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Principles of the Adhesion of High Polymers

Part 2 *The Bonding of Polyolefins*

D. M. BREWIS*
Imperial Chemical Industries Ltd, Petrochemical and Polymer Laboratory, The Heath, Runcorn, Cheshire, UK

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Data are presented relating to the surface treatment of various polyolefins with chromic acid, organic peroxides, and γ-radiation. The mechanisms of these surface treatments are discussed, in particular the relative importance of oxidation and crosslinking reactions. Adding a region of low strength to an oxidised polyethylene surface had little effect on the resultant bond strength.

1. Introduction

The adhesion problems associated with polyethylene and polypropylene are well known, being manifested in printing, coating, and bonding operations. In order to achieve a high bond strength with these polymers, it is generally necessary to pre-treat the polyolefin surfaces, unless a hot melt adhesive or a heat sealing technique is used. Also, to be able to print satisfactorily on polyolefins, it is generally necessary to pre-treat the surfaces. There are numerous surface treatments available including: corona discharge treatment [1, 2], chromic acid treatment [3, 4], treatment with chlorine gas [5], treatment with halogen hydra-acids [6], flame treatment [7], plasma jet treatment [8], and solvent treatments [9].

The treatment used for a particular application will depend on a number of factors, in particular cost, efficiency, and safety.

In the case of films, direct heat sealing is often employed, except with oriented films, and therefore printability rather than bondability is the more important feature. The most commonly used treatment for films is the corona discharge method. Where thick sections of polymer are involved, e.g. bottles, treatment with a flame [10] or chromic acid is generally more suitable.

It has generally been assumed that the success of many of these treatments is due to the fact that they increase the polarity of the surface and thereby increase the "wettability". There is in fact much direct and indirect evidence to show that many of these pre-treatments introduce polar groups into the polyolefin surface [11-13]. However, there has, for some time, been good evidence to suggest that regions of low molecular weight exist on the surfaces of at least some grades of polyethylene [14], and any discussion on the mechanism of these treatments must consider this potential weak boundary layer. Recent work by Hansen and Schonhorn [15] indicates that the importance of surface energy has been overestimated. By bombarding polyethylene and certain other polymers with inert gas ions, they obtained very large increases in bond strength, apparently without increasing the polarity of the polymer; they conclude that the weak boundary layers are crosslinked to the long polymer chains.

Although crosslinking and moderate oxidation should generally facilitate bonding operations, crosslinking will have an adverse effect on heat sealing operations involving uncoated substrates. The efficiency of heat sealing depends on the mobility of the polymer chains, on or near the surface, and this will clearly be reduced by crosslinking [2, 16]. Excessive oxidation can also lead to lower bond strengths [7], presumably due to the formation of regions of low strength.

New data are presented in this paper relating to the treatment of polyolefins with organic peroxides, chromic acid, and γ-radiation, and the mechanisms of these treatments are discussed.

*Current address: Rugby College of Engineering Technology, Warwickshire, UK

This work includes a study of the effect of adding a "weak boundary layer" to a chromic acid treated polyethylene.

2. Experimental

2.1. Materials Used

"Araldite" AV100 is an epoxy resin made by Ciba (ARL) Ltd.* "Araldite" HV100 is the appropriate curing agent which is used in the ratio of 1:1.

"Rigidex" 50 is a high density (0.960) polyethylene, marketed by British Resin Products Ltd,† and has a melt flow index of 5.0.

"Alkathene" WJG 11 is a low density (0.918) polyethylene with a melt flow index of 2. "Propathene" HWM 25 is a polypropylene with a melt flow index of 3.0. The latter two materials are products of Imperial Chemical Industries Ltd.

Lauryl and dicumyl peroxides were obtained from Novadel Ltd,‡ as "Laurydol" and "Perkadox B" respectively.

2.2. Pre-Treatments

The formulation in ASTM Designation D2093-62T was used for the chromic acid treatment. The polyolefin films were immersed in the chromic acid at room temperature for 1 h. They were then washed thoroughly with distilled water, and dried under vacuum for 30 min at 60° C. The films were then bonded as described below.

The treatments with the organic peroxides involved immersing the polyolefin films in a solution of the peroxide for 5 sec, removing the polyolefins and then heating the films in an oven for the appropriate time.

The polyolefins were irradiated using a Cobalt-60 source. The total doses used are given in tables I and II.

2.3. Bond Strength Determinations

Laminates similar to those described by Sharpe and Schonhorn [17] were used, except that double lap joints were formed. Films (0.006 in.; 1 in. = 2.5 cm) of the polyolefins were used, and these were bonded to aluminium strips with "Araldite" AV100, a glue-line thickness of 0.005 in. being maintained by means of wire spacers. The adhesive was cured with "Araldite" HV100 (ratio 1:1) in an oven at 60° C for 3 h under a pressure of 0.5 kg/cm^2. The joints were removed from the oven and their bond strengths were determined 1 h later, using a Hounsfield Tensometer (type W) at a withdrawal rate of 0.25 in. per min. The results quoted in tables I to V are the mean of at least ten determinations.

2.4. Contact Angle Measurements

These were determined using a telescope goniometer [18] with a linear magnification of about 25. The polymer films were clamped to a metal plate which could be rotated, and which was contained in an air-cell to prevent atmospheric contamination.

3. Discussion

One of the objects of this work was to attempt to crosslink the region of low molecular weight that apparently exists on polyolefin surfaces [15], by means of organic peroxides, and by γ-radiation. The results in tables I and III show that treat-

TABLE I The effect of treating polyolefins with γ-radiation in air.

Polymer	Conditions of treatment	Lap shear strength* (kg/cm^2)	θ_{adv}
"Alkathene" WJG 11	—	11.0	99
"	5 Mrad	68.3	99
"	10 Mrad	93.7	98
"Rigidex" 50	—	18.3	99
"	5 Mrad	76.1	—
"	10 Mrad	112.0	97
"Propathene" HWM 25	—	14.1	100
"	5 Mrad	29.2	—
"	10 Mrad	34.5	—

*For comparison, the average shear strength of a lap joint formed by melting paraffin wax between two strips of aluminium was 11 kg/cm^2.

TABLE II The effect of treating polyolefins with γ-radiation in a nitrogen atmosphere.

Polymer	Conditions of treatment	Lap shear strength (kg/cm^2)	θ_{adv}
"Rigidex" 50	—	18.3	98
"	9 Mrad	22.5	100
"Propathene" HWM 25	—	14.1	100
"	9 Mrad	14.1	99

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*Address: Duxford, Cambridge, U K
†Address: Devonshire House, Piccadilly, London W1 U K
‡Address: St Ann's Crescent, London SW18, U K

TABLE III The effect of treating "Rigidex" 50 with organic peroxides.

Peroxide	Conditions of treatment	Lap shear strength (kg/cm^2)	θ_{adv}
—	—	18.3	99
—	Heated at 120° C for 24 h in air	21.5	98
—	Immersed for 5 sec in methylene chloride, then dried at 60° C for 20 min	17.3	97
—	Immersed for 5 sec in methylene chloride, then heated at 120° C for 24 h in air	27.4	—
—	As above, but heated under nitrogen	25.6	—
Dicumyl peroxide	5% solution in methylene choride, then heated at 120° C for 24 h in air	95.8	97
,, ,,	As above, but heated under nitrogen	33.8	—
Lauryl peroxide	5% solution in methylene chloride, then heated at 120° C for 24 h in air	65.2	97
,, ,,	As above, but heated under nitrogen	37.4	—
,, ,,	20% solution in methylene chloride, then heated at 120° C for 24 h in air	57.1	—
,, ,,	5% solution in methylene chloride, then heated at 90° C for 16 h in air	14.8	—

ment in air of "Rigidex" 50 with dicumyl or lauryl peroxides, or with γ-radiation, leads to a substantial increase in bond strength. However, if the treatments are carried out under nitrogen, a much smaller increase in bond strength is obtained (tables II and III). This indicates that the increase in bond strength is due largely to oxidation, although there is a surprisingly small decrease in the contact angle between the polyethylene and water. Further, when the treatment with lauryl peroxide was carried out at 90° C for 16 h (table III), no increase in bond strength was obtained despite the fact that the decomposition of the peroxide would be virtually complete ($t_{\frac{1}{2}}$ at 85° C $\simeq$ 30 min). However, increasing the temperature of treatment to 120° C resulted in a large increase in bond strength.

Results in table IV show the effect of treating various polyolefins with chromic acid. As has been shown by other workers [11-13], and as would be expected, treatment with chromic acid results in a considerable increase in polarity. However, the relatively high results obtained with chromic acid in the present work are not necessarily due to improved "wetting", although if other factors are equal improved "wetting" should result in higher bond strengths [19]. The higher bond strengths may be due merely to the fact that no serious attempt was made to optimise the treatments with γ-radiation, or with the organic peroxides.

Of more importance from the mechanistic viewpoint are the results in table V, which show the effect of deliberately placing a region of low strength on the surface of a chromic acid treated polyethylene. Despite the fact that the thickness of this layer is probably thicker (average thickness 2×10^4 Å) than a normal weak boundary layer, relatively high bond strengths are still obtained, although some reduction in bond strength does occur. This indicates that the interaction between the epoxy resin and the polar

TABLE IV The effect of treating polyolefins with chromic acid.

Polymer	Conditions of treatment	Lap shear strength (kg/cm^2)	θ_{adv}
"Alkathene" WJG 11	—	11.0	99
,, ,,	Treated as recommended in [3]. Then dried at 60° C for 1 h under vacuum	140.9	72
,, ,,	As above, but bonded after 7 days	145.1	—
"Rigidex" 50	—	18.3	98
,, ,,	Treated as recommended in [3]. Then dried at 60° C for 1 h under vacuum	176.1	75
,, ,,	As above, but bonded after 7 days	167.7	—
"Propathene" HWM 25	—	14.1	100
,, ,,	Treated as recommended in [3]. Then dried at 60° C for 1 h under vacuum	236.1	—

TABLE V The effect of adding petroleum jelly to chromic acid treated "Rigidex" 50.

Conditions of treatment	Lap shear strength (kg/cm^2)	θ_{adv}
—	18.3	98
Treatment as recommended in [3], then dried at 60° C for 1 h under vacuum	176.1	75
As above, then a layer of petroleum jelly ($\simeq 2 \times 10^4$ Å) was spread on to the polymer	126.8	96

groups on the polyethylene surface is sufficiently large to displace much of the weak boundary layer; the decrease in bond strength may be due to a reduction in the strength of the epoxy resin. Therefore it is not necessarily true that surface oxidation treatments remove the low molecular weight material from a polymer surface, as suggested by Hansen and Schonhorn [15]; in the treatment with peroxides described above, it is probable that regions of low strength remain on the polymer surfaces after the treatment.

It is clear that the bonding of polyolefins is highly complex and certain factors remain obscure; in particular the relative importance of oxidation and crosslinking reactions during certain surface treatments is still uncertain. It should also be remembered that in addition to forming good contact with the substrate, a suitable adhesive must have tensile properties appropriate to the service conditions of the adhesive joint. For example, when the substrates are in the form of a film, the flexibility of the adhesive is important [19]. Thus, although the epoxy resin used in the present work gives high bond strengths in shear with the treated polyolefins, the bond strengths of unsupported films would be low because peeling forces would then be important.

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