Corona-discharge Treatment of Polypropylene films-Effects of Process Parameters

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Corona-discharge Treatment of Polypropylene films—Effects of Process Parameters

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Corona treatment of films, mainly polypropylene (PP)-copolymers, was studied at commercial levels in a 2.7 kVA treater. The films were produced on a flat-film extruder with chill rolls. Degree of treatment was characterized by power of the generator divided by web speed and width of film (m Ws/cm²).

The effectiveness of the treatment was measured in terms of the polar and dispersion components of surface-energy, the peel adhesion of pressure sensitive tape (similar to ASTM Adhesion Ratio) and the peel adhesion of polyurethane adhesives.

The polar component of surface energy is a measure of the effectiveness of corona pretreatment.

For a given degree of treatment, the polar surface energy component becomes greater as the film cooling rate increases (and the degree of crystallization falls).

A comparison of homopolymers and copolymers does, however, reveal that even where these have the same density or the same degree of crystallization one cannot count on them having equally-sized polar components.

Peel strengths of pressure-sensitive tapes and polyurethane-bonded patches confirm the influence of cooling conditions on wetting properties.

Contrary to the case for tape adhesion, the polyurethane adhesive strengths reach their maximum value at much lower treatment intensities, i.e. with much lower polar surface energy components, and thus question the validity of the ASTM tests for adhesion properties.

1. INTRODUCTION

Corona-discharge treatment is a proven method used to activate polyolefin surfaces. In spite of the wide use, there remain certain imponderables with regard to the measurement of the effectiveness of this treatment—in some

cases, the continuous measurement. These arise on the one hand from the fact that the physical chemical mechanisms operative during the treatment are too little known, and on the other that the process parameters vary in their individual effects on the effectiveness of the treatment.[1-5]

2. EXPERIMENTS

Test set-up

Figure 1 shows the layout of the extrusion and pretreatment plant. Apart from a few exceptions, an "in-line" operation was used, under suitable practical conditions.
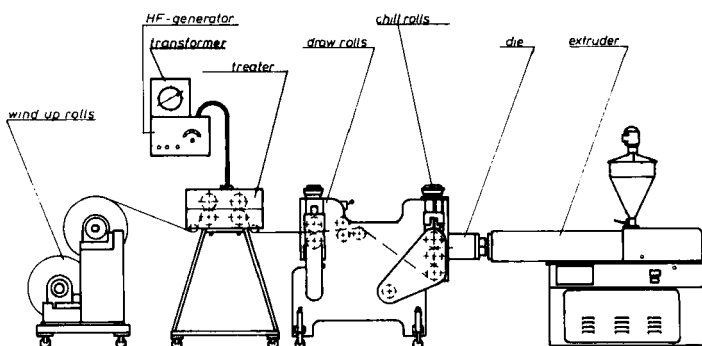

FIGURE 1   Layout diagram of in-line extrusion and treating equipment.

A "45 mm screw" extruder was used and with the aid of the heat expansion bars for slit width adjustment on the slot die, the roller tape-up and the rotational velocity PP film, approximately 100 μm thick, were produced at different extrusion velocities. Film width was approximately 75 cm. The film was cooled over three cooling rollers at temperatures varied between 10° and 110°C. Then before being wound up the film was passed through the treatment unit, which had a 2.7 kVA power input and a frequency range of 20 to 40 kHz. In all the tests the gap between the rotating star-shaped profile electrode and the earthed carrier roller with its dielectric silicone rubber coating was 1.3 mm. Power output was infinitely variable and controlled via a transformer.

The corona pretreatment intensity, J, was defined as the power, W, on the primary side of the transformer, expressed in terms of the film thickness, b, and the film velocity, v ($J = W/b \cdot v$). It was thus possible to set comparable intensities with higher or lower film velocities. The power could not be

adjusted to below 100 W, however, since this gave too irregular a discharge on the surface of the PP.

So as to achieve a larger cooling temperature range, freshly extruded pieces of film were melted down again and cooled at higher and lower temperatures. Figure 2 shows the basic method used here. To avoid any
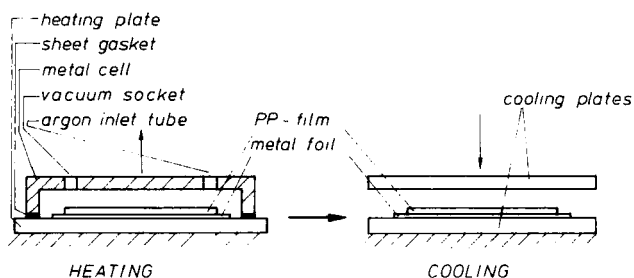
FIGURE 2   Heating and cooling device.

oxidation of the PP the heat cell was evacuated several times and filled with argon. After the PP had been melted (12 minutes at 240°C) it was cooled, together with the aluminium foil, for up to 5 minutes between two chromium-plated steel plates. The temperature of the cooling plates was controlled with liquid nitrogen or oil at 10° and 160°C. Pieces of film, 4×4 cm, were then bonded over similarly sized cutouts in a PP film and sent through the corona treatment unit at different treatment intensities.

Material

The majority of tests were carried out using an ICI random copolymer (Type PXC 2907). For comparison purposes a CWH lubricant-free homopolymer (Type 5200) was also taken for a number of tests. A Henkel polyurethane laminating adhesive (40 parts Liofol UK 3640, 1 part setting agent UK 6000) was used to bond the PP film and this was applied with a blade. Its definitive adhesive strength was achieved after 5 days at room temperature.

Physical Tests

The following tests were carried out so that the change in PP physical properties brought about by the corona pretreatment and the extrusion conditions could be characterized:

—measurement of surface energy

—peel strength of pressure-sensitive tapes and polyurethane bonds

—density determination

—DSC analysis

—microscopic structural investigations.

Details of the chemical analyses that were also carried out in this context (IR spectroscopy, GPC analyses and SIMS measurements) are given elsewhere.[6]

Surface energy

This work involved contact angle measurements which were taken using the "sessile drop" method. Table I lists the fluids with their polar and dispersion

TABLE I   Liquids and equation of state.

	σ_i	σ_i^p	σ_i^d
dest water	72,8	50,7	22,1
glycerin	65,2	36,9	28,3
formamide	59,0	19,6	39,4
methylene iodide	50,8	6,7	44,1
ASTM 40	40	8,2	$31,8 \frac{mN}{m}$

$$\sigma_{s,i} = \sigma_s + \sigma_i - 2\sqrt{\sigma_s^d \sigma_i^d} - 2\sqrt{\sigma_s^p \sigma_i^p}$$

$$+$$

$$\sigma_{s,i} = \sigma_s - \sigma_i \cos \vartheta$$

$$\downarrow$$

$$\frac{1+\cos \vartheta}{2} \frac{\sigma_i}{\sqrt{\sigma_i^d}} = \sqrt{\sigma_s^d} + \sqrt{\sigma_s^p}\sqrt{\frac{\sigma_i^p}{\sigma_i^d}}$$

$$\pi_1 = \sqrt{\sigma_s^d} + \sqrt{\sigma_s^p} \; \pi_2$$

surface energy components. These components were established through contact angle measurements on PTFE. The equation of the geometric mean was then used in mathematical calculation. The PP surface energy components were determined by the graphic method (as shown in Figure 3) and by calculation—again using the equation of the geometric mean.[7,8] In this figure the polar component is equal to the square of the gradient of the compensating lines and the dispersion surface energy component equal to the square of the ordinate value.

The critical tension of wetting according to Zisman was not always established because with such low corona treatment intensities the scatter of
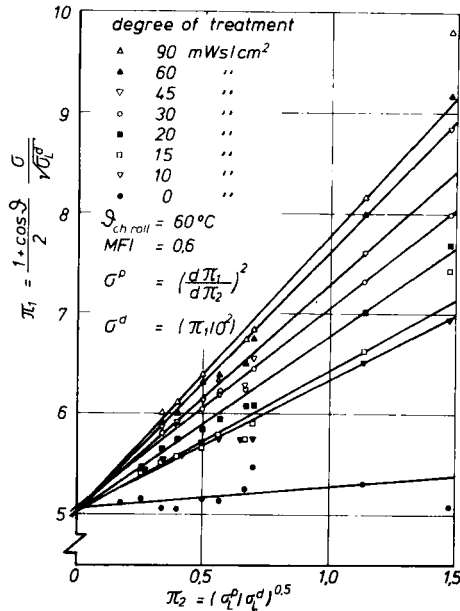
FIGURE 3   Graphical determination of σ^p and σ^d.

the extrapolated values was too great. Again, with the "wipe test" as per ASTM D 2567–67, the differentiation of measured values was not satisfactory.

Peel test

The amount of force required to peel pressure-sensitive adhesive tape from the film surface was established on the basis of ASTM Standard D 2141-63 T. The same test set-up was used to measure the peel strength of the PP films bonded with polyurethane adhesive.

3. RESULTS AND DISCUSSION

Wetting properties

As already mentioned, it was appropriate to relate treater power input to film width and velocity since all the physical and chemical processes to be carried out on the surface of the PP were to be expressed as a direct function of the energy applied per unit area.

Figure 4 now shows that the degree of treatment, defined in this same way, clearly determines the size of the polar energy component. It is quite
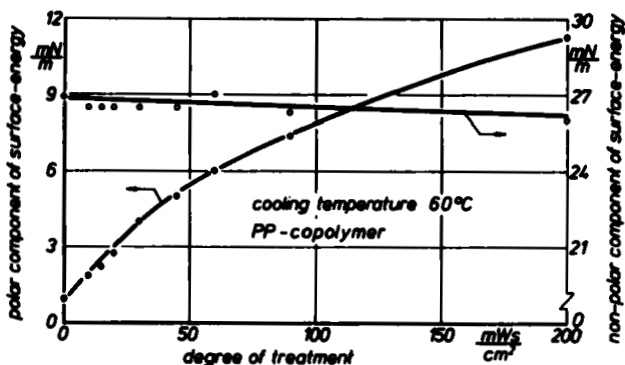
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FIGURE 4   Wetting result

evident that the increase in σ^p with increasing corona intensity obeys the law of an e-function.

This does not just apply for the 0–200 range covered here, but holds true right up to 10^5 mWs/cm². However, only the 0–100 range is of technical interest, extending up to 200 mWs/cm² in exceptional cases. The non-polar component of surface energy remains virtually constant. With higher degrees of treatment this can be seen even more clearly to fall slightly.

The increase in the critical surface tension of wetting also follows an exponential curve similar to that of σ^p, though reference has already been made to the extrapolation difficulties encountered here.

The strict dependence of the polar surface energy component on the degree of treatment prompted us to take σ^p as a measure for the effectiveness of corona pretreatment and to look into σ^p as a function of processing conditions.

Figure 5 gives σ^p as a function of roller temperature or cooling tempera-
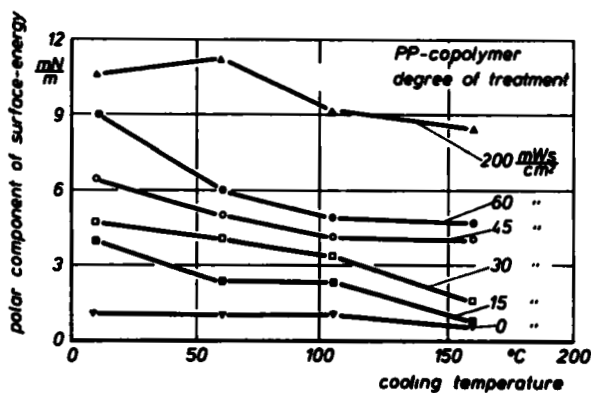

FIGURE 5   Surface-energy component vs cooling temperature

ture for different levels of treatment. The curve for cooling at the tempera-
ture of liquid nitrogen has not been plotted—this is because no significant
differences were found between σ^p values for $-190°C$ and the values for
room temperature.

It is, however, clear to see that σ^p falls as the cooling temperature increases.
This relationship becomes particularly evident at intensities below 100 m
Ws/cm^2. At intensities greater than 200 mWs/cm^2, not plotted here, there
is no longer any evidence that σ^p is still influenced by the cooling temperature.

On the basis of this figure the next step would now seem to be to correlate
the effectiveness of corona pretreatment with either crystallite size in the
PP, the degree of crystallization or simply with density, since the cooling
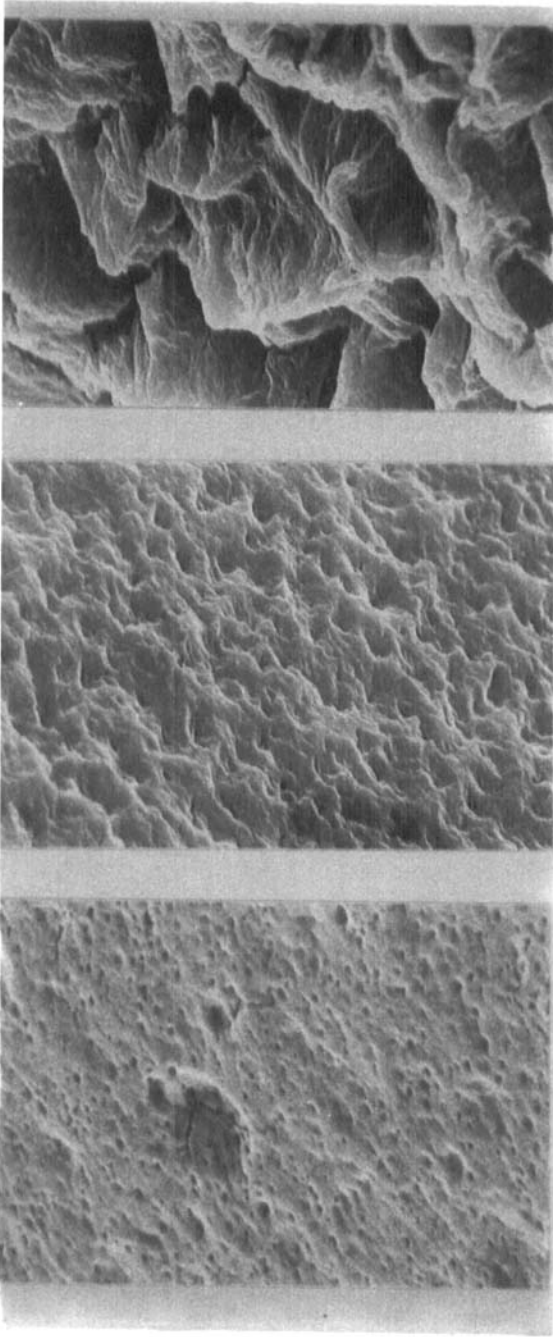rate has a marked influence on the crystalline structure of the PP.

Photographs taken on an optical microscope did not provide much in-
formation of the crystalline structure of the PP. The differences are brought
out more clearly on etched samples under a scanning electron microscope.
Figure 6 gives a comparison of PP film surfaces cooled at 10, 60 and 160°C.

It is clear to see that the film which is cooled quickly possesses a large
number of small crystalline zones whereas the film which cools more slowly
has a small number of larger crystalline zones. The PP copolymer does not,
however, crystallize in the form of α spherulites as are generally observed
in homopolymers (Figure 8). This non-uniform crystallization is due to the
irregular chemical composition of the random copolymer. Figure 6 gives
values for density and the degree of crystallization too. These provide
evidence of the fact that the low density PP can be pretreated more effectively
than the high density PP.

All the same, this statement is not very satisfactory—the reason for this
becomes evident in Figure 7. It shows a comparison between a homopolymer
and two copolymers of different molecular weights. It can be seen (even
though the relatively high degree of scatter in measurement results is
inevitable) that the PP homopolymer is more responsive to pretreatment
than are the two copolymers. The copolymers behave in virtually identical
manner, despite their marked difference in molecular weight, which is
indicated here by means of the melt flow index.

All the PP films were produced under identical cooling conditions,
namely with a cooling roller temperature of 60°C. Figure 8 gives an impression
of the crystalline structure of the homopolymer, indicating the corresponding
values for density and degree of crystallization. The different degrees of
pretreatment effectiveness achieved when pretreating homopolymers and
copolymers cannot be explained on the basis of density, since under cooling
conditions such as these the density of the homopolymer is even slightly
greater than that of the copolymer and its degree of crystallization is higher.

This means that the effectiveness of corona pretreatment will be all the

cooling – temperature	10°C	60°C	160°C
magnification	2000 x	2000 x	2000 x
crystallinity	30 %	32 %	45 %
density	0,886 g/cm³	0,897 g/cm³	0,905 g/cm³

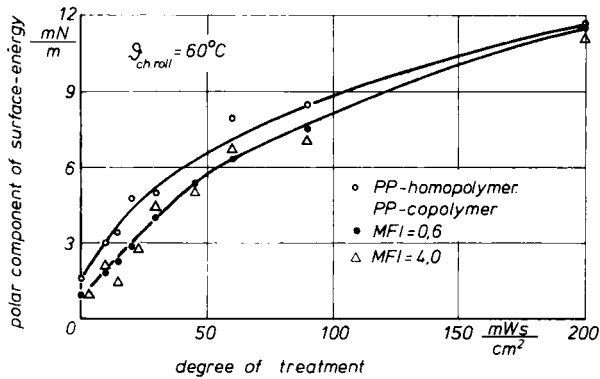FIGURE 6   Etched surfaces of PP-copolymers.

FIGURE 7 Polar surface-energy components of PP-homopolymer and PP-copolymers.

greater the lower the density of the PP; this, however, only applies for one type of PP under different cooling conditions. A comparison of different types of PP, on the other hand, shows that despite the PP types having the same or similar density, there can be marked divergences in the effectiveness of the corona pretreatment. The reason for this then lies in the different type of crystallization and the resultant crystalline structures.

Adhesion properties

The peel test with pressure-sensitive tape served to confirm the wetting measurements, despite the relatively high scatter. Figure 9 shows that for the same level of pretreatment, low density films have higher peel strengths than film which has been cooled slowly and hence has a higher density. At intensities above $100 \, mWs/cm^2$ there is virtually no further change in peel strength.

The patches of film applied with polyurethane adhesive and put into normal technical use were, however, of greater interest than the peel strength with pressure-sensitive tape, as indeed was the question as to how far these peel strengths are influenced by cooling conditions.

The results are presented in Figure 10 with the peel strength plotted against the degree of treatment. For the sake of clarity, measured values are given only for the films with the highest and lowest cooling rates. Here again, it is evident that the less crystalline film obviously responds better to pretreatment than does the high-crystalline film. It achieves higher peel strengths even at low-level treatment intensities. All the same, it is entering the region where cohesion falls below the adhesion between PP and poly-urethane. The high-crystalline film has a strength at break which is greater

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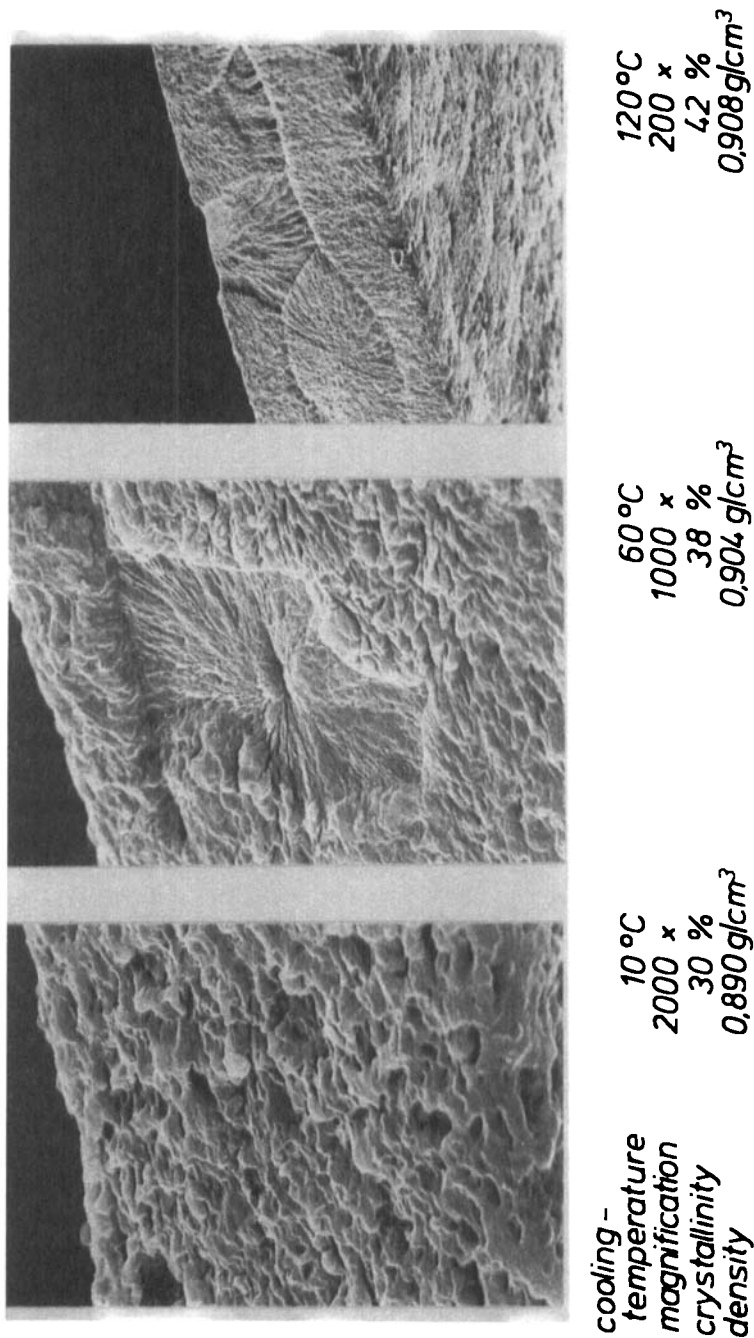|		
cooling–		
temperature	10 °C	60 °C	120 °C
magnification	2000 ×	1000 ×	200 ×
crystallinity	30 %	38 %	42 %
density	0,890 g/cm³	0,904 g/cm³	0,908 g/cm³

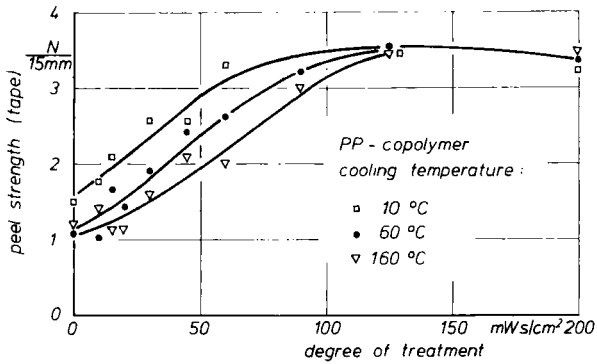FIGURE 8 Etched surfaces of PP-homopolymer.

FIGURE 9   Influence of cooling temperature on tape adhesion.

by a factor of 2 than that of the amorphous film and in this respect it also gives higher peel strength measurements.

If we now express peel strength in terms of the strength at break of the film and plot these values against the polar surface energy component (Figure 11) a certain universality can be seen in the ratio of adhesion properties to surface energy.

Compared with the peel strengths as per the ASTM "Adhesion Ratio",
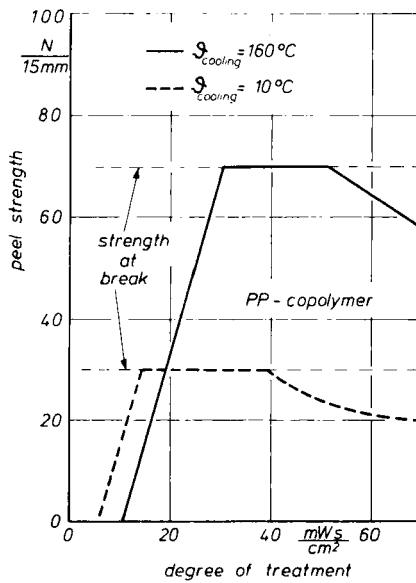

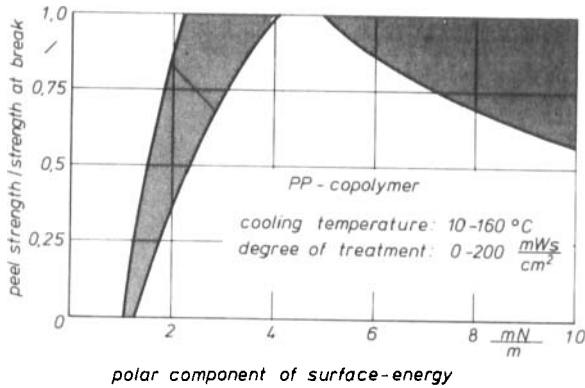FIGURE 10   Peel strength of polyurethane adhesive.

FIGURE 11   Peel strength results of polyurethane adhesive.

where a continuous increase is observed as the polar surface energy component increases, it is clear here that the adhesion properties reach their maximum value very rapidly, i.e. with a relatively low polar component, and then remain constant. Furthermore, the polyurethane-bonded patches clearly highlight the effect of overtreating film surfaces. Adhesion falls so sharply on account of surface degradation that in some cases it is well below film cohesion. This relationship applies both for the copolymers and the homopolymer.

4. CONCLUSION

This work shows that process parameters—e.g. cooling rate—influences the effectiveness of corona–discharge treatment. There should be made more investigations on process parameters such as stretching ratio, temperature of film during treatment and lubricant concentration of films.

References

1. J. F. Carley and P. T. Kitze, *Polymer Eng. and Sci.* **18,** 326 (1978).
2. J. F. Carley and P. T. Kitze, 37th Annual Tech. Conf., May 7–10 (1979), New Orleans, SPE Manual, pp. 728–733.
3. R. van der Linden, *Kunststoffe* **69,** 71 (1978).
4. W. Bartusch, *Verpackungs–Rundschau* **27,** 87 (1976).
5. J. M. Evans, *J. Adhesion* **5,** 9 (1973).
6. R. Krüger and H. Potente, *Adhäsion* **23,** 381 (1979).
7. W. Rabel, *farbe + lack* **77,** 997 (1971).
8. U. Zorll, *Gummi, Asbest, Kunststoffe* **30,** 634 (1977).