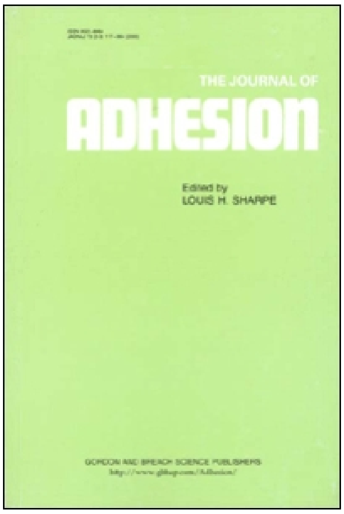

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The Corona-Induced Autohesion of Polyethylene: The Effect of Sample Density

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With increase in sample density, corona treatment was found to be decreasingly effective in enhancing the autohesion of polyethylene sheets. The effect of higher density could be offset in part by an increase in temperature of lamination. This parallel behaviour suggests that similar molecular mechanisms govern the phenomena of thermally-induced and corona-induced autohesion.

INTRODUCTION

Treatment with an electrical discharge is known to be an effective method for enhancing the autohesion of low density polyethylene.[1-3] A question of some interest is whether the increase in bonding is affected by the bulk density and thus the crystallinity of the polymer. The present investigation into dependence of corona-enhanced autohesion on polymer density was therefore undertaken in order to elucidate this question and thereby to gain a further understanding of the mechanism of the process.

CHARACTERIZATION OF POLYETHYLENE SAMPLES

Sample preparation

Test specimens were prepared by compression molding against a glass plate at 155°C, followed by cooling in the press. The sheets had a thickness of 0.75 mm and only scratch-free areas were used. The characterization of polyethylene resins used is summarized in Table I.

TABLE I

Characterization of polyethylene resins

Specimen	Designation/ manufacturer	Density (g/cm^3)	Melt index	Melting point (°C)	Estimate of crystallinity (X_v) %
A	220G C.I.L.	0.919	1.9	106	44
B	DHDY-5876 Union Carbide	0.928	2.5	113	50
C	DHDB-4700 Union Carbide	0.935	1.8	119	54
D	Sclaire 29B DuPont	0.948	5.0	134	64

Density

Densities were determined on the molded polymer sheets by the pyknometric method at 20°C using water as an immersion liquid.

Melt index

The values of melt index given in Table I were supplied by the manufacturer.

Melting temperature

A Perkin-Elmer Differential Scanning Calorimeter (DSC) was used to determine the melting temperatures of the specimens. The melting points were identified with the peaks on respective thermograms. The scanning speed was 10°C/min and the instrument was calibrated with benzoic acid as a calorimetric standard.

Crystallinity

The crystallinity of the specimens was calculated from the equation

$$X_v = 100\,(6.944\rho - 5.944) \qquad (1)$$

where X_v is the crystallinity in % by volume and ρ is the density. Equation (1) was derived from the nomogram given in Ref. 4 for which the densities of crystalline and amorphous domains were taken as being 1.00 g/cm^3 and 0.856 g/cm^3 respectively.

ADHESIVE BEHAVIOUR

Corona treatment was carried out in a flat plate cell enclosed in a glass vessel. The oxygen gas used was stated to have a purity of 99.6%. Before admission of the gas, the cell was evacuated to a pressure of one Pa (10^{-2} torr.). The gas was demoisturized by passage through a liquid nitrogen trap, prior to entering the cell and the flow rate was maintained at 50 ml/min at atmospheric pressure.

The discharge was generated by a 19 kV, 45 Hz square wave potential produced by a d.c. power supply in conjunction with a mechanical chopper. A time of treatment of 4 seconds was used throughout. The adhesive joints were made by 5 mm overlap of 20 × 5 mm strips cut out from the polyethylene sheet to give a bonded area of 5 × 5 mm. The lap joints were then pressed together at the required temperature for 3 minutes under a load of 7 kg/cm^2. The bonded specimens were then broken in tension. Further details of the application of the corona treatment and the procedures used in testing are given elsewhere.[5]

TABLE II

Effect of temperature of lamination and sample density upon the autohesion of untreated and corona-treated polyethylene

Temperature of Lamination →		Bond strength (kg/cm^2) 16°C		36°C		55°C	
Sample	(g/cm^3)	Untreated	Treated	Untreated	Treated	Untreated	Treated
A	0.919	0.3	12	0.8	>20	2.0	>20
B	0.928	0	1.5	0.5	7.7	0.9	>20
C	0.935	0	0	0.3	1.3	0.7	3.7
D	0.948	0	0	0	0	0	1.8

Table II summarizes the results of bonding experiments on untreated and treated samples. It is apparent that the most pronounced enhancement of bonding is observed with the specimens of lowest density. With sample A, corona-induced autohesion was so strong at a laminating temperature of 36°C that the strip broke instead of the bond. At 55°C, this type of failure was observed for both A and B. However, as the polymer density increased the effect of treatment diminished for any given temperature of lamination.

As shown in Table I, the melting temperature of the polyethylene resins increases with increase in density. Thus it may be argued that part of the higher corona-induced bonding in the low density specimens was due not to the intrinsic effect of the corona discharge but rather to the greater thermoplastic conformability of low density material compared with high

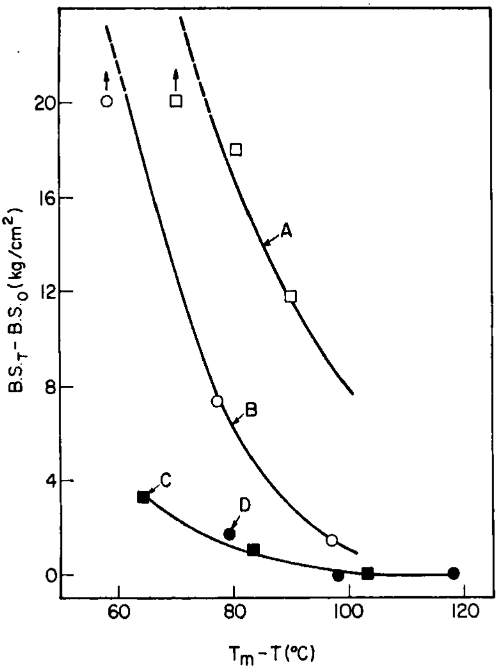

FIGURE 1 The effect of temperature of lamination (expressed as a difference between melting temperature and laminating temperature, $T_m - T$) on the enhancement of bonding due to corona treatment. For sample A, a point corresponding to a lamination temperature of 25°C is included.

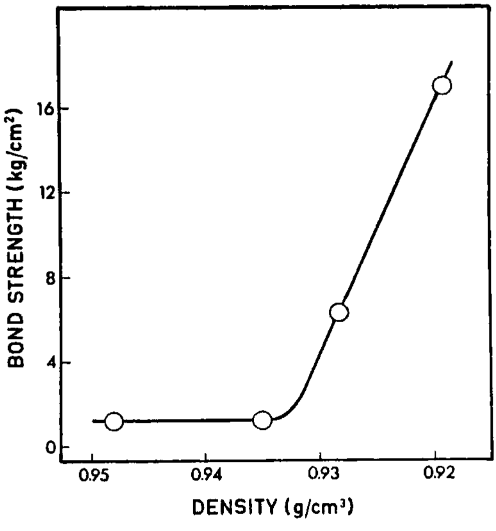

FIGURE 2 The effect of the density upon the corona-induced autohesion of polyethylene.

density material at any particular temperature. As an approximate compensation for the thermoplastic effect, the corona-induced enhancement of autohesion was compared for the different samples, not at the same temperature, but at equal decrements below the melting temperature. The additional bond strength produced (i.e., the difference between the bond strengths of a treated sample and an untreated sample ($B.S._t - B.S._o$)) was plotted against the difference between the melting and laminating temperature ($T_m - T$). As shown in Figure 1, the results indicate that the corona-induced bonding thus normalized is much stronger for samples in the low density range.

The dependence of the corona-enhanced bonding upon sample density is illustrated in Figure 2 for values of $(T_m - T) = 80°$. It is interesting to note that the relationship between the density and autohesion is strongly nonlinear. It appears that the effect is very small until the density decreases to 0.93 g/cm^3. At densities below this value, the corona-induced bonding increases rapidly with further decrease in density.

THE EFFECT OF TRANSCRYSTALLIZATION

A useful confirmation of the trend shown in Figure 2 could be obtained if the density near the surface of a sample could be altered without changing the chemical characteristics of the polymer. Polymers which are nucleated and crystallized against high-energy surfaces such as gold or aluminium, have

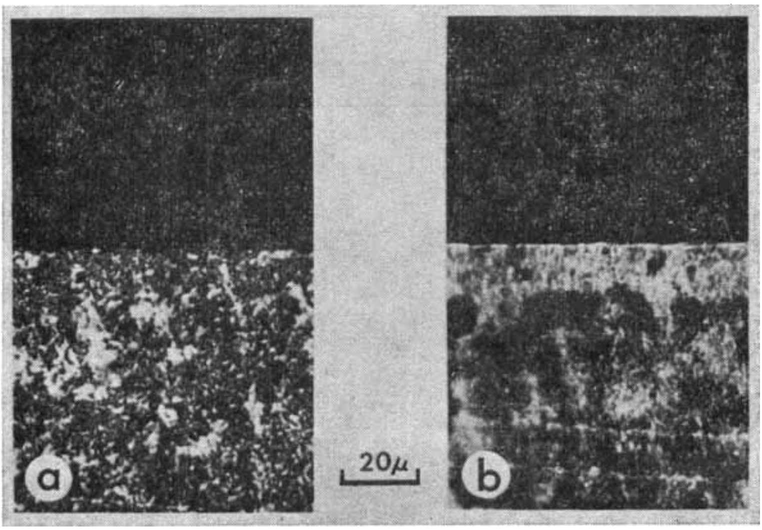

FIGURE 3 Surface morphology of polyethylene (sample D) produced by crystallization of the resin adjacent to (a) glass surface, (b) gold surface.

high surface densities compared to densities generated by solidification against low energy media such as air, glass or other polymers.[6,7] By exploitation of such transcrystallization phenomena, the surface of a medium density polyethylene sheet was modified and then examined for response to corona treatment.

In Figure 3, micrographs of the transverse sections of the polymer sheet crystallized against a glass surface and a freshly vacuum-deposited gold surface are illustrated. No morphological changes between the bulk and surface region are observed on the surface solidified against the glass. However, there is clear visual indication of a transcrystalline region on the surface made facing the gold.

The data on adhesion tests are shown in Table III. A substantial reduction of bonding results both for the untreated and corona-treated sheets when the surface is modified by transcrystallization against a freshly deposited gold surface. Since the density of the transcrystalline layer is almost certainly higher than that of the bulk polymer, this result is in agreement with the trends shown in Figure 2.

TABLE III

Effect of surface preparation upon the autohesion of untreated and corona-treated polyethylene†

Surface preparation	Bond strength (kg/cm^2) Untreated	 Treated
"Glass Nucleated"	1.9	15.5
"Gold Nucleated"	1.5	7.1

† Sample D, temperature of lamination 98°C.

DISCUSSION

According to the widely accepted diffusion theory of autohesion,[8] an increase in temperature improves the viscoelastic behaviour and diffusion properties of the materials being bonded together thus facilitating "sewing" together of the two polymer surfaces placed in contact. The microbrownian motion that is essential for macromolecular diffusion to take place can be exhibited only by polymer chains in the non-glassy state, i.e. in case of a semi-crystalline polymer by chains in the amorphous regions above T_g. The presence of an extensive supramolecular structure due either to crystallinity or to a cross-linked network restricts the interpenetration of the polymer chains across the interface and thereby causes the bonding properties to deteriorate. This has been demonstrated clearly by a progressively detrimental effect of radiation crosslinking upon weldability of polyethylene.[9] A similar effect was produced by vulcanization of rubber.[8]

The results of the present work show that the effects of polymer density on corona-induced autohesion and on thermally-induced autohesion are analogous. In a previous paper[1] it was suggested that corona treatment produced a charged matrix on the surface which lowered the softening temperature and thereby enhanced the interdiffusion of the polymer chains when the surfaces were pressed together. The present work neither supports nor contradicts the concept of a charged layer being responsible for the behaviour observed. However, the results described do indicate that similar molecular mechanisms govern the phenomena of thermally-induced and corona-induced autohesion.

In a recent paper, Owens[2] noted that corona-induced autohesion of polyethylene was destroyed by the application of hydrogen-bonding liquids to the adhesive joint. He proposed that the corona-induced bond is a hydrogen bond between the enolic hydrogen of an enolized keto group and a carbonyl group on the adjacent sheet. Owens suggested that enolized ketones are formed at the sites of chain branching. High density polyethylene has fewer branches than low density polyethylene. Thus fewer hydrogen bonds would be formed when high density polyethylene was treated and laminated. The results given in Table II are in agreement with this concept. However, the decrease in corona-induced autohesion upon transcrystallization cannot be explained by this mechanism since presumably the degree of crosslinking in the sample remains unchanged by the transcrystallization phenomenon.

It is important to note, however, that if, as Owens claims, hydrogen bonding is the dominant mechanism, chain mobility must play an important role in facilitating the close molecular approach necessary for hydrogen bonding to be effective. It would be expected that such chain mobility would be more prevalent in the low density samples. However, previous investigations[1,3] have cast some doubt on the importance of oxidation in the corona-induced autohesion of polyethylene. More definitive characterization of the corona-treated surfaces by means of techniques such as ESCA would help to elucidate the mechanism of bonding.

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