Influence of an Electric Field on Polar-Group Orientation and Adhesion at Poly(ethylene terephthalate) Surfaces

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SYNOPSIS

Application of a high continuous electrical field accelerates the orientation kinetics of polar groups at a polymer–water interface and so improves the surface polarity. This is preliminary to adhesion establishment on a polar substrate. Adhesion of PET and gelatin performed under an electric field leads to an increase of the interfacial adhesion properties, due to simultaneous effects of the electric field at the interface. Polar-group orientation at a polymer surface and electrical aspects of adhesion are therefore self-consistent.

INTRODUCTION

Numerous electrical treatments are commonly applied to poly(ethylene terephthalate) (PET) surfaces, such as an electrical discharge,[1,2] in order to modify their wettability. These treatments lead to the formation of chemical species: phenolic —OH, carboxylic acid, —COOH (Ref. 1), and carbonyl groups, =C=O (Ref. 2). Another way to improve wettability consists of the reorientation of polymer surfaces during contact with a polar medium, like water, especially.[3-6] All these modifications can increase adhesion by creation of polar sites, and this has been observed with PET films.[7] But these treatments can provoke chain scissions, which, in turn, lead to a weak cohesion boundary layer and then adhesion decreases.[1,8]

Recently, it has been shown that the main parameter for the thermodynamic orientation properties at the polymer interface is the dielectric constant of the polar liquid medium.[9] Electrostatic interactions between the dipoles of the polymer surface and of the liquid are involved in the orientation of the polar groups initially contained in the polymer and migrating to the interface. These phenomena are favorable to adhesion establishment on a polar substrate.[10]

A few published works and patents have dealt with the influence of an electric field on bonding[11-15] for polar polymers like poly(vinyl chloride) or epoxy on metallic substrates. Studies on the adhesion of allylic resins on dichromate-treated copper foils under an applied electric field[14] have shown that, owing to the orientation under the applied continuous voltage, the peel strength increases with the applied voltage. This is valid only when the allylic negative group is oriented to the electron positive side and reversely. A covalent bonding between the allyl group and the chromium on copper is responsible for the adhesive strength of the resin to a treated copper foil.

To achieve the orientation process at polymer–water interfaces, it seemed interesting to examine the influence of an electric field applied and to extrapolate the results to the adhesive properties of gelatin to PET, this being an interesting example in photographic film applications.

First, experiments of aging on water under the electric field are performed. Surface properties are examined by contact-angle measurements with the two-liquid-phase method,[16] which permits the determination of the dispersive component γ_S^D and polar component γ_S^P of surface energy, in water. The evolution of the polar component is a good estima-

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tion of the orientation of functional groups at the polymer interface. Usually, when the polymer is kept in contact with water, there is a continuous increase of polarity as a function of time of contact on water, at room temperature.[5] This increase leads to a higher surface energy and the polymer surface exhibits, then, the so-called potential surface energy property[5,10] that is correlated with the ability to adhere on a selected substrate.

EXPERIMENTAL

Materials

Poly(ethylene terephthalate) (PET) films of 100 μm thickness were used. They were obtained from Toray Co. in the form of flakes and transformed into thin sheets by extrusion and biaxial stretching at Fuji Photo Film Co. Thus, the film surface was in contact with the atmosphere. The molecular weight (Mw) is roughly 30,000 g/mol and the degree of crystallinity is about 50%.

The gelatin powder is in the form of 250–500 μm-diameter grains. Films of 10 μm thickness are obtained by coating from a hot diluted gelatin solution (pH 6,2) of low concentration (1–2%).

Surface-property Determination

Two methods are used: The contact angle of a drop of water of controlled pH is measured by the one-liquid method as in Ref. 7. The surface properties are determined by the classical two-liquid-phase contact-angle measurements.[16] The sample being immersed in water and the contact angle of different alkane drops (hexane to dodecane) are measured. This allows us, using a graphical method, to determine the dispersive component γ_S^D and the polar component γ_S^P of the surface energy of the film, knowing the surface properties of the alkanes and water.

These measurements were undertaken to estimate the surface-property evolution in function of previous contact time on water with or without an electric field applied. For gelatin, the reverse method is used, a drop of water being deposited on the gelatin surface immersed in various alkane environments.

Electric-field Application

Two different treatments are performed under the electric field: one on the PET film deposited on water in order to accelerate the orientation of polar groups; the other on the gelatin-coated PET film in order to improve the adhesion.

The experimental method applied to the PET film on water is shown on Figure 1. The film is deposited on water in a glass vessel between two electrodes connected to a high-voltage supplier (Keithley 247). The applied fields are of the order of 1–50 kV/m, applied through the water. One electrode is in contact with the glass vessel containing the water.

With the coated PET, the assembly is placed for 18 h in an electric field of a few kV/cm, between two electrodes with insulating spacers, until the thin layer of gelatin has dried out. The schematic figure of the experiment is shown in Figure 2. The electric field was applied immediately after coating with the gelatin solution. This type of apparatus was preferred to the dip coating of PET in the presence of an electric field, which is much more difficult to monitor.

Adhesion Measurements

The adhesion of the PET–gelatin assembly is characterized by a classical peel test at 180° on 60 mm-long samples. The separation energy is measured both in air and in a liquid medium, allowing an estimation of the chemical contribution to adhesion to be made.[17] Results are given with an accuracy of ± 0.2 J m^{-2}.

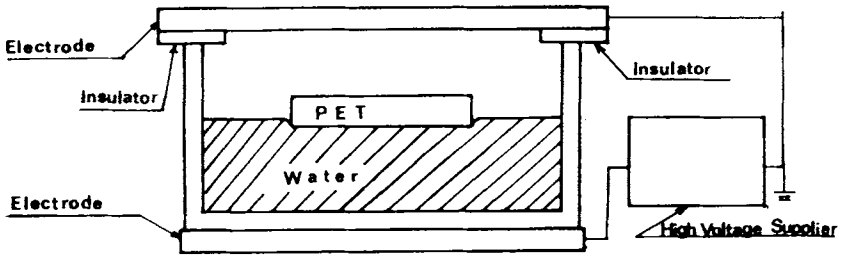

Figure 1 Schematic view of apparatus for PET orientation on water through an electric field.

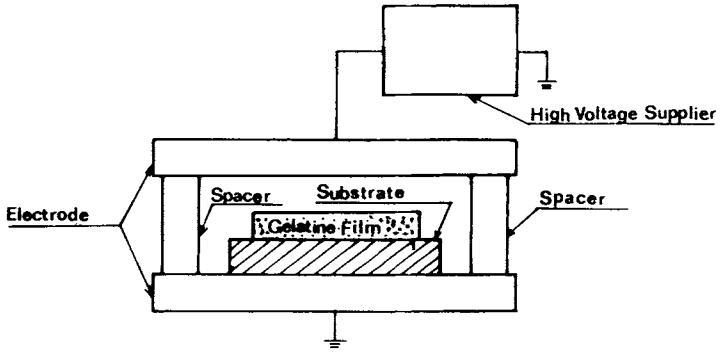

Figure 2 Schematic view of apparatus for application of an electrical field on gelatin–PET assembly.

RESULTS

PET Surface Properties on Water

Results of the contact angle of a drop of decane in water are compared as a function of contact time on water, at room temperature (Fig. 3). In Table I, taking into account the precision of the determination (±3 mJ m^{-2}), at equilibrium, only the nondispersive component of the PET surface energy is significantly increased, the dispersive component remaining constant. The difference appears clearly for an applied electric field of 52 kV/m. With 17.5 and 35 kV/m fields, the results remain very near those obtained when no field is applied, as shown on Figure 3. The sense of the applied field seems to have no influence on the final equilibrium value, but the kinetics seems slightly affected: The evolution is more rapid with a positive applied field. Typical results are given on Table I. After 24 h on water, the difference is already neat: For PET on water without an applied field, γ_S^P is 9 mJ m^{-2}, and with the application of an electric field (52 kV/cm), the nondispersive component reaches 18 mJ m^{-2}, which corresponds to the value attained after a 20-day orientation on water at room temperature without a field.

ESCA XPS analysis performed on the different PET surfaces shows no clear difference in the peak height ratios of the carbonyl C=O to aliphatic C—H groups. In the case of the carboxylic groups O—C=O, the calculated ratio for the nontreated PET to the treated one corresponds to an increase in carboxylic-group concentration on the treated surface.

With the one-liquid method as used in Ref. 7, the contact angle of a drop of water at variable pH is measured. A decrease is observed with increasing pH as shown in Figure 4. This corresponds to an increase of surface polarity as shown by the increase of the nondispersive interaction term: $I_{SW}^{ND} = 2\sqrt{\gamma_S^P \cdot \gamma_L^P}$, where γ_L^P is the polar component of the

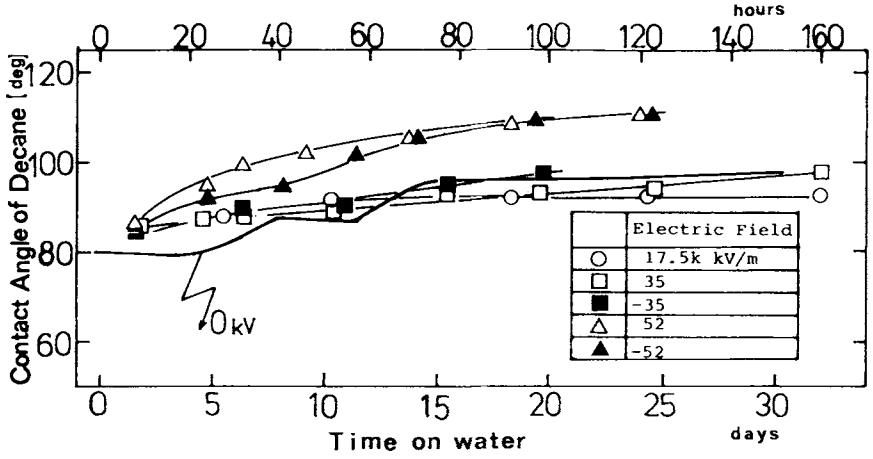

Figure 3 Decane contact angle for PET in water as a function of time of contact on water, with different applied electric fields (two-liquid-phase method).

Table 1 Surface Energy of PET Film and Gelatin Layer Equilibrated on Water with an Electric Field Applied

PET Film (mJm^{-2})		
Component of surface energy	Under electric field (50 kV/m)	Without electric field
Dispersive	41 ± 3	43 ± 3
Nondispersive	23	18
Gelatin Layer (mJm^{-2})		
Component of surface energy	Under electric field (80 kV/m)	Without electric field
Dispersive	21 ± 3	24 ± 3
Nondispersive	12	9

surface energy of the liquid. It can be concluded that after application of an electric field the PET surface becomes more acidic. With gelatin, the results, also given in Table I, show an increase in surface polarity. However, the variation from 9 to 12 mJ m^{-2} is at the limit of accuracy.

Adhesion between PET and Gelatin

For nontreated assemblies, the separation energy measured in air is 0.7 J m^{-2} at a peeling rate of 2 mm mn^{-1}. If an electric field is applied on the assembly, the separation energy increases linearly with the applied electric field (1.5 kV/cm) for a given peeling rate (2 or 10 mm min^{-1}) to 1.6 J m^{-2}, as represented in Figure 5. The influence of the electric field appears also to be slightly affected by the peeling rate, as seen in Figure 6, taking into account the 0.2 J m^{-2} accuracy on separation energy. In all cases, adhesion is enhanced after application of an electric field to the gelatin-coated PET. Application of the electric field leads to a permanent adhesion increase, which remains constant whatever the time lag between removal of the field and testing. The applied electric field has definitely a positive and permanent influence on adhesion.

DISCUSSION

Surface Properties on Water with an Electrical Field Applied

The results obtained on PET surfaces by contact-angle measurements show that the application of an electric field favors a slight increase of surface polarity, with a more rapid kinetical evolution than

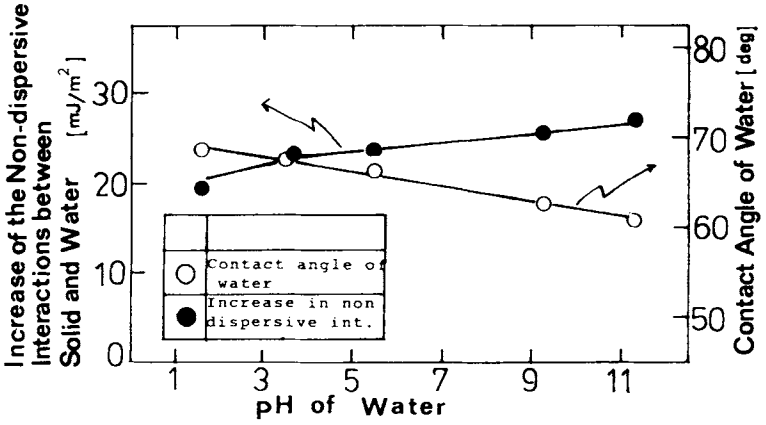

Figure 4 Contact angle of water on PET surface after application of an electric field as a function of pH of water (one-liquid-phase method).

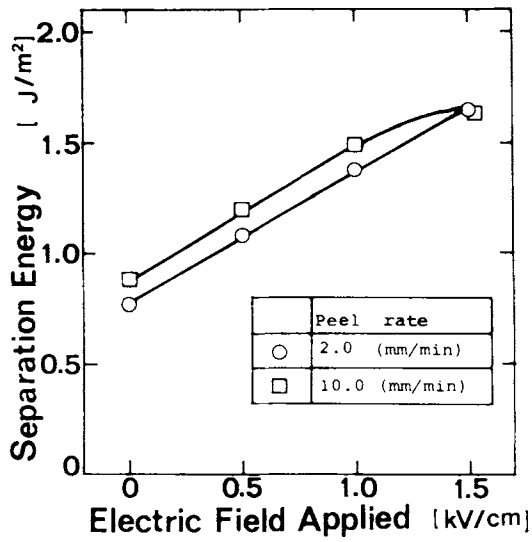

Figure 5 Separation energy as a function of the applied electric field for PET–gelatin assemblies.

without an electric field. There is faster enhancement of surface polarity when an electric field of the order of 50 kV/m is applied. The ESCA spectroscopy data show that the carboxylic-group concentration is higher on the PET surface after orientation on water in the presence of an electric field.

The amphoteric properties of PET have recently been determined by inverse gas chromatography[7]: The surface has an acidic and, simultaneously, slightly basic character. The results obtained as a function of the pH of water drops show that wettability is increased at higher pH's and that surface acidity is increased. The fact that surface polarity is higher whatever the direction of the electric field could be connected with the amphoteric character of PET.

The gelatin surface polarity increase from 9 to 12 mJ m^{-2} for a sample oriented on water under an electric field is not really significant. It can be supposed that gelatin as prepared is already oriented. Gelatin has a rather basic character.[7] By application of an electric field under a steady state, PET surface acidity is increased, and this should favor adhesion with gelatin through acid–base interactions according to Fowkes analysis.[18,19]

Adhesion between PET and Gelatin

It is observed through peeling that the separation energy of the PET–gelatin assemblies increases with increasing applied electric fields. As an example, the maximal value of 1.65 J m^{-2} observed under a 1.5 kV/cm field is close to the value of 2 J m^{-2} attained with a flame treatment of PET.[7] Different hypotheses can be given in order to explain these results:

- The first one assumes that the electric field orientates the polar groups of PET and favors interactions with the basic gelatin, in agreement with the acid–base theory.
- The second one concerns the ionization of the oriented end groups of PET, leading to a higher reactivity with the basic end groups of the gelatin.
- Third, it can be envisaged that under a high electric field there is an increase of temperature of the assembly, increasing the mobility of the macromolecular chains and allowing an interdiffusion at the interface. According to Voyutskii,[20] these phenomena can be at the origin of adhesion between polymers.
- Finally, the temperature increase could also accelerate the kinetics of orientation of the groups. Simultaneous mechanisms could so be responsible for the observed data.

According to recently published results,[7] orientation of polar carboxylic groups on water is obtained at room temperature and is enhanced in the presence of a continuous applied field. This is at the origin of the adhesion increase of thin films of gelatin deposited on PET and submitted to a high electrical field.

This method appears to be a good way to improve adhesion. The electrical theory of adhesion proposed by Deryagin et al.[15] takes into account the electrical charge separation at the adhesive contact. Recent

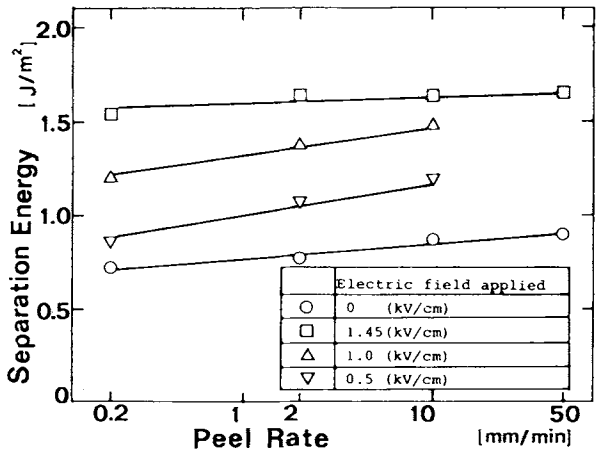

Figure 6 Separation energy as a function of peeling rate after electric-field application on PET–gelatin assemblies.

results on an electrical analytical model of adhesion between acrylic acid-grafted polyethylene and aluminum[21] show the influence of a space charge between the metal substrate and the polymer on adhesion properties. Following the same analysis, it could be assumed that the separation of electrical charges between the two polymers could be modified by the electric field. This leads to a higher adhesion at the interface.

CONCLUSION

It is well known that the orientation of acid polar groups of a polymer at the interface with a polar medium, like water, is responsible for the polarity increase and favors adhesion to a basic polar substrate. In this study, it has been shown that under application of a continuous electrical field (a few kV/m), orientation is favored on water and the PET surface is enriched in acidic groups. This can be due to the activation of the orientation by electrical or by thermal effects.

Adhesion of gelatin coated from a solution to PET is increased by a subsequent application of a high electric field. The continuous electric field can orientate the dipoles at the interface and, as a consequence, enhance the final adhesion. This mechanism concerns only polar polymers.

A study of polar-group orientation at the polymer surfaces has shown the influence of dielectric interactions.[9] Electrical aspects of adhesion take into account the presence of space charges at the interface. It appears, therefore, that the two approaches are self-consistent.

Some rather old patents[12,22] are devoted to the effect of an electric field on adhesion, but only a few scientific works have been published on this aspect. The purpose of this study was to bring some light on this complex problem of improving adhesion by use of a high electric field.

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