution of physical and chemical interactions to the interfacial adhesion according to a method developed by Schultz and co-workers [12, 13].

The experimental decrease of peel strength, $\Delta W/W$, in an ethanol environment is compared to the decrease of the reversible energy of adhesion, $\Delta W_O/W_O$, calculated from the surface energies of the liquid and the solids. The observed difference is easily related to the chemical contribution, $W_{o\,\mathrm{chem}}$, to adhesion which is not supposed to be affected by the presence of the liquid.

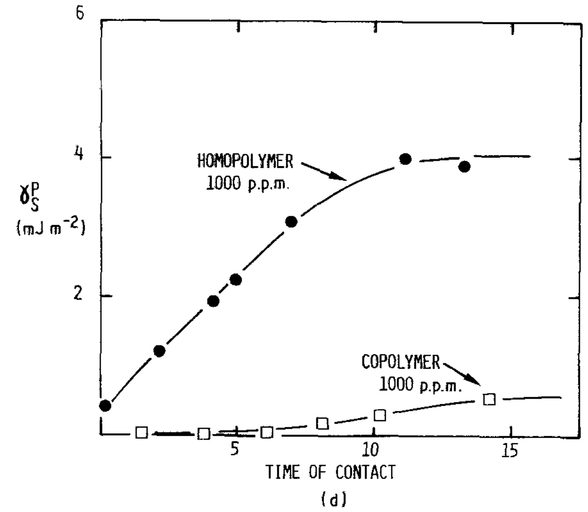


Figure 1 Variation of surface polarity of polymers with time of contact with water at room temperature.

Equations 3 and 4 give the values of both the chemical and physical contributions, $W_{o\,\mathrm{chem}}$ and $W_{o\,\mathrm{phys}}$

$$W_{o\,\mathrm{chem}} = \frac{W_{o\,\mathrm{phys}} - W_{oL\,\mathrm{phys}}}{\Delta W/W} - W_{o\,\mathrm{phys}} \qquad (3)$$

$$W_{o\,\mathrm{phys}} = 2(\gamma_S^D\gamma_{Al}^D)^{1/2} + 2(\gamma_S^P\gamma_{Al}^P)^{1/2} \qquad (4)$$

where $W_{oL\,\mathrm{phys}}$ is the reversible energy of adhesion between polymer, S, and aluminium, Al, in the presence of the liquid, L.

3. Results

3.1. Surface properties

Fig. 1 gives an example of the evolution of the surface polarity of the polymer mixtures at a 1000 p.p.m. maleic anhydride content. There was an increase of surface polarity of the polymer with time of contact on water at room temperature. As shown in earlier work [7], this increase can be attributed to a movement of the macromolecular chains followed by a preferential orientation of the carboxylic polar groups, initially buried in the bulk of the polymer, towards the water interface. XPS analysis of the oriented polymer clearly showed the presence of a carboxylic acid component in the C_{1s} peak.

In order to accelerate the kinetics of orientation of the grafted species, the contact on water was done at 80° C. After 3 d, a maximum value of the polar component, γ_S^P, was obtained. Fig. 2 shows the variation of

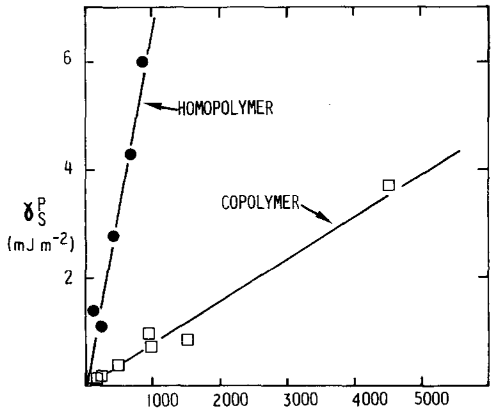


Figure 2 Variation of surface polarity with maleic anhydride content of the polymers after 3 d contact with water at 80° C.

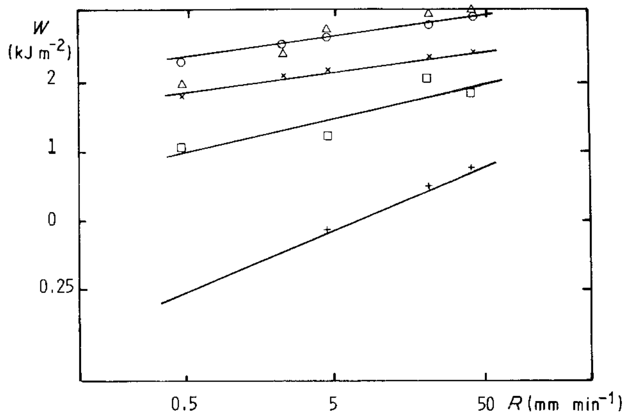


Figure 3 Peel energy, W, plotted against peel rate, R, for copolymers at different maleic anhydride contents: (×) 5000, (○) 2000, (△) 1000, (□) 400, (+) 200 p.p.m.

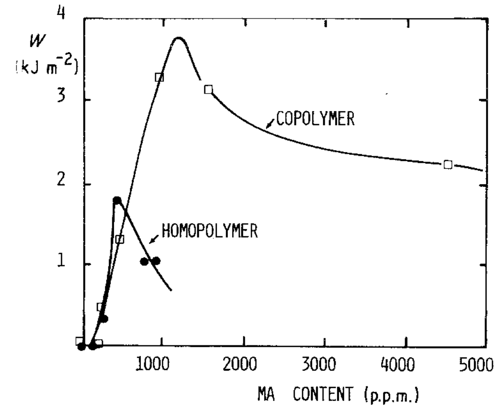


Figure 5 Peel energy, W, (at a peel rate of 5 mm min^{-1}) plotted against maleic anhydride content for homo- and copolymers.

this maximum surface polarity value as a function of the MA content of both the homo- and copolymer mixtures.

It is clearly seen that the higher the MA concentration, the higher the surface polarity. It can be concluded that the surface polarity which can be attained when the polymer surface is put in contact with a highly polar environment is directly proportional to the number of polar groups available in the bulk polymer.

It must also be mentioned that the dispersive component, γ_S^D, is approximately constant and equal to (33 ± 2) mJ m^{-2}.

It also appears that for a given amount of MA present in the polymer, that is to say for the same dilution ratio of the grafted polymer into the polymer matrix, a much higher surface polarity (about eight times higher) is obtained with the homopolymer than with the copolymer. Although we have no definite explanation, this phenomenon is attribued to a different chain mobility of the homo- and copolymers (because of molecular weight, degree of crystallinity, . . .) and probably to a different localization of the MA grafts into the chain.

This section shows that a polar medium, such as water but also aluminium in accordance with earlier work done in our laboratories [5, 7], is capable of orienting the polar groups of the polymer mixture to the interface, the driving force being the minimization of the interfacial energy.

3.2. Adhesive strength

The variation of the energy of separation, W, with the peel rate, R, as a function of MA content for the co- and homopolymers is presented in Figs 3 and 4. As expected from simple rheological considerations, the peel strength increases with increasing peel rate.

However, for a given peel rate, the adhesive strength of the assembly goes through a maximum when the MA content is increased. This phenomenon is better seen in Fig. 5 where the energy of adhesion, W, is plotted as a function of MA content for a given peel rate of 5 mm min^{-1}. The maximum value of peel energy is obtained for an MA content of about 400 p.p.m. for the homopolymer and 1200 p.p.m. for the copolymer.

Fig. 6 shows an example of the results relative to the 1000 and 2000 p.p.m. MA polypropylene copolymers when peeling is performed in air and in an ethanol environment. As explained in Section 2, the observed decrease of 68% in peel strength in ethanol allows the chemical and physical contributions to the interfacial interactions to be determined. In this case it was found that the chemical interactions represent 31% of the total energy of adhesion. Following an experimental procedure proposed previously [5], it was verified by infrared spectroscopy that these chemical interactions corresponded to the formation of an aluminium

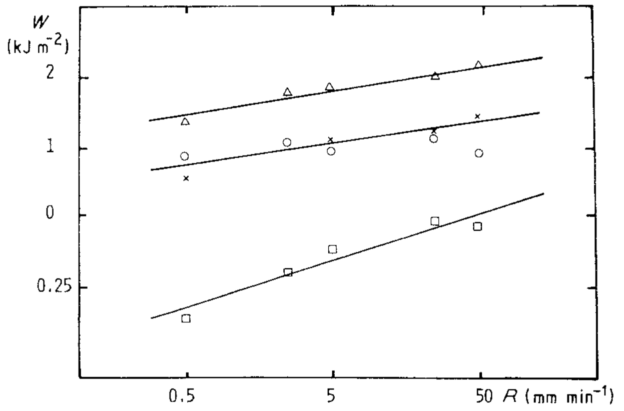


Figure 4 Peel energy, W, plotted against peel rate, R, for homopolymers at different maleic anhydride contents: (×) 1000, (○) 750, (△) 400, (□) 200 p.p.m.

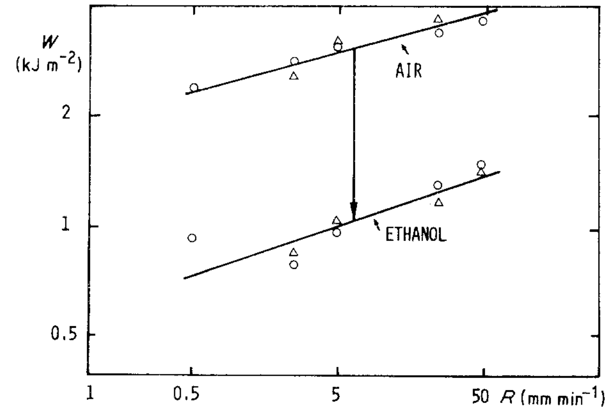


Figure 6 Peel energy, W, plotted against peel rate, R, for copolymers at 1000 and 2000 p.p.m. maleic anhydride, in air and in ethanol: (△) 1000, (○) 2000 p.p.m.

carboxylate resulting from the reaction of the hydrolyzed MA grafts of the polymer with the aluminol groups at the surface of the metal.

4. Discussion

4.1. Proposition of an adhesion mechanism

It is rather surprising to find that there is no simple correlation between the surface properties of the polymer as measured by wetting and the adhesive strength of the polymer–aluminium assembly as determined by peeling. The surface polarity, which measures the capacity of the polymer to form chemical bonds, increases in a continuous manner with the amount of grafted MA whereas the adhesion to aluminium goes through a maximum. It was shown through static and dynamic testing that the bulk mechanical and rheological properties of the polymer are not altered by the addition of the grafted polymer. It was also easily shown that the optimal value of MA content leading to the highest adhesive strength was not an intrinsic property of the aluminium substrate. As shown in Fig. 7, the use of other substrates with hydroxyl groups such as poly-ethylene terephthalate (PET) or an ethylene–vinylalcohol copolymer (EVAL) led to the same optimum value of the MA content ($\simeq$ 1200 p.p.m.) although the number of hydroxyl surface groups is considerably different from one substrate to the other. However, as expected from their hysteretic properties, the level of adhesion, even at the maximum, depends strongly on the nature of the substrate.

Having examined several potential explanations, the difference between the surface properties and the adhesive strength was attributed to the formation of a weak boundary layer [14] at the polymer–metal interface. During the grafting reaction through the peroxide radical, a chain scission occurs according to Scheme I [15]. Therefore, each grafted polypropylene chain will present a molecular weight lower than that of the non-grafted polymer chains in which it is incorporated. Because of the driving force resulting from interfacial attraction, the grafted chains of lower molecular weight will migrate easier and faster and enrich the surface in low molecular weight fraction thus provoking the formation of an "interphase" of low cohesion.

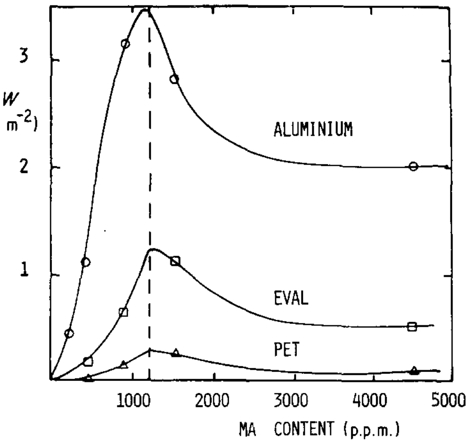
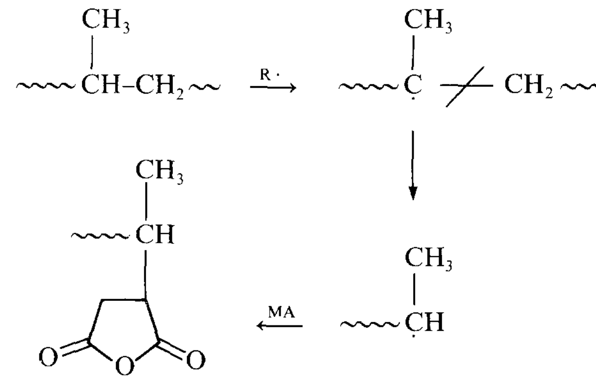


Figure 7 Peel energy, *W*, plotted against maleic anhydride content of the copolymer for different substrates (aluminium, ethylene–vinylalcohol copolymer, polyethylene terphthalate).



(I)

The experimental curves of Fig. 5 giving the energy of adhesion *W* against the MA content of the polymer can therefore be explained by the existence of two simultaneous mechanisms illustrated in Fig. 8. Curve (a) corresponds to the formation of physical and chemical bonds at the polymer–metal interface through migration and orientation of the grafted polymer chains. Therefore, the adhesive strength, *W*, increases with MA content until a plateau is reached corresponding to the saturation of all the aluminol groups present on the surface of aluminium (about 1 OH group per nm^2 [16, 17]). Curve (b) corresponds to the cohesive strength of the polymer as a function of MA content. As the MA content increases, the cohesion of the polymer near the interface decreases as the low molecular weight fraction accumulates, from a value corresponding to the cohesion of the non-grafted polypropylene to a constant value corresponding to the cohesive strength of the grafted polypropylene.

To explain the experimental curves of Fig. 5, it is assumed that, first (Region I), adhesion increases along Curve (a) due to the bond formation. When the cohesion of the polymer in the interphase (Curve b) becomes smaller than the interfacial adhesion (Curve a), the experimental curve will follow Curve (b) (Region II). This leads to a *W* against MA content diagram exhibiting a maximum as experimentally observed.

This proposed mechanism also implies that in Region I, for low MA contents, the failure should appear purely interfacial, whereas in Region II, for high MA contents, the failure should propagate cohesively within the polymer interphase.

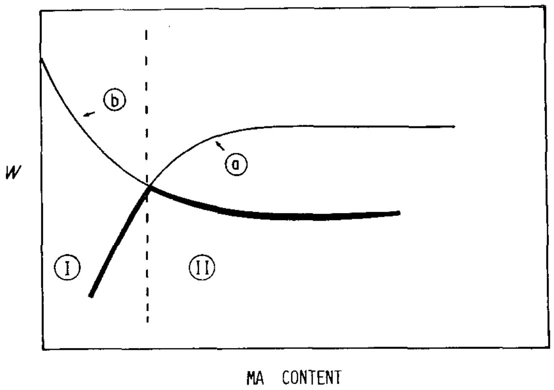


Figure 8 Schematic representation of peel energy, *W*, plotted against maleic anhydride content of the copolymer according to the hypotheses of (a) bond formation and (b) weak boundary layer formation.

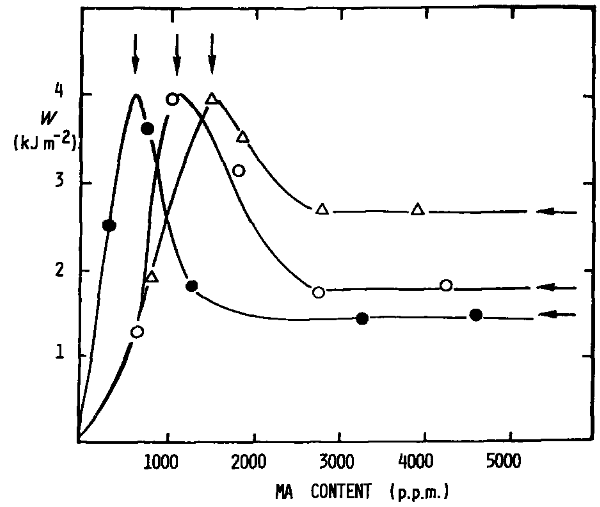


Figure 9 Peel energy, W, plotted against maleic anhydride content of the copolymer at different grafting ratios: (●) Polymer A, (○) polymer B, (△) polymer C.

4.2. Verification of the proposed mechanism of adhesion

In order to check this two-step mechanism, three series of copolymer mixtures were prepared in which the grafting ratio of the MA grafted polymer was varied from 3.0% to 4.5%.

At the same dilution in the non-grafted polypropylene copolymer, the only difference will be the average molecular weight of the chains carrying the MA grafts. The molecular weights were determined by gel permeation chromatography (GPC) and are shown in Table I. Assemblies were prepared with these three series of polymer mixtures at dilutions ranging from 300 to 4500 p.p.m. Peel strength against MA content is presented in Fig. 9.

It is clearly seen that the curves corresponding to the three series exhibit the same general shape with a maximum value of adhesion but are shifted according to the grafting ratio of the polymer. The value of MA content at the maximum of adhesion is inversely proportional to the grafting ratio, that is to say the lower the molecular weight of the grafted polymer, the lower the value of the MA content corresponding to the maximum of adhesion.

At low MA content or high dilution, i.e. below the maximum of adhesion, the diffusion of the grafted species is easier as the molecular weight is lower as a result of higher chain mobility or lower chain entanglements. At the same dilution for the three series, the grafted chains of polymer A will appear in greater amount at the interface than grafts of polymer C. Fig. 10 shows that there is a good correlation between the MA content corresponding to the maximum adhesive strength and the inverse of molecular weight at power 2/3. This constitutes an indication that the observed phenomenon is controlled by a kinetic effect related to the diffusion of grafted chains of low molecular weight [18].

TABLE I Molecular weights determined by GPC

	Designation of the polymer mixture			
	Non-grafted	A	B	C
Grafting ratio (%)	0	4.5	4.0	3.0
M_W (g mol^{-1})	320 000	49 000	52 000	64 000

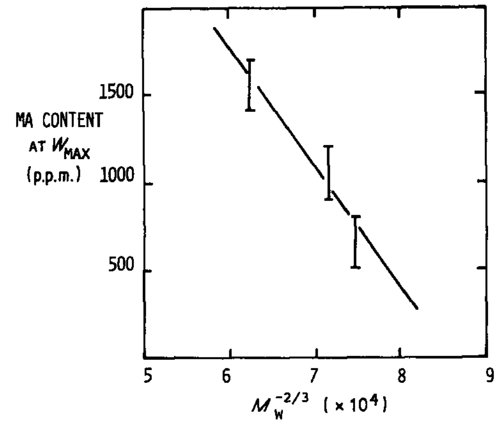


Figure 10 Relationship between the optimum concentration of maleic anhydride of the copolymer and its molecular weight, M_W.

At higher MA content (above the maximum of adhesion), a plateau value for adhesion is observed; the higher the grafting ratio (i.e. the lower the molecular weight of the grafts), the lower the value of adhesion at the plateau. The plateau value corresponds, according to our hypothesis, to the cohesive strength of the grafted polymer. A strong correlation is observed in Fig. 11 between this plateau value and the average molecular weight of the grafted chains.

The experimental curves of Fig. 9 can therefore be described by the schematic representation of Fig. 12. In the curves corresponding to bond formation, adhesion increases "faster" for series A than for series B or C starting from a zero value (no adhesion) to a common limiting value corresponding to the saturation of all hydroxyl groups available on the aluminium oxide surface. In the curves corresponding to the cohesion of the polymer in the interphase, the energy of separation decreases starting from a common value corresponding to the cohesive strength of the non-grafted polymer of molecular weight 320 000 and reaching values corresponding to the intrinsic cohesion of the grafted polymers. The composite curves obtained when following the adhesion curve (until cohesion becomes lower than adhesion) and then the cohesion curves describe satisfactorily the experimental curves of Fig. 9.

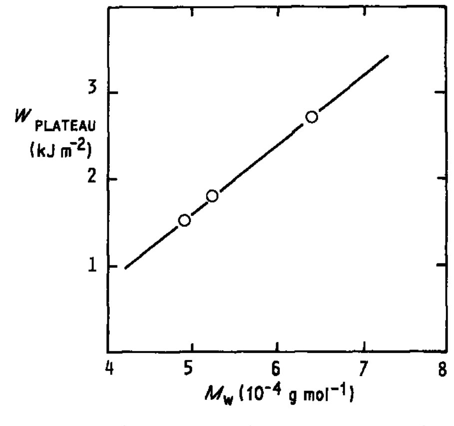


Figure 11 Relationship between the plateau value of adhesion for high maleic anhydride concentrations of the copolymer and its molecular weight, M_W.

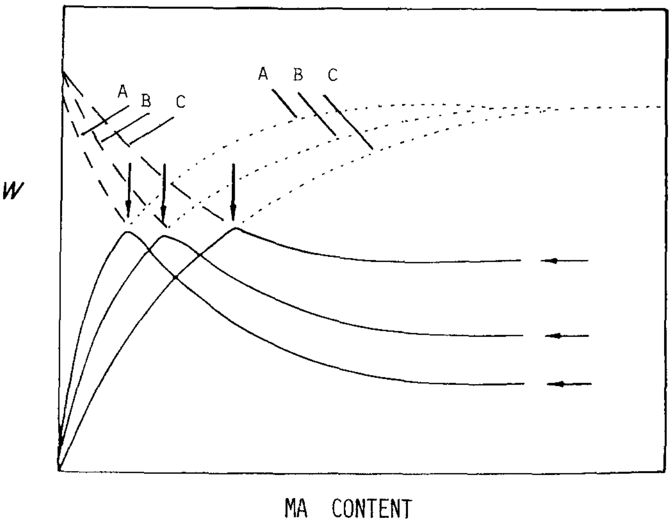


Figure 12 Schematic representation of peel energy, *W*, plotted against maleic anhydride content of copolymers of different grafting ratios.

It must be mentioned that this dual mechanism implies that the locus of failure should be at the interface for low MA content whereas it should be cohesive in the polymer for higher MA content. This was verified by examining the surface composition of the aluminium substrate after separation from the polymer using ESCA analysis. Samples of series B at MA dilutions of 500 p.p.m. (below the maximum of adhesion) and 2500 p.p.m. (above the maximum) were chosen.

On aluminium having been in contact with the 500 p.p.m. polymer, ESCA peaks identical to those observed on the virgin substrate are seen, i.e. peaks corresponding to Al_{2s}, Al_{2p} and O_{1s}. However, with aluminium having been in contact with the 2500 p.p.m. polymer, these peaks have totally disappeared leaving only the C_{1s} peak characteristic of the polymer. It can be concluded that, in the first case, the failure is purely interfacial and in the second case, a polymer layer is left on the surface as a result of the cohesive failure and totally conceals the surface of aluminium. This experiment constitutes further evidence for the validity of the proposed mechanism of the adhesion of polyolefins modified by the incorporation of small quantities of the same grafted polymer.

5. Conclusion

It has been shown that the addition of small quantities of a maleic anhydride grafted polypropylene to the same non-grafted polymer could constitute an interesting way for the improvement of the adhesion of polyolefins to polar substrates such as aluminium.

Before contact with aluminium, the polymer mixtures, independent of the grafting ratio and the dilution in the non-grafted matrix, exhibit zero surface polarity. During the bonding procedure when in contact with the orienting medium, i.e. aluminium, the low molecular weight chains carrying the maleic anhydride grafts will migrate and orientate at the interface. After orientation, chemical bonds are formed by the reaction of the grafted carboxylic groups with the hydroxyl groups of the metal surface. Secondly, this migration leads to an enrichment of the interfacial zone in low molecular weight chains thus creating a boundary layer of low cohesive strength. The cohesion of this interphase is inferior to the interfacial adhesion and the failure will therefore propagate cohesively within this weak boundary layer. This mechanism leads to an energy of separation of the polymer–aluminium assembly which first increases and then decreases with increasing maleic anhydride content.

On a practical level this study also constitutes a good base for the selection of optimum grafting ratios and composition of the polymer mixtures in order to obtain improved adhesion behaviour of polypropylene.

During this work, two important phenomena were clearly illustrated:

(i) orientation of macromolecules at the interface which led us to propose the concept of "potential surface energy" of polymers;

(ii) interphase formation which creates near the interface a polymer layer presenting properties different from those of the bulk polymer.

We believe that in most adhesion problems we are faced with these two important phenomena of restructuring of the polymer surface and interphase formation. The challenge is to gain a better understanding of the fundamental mechanisms in order to be able to predict and master these phenomena.

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