

Characterization of Treated Polyolefin Surfaces by a Liquid Mixture Spreading Technique

INTRODUCTION

Surface properties of polymers are of great importance in many practical applications.¹⁻⁴ A typical and most common example is the adhesion of polar printing inks to polyethylene, which is essential in the packaging industry. Since the surface energy of polyethylene is too low to allow good adhesion of polar liquids, pretreatment is usually required. The most common methods of pretreatment designed to raise the surface energy of the polymer include flame or corona discharge treatments, oxidation by acids, and chlorination.

Obviously, methods of testing the surface of the polymer are required to assess the effect of the pretreatment. The methods in use³ can be divided into two groups: (1) methods that attempt to elucidate the surface free energy, such as contact angle measurement and the wetting tension test, and (2) methods that approximate the actual process of adhesion, under standard conditions, such as the tape adhesion tests and printing ink adhesion. In this note, methods related to only the former group will be discussed. Contact angle measurement has been used widely in scientific studies of polymer surface treatments. However, as is well known, contact angle measurement presents some difficulties, regarding both reproducibility and theoretical interpretation. In particular, it seems that the major changes in contact angles of water on polyethylene and polypropylene occur during about the first minute of treatment,⁵⁻⁷ and thereafter the changes are only of about 5–10 degrees. Taking into account the accuracy of the measurement, which is about two degrees, the changes that occur in the contact angle for a period of treatment longer than 1 min are somewhat inconvenient. The wetting tension test³ consists of using a range of liquid mixtures having different surface tensions to find the mixture of the highest surface tension that does not contract into droplets within 2 sec after brushing it on the surface.

According to Sharples,³ this test is used more often in industry; it is quick but requires experienced operation and has many pitfalls. Thus, the two tests mentioned have their own advantages and drawbacks but, surprisingly, have not been compared to each other regarding their sensitivity to modifications of the surface properties.

In the present note we suggest a technique for surface characterization based on watching the spreading of a mixture of polar and nonpolar liquids on the solid surface. Its sensitivity is compared with that of measuring contact angles on polyethylene treated with chromic acid solution, and the differences between this technique and the wetting tension test are discussed.

EXPERIMENTAL

Treatment of Powder and Film Preparation

The polyethylene powder used was low-density polyethylene (LDPE) (Israel Petrochemical Enterprise Ltd., density 0.919 g/cm³, MFI 2.0 g/10 min, mean diameter 210 μm). Antioxidants were extracted by chloroform at 62°C for 14 hr. The powder was then dried in a vacuum oven at 40°C for 2.5 hr under continual vacuum. Chromic acid solution was prepared by mixing 100 parts sulfuric acid, 5 parts potassium dichromate, and 8 parts water, by weight. The polyethylene powder was mixed with the chromic acid in Erlenmeyer flasks which were placed in a shaker bath for a specified period of time at a specified temperature. Separation of the powder from the acid was accomplished by filtering, followed by flushing with distilled water. The wet material was dried in a vacuum oven for 3 hr at 40°C. The dry powder was spread between two sheets of Mylar, which had been cleaned with chemically pure methanol. The Mylar sheets were sandwiched between two flat pieces of nickel-plated brass. After compression molding, the film was immediately sealed in a plastic bag and stored in a dark cabinet until the performance of the surface characterization tests.

Contact Angle Measurement

Prior to measurement, a 2-cm square of the polyethylene film had been cleaned by triple-distilled water in an ultrasonic bath for 5 min and dried in the ambient air for 2 hr. The specimen was then placed on the stage of a reflective-type goniometer. Flatness of the film surface was ensured by placing a small weight over it, with a suitable gap for placing and watching the drop. A thoroughly cleaned glass syringe was used for placing the drops. Two liquids were used for these measurements: triple-distilled water and propylene carbonate.

Alcohol-Hydrocarbon Spreading Test

Various mixtures of ethanol and octane were used for this test. They were prepared in volume proportions ranging from 95:5 to 5:95, in 5% increments, and stored in bottles sealed securely to avoid evaporation. The polyethylene samples were cleaned as for the contact angle measurements. To perform the test, a precleaned syringe was filled quickly with a small amount of a particular test solution, and a drop was placed on the specimen. The drop was watched for continuous spreading, defined here as a rapid advance of the drop periphery to a very low contact angle. Beginning with solutions of high ethanol concentration, the test was performed with successively lower concentrations of ethanol until continuous spreading occurred. The concentration at which continuous spreading was first observed was recorded.

RESULTS AND DISCUSSION

Figure 1 presents the contact angles of water drops on polyethylene films made of powder treated with chromic acid versus time of treatment for various temperatures. Figure 2 presents the same type of data, using propylene carbonate as the liquid. This liquid was chosen in addition to water because of its lower contact angle on polyethylene. Both figures show, as expected, that the contact angles decrease with treatment time and with increasing temperature. The important point, however, is that the changes in contact angles are within 5° , while the accuracy is about ± 1 .

Figure 3 presents results for the alcohol-hydrocarbon spreading test. It is clearly seen that with increasing treatment time at a given temperature the solution which exhibits continuous spreading

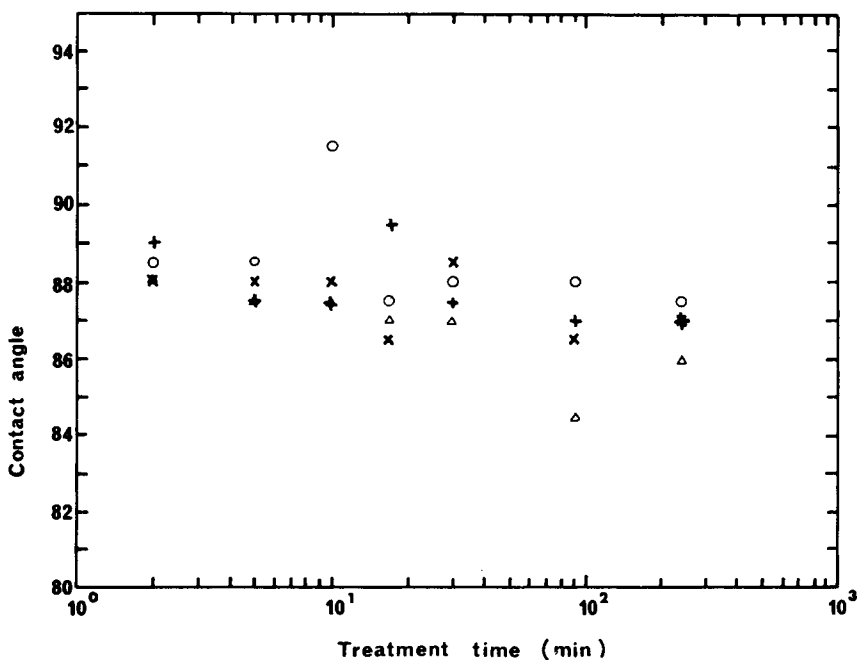


Fig. 1. Water contact angles on films formed from LDPE powder treated with chromic acid: (O) 30°C; (X) 40°C; (+) 50°C; (Δ) 60°C.

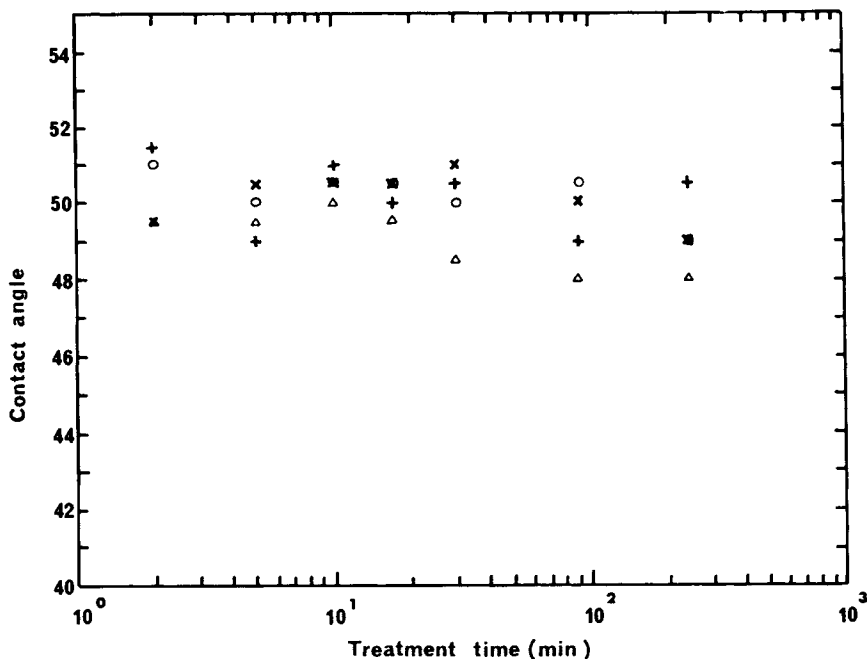


Fig. 2. Propylene carbonate contact angles on films formed from LDPE powder treated with chromic acid. See Fig. 1 for legend.

becomes more polar, i.e., has a higher ethanol content. The same holds true for increasing the treatment temperature at a given treatment time. In comparison with the measurements of contact angles for the same treatment conditions it is quite obvious that the alcohol-hydrocarbon spreading technique is much more sensitive.

Since the alcohol-hydrocarbon spreading test may seem somewhat similar to the wetting tension test, it is of interest to discuss the differences between the two techniques, as follows:

(1) The wetting tension test is based on forced formation of the liquid film, followed by inspection of its contraction, while in the present test the composition of a drop that forms a thin film by continuous spreading is searched for.

(2) The wetting tension test involves an element of time (contraction should occur within 2 sec), and thus the viscosity of the solution is playing a part in the test. This complicates the interpretation of the results, since the purpose is to characterize the surface of the solid through the surface properties of the solution. The alcohol-hydrocarbon spreading test, on the other hand, uses an inspection of a dynamic process, i.e., continuous spreading, only to determine the composition of the solution which yields a contact angle that approaches zero. Thus, the dynamic process is used only as a convenient means for assessing a thermodynamic property, i.e., the composition which leads to approximately zero contact angle, and the rate of the process is not considered.

(3) In the wetting tension test a mixture of liquids having different surface tensions is used, and the result is given in terms of the surface tension of the appropriate solution. This is based on the assumption that the surface tension thus given is characteristic of the surface energy of the polymer (a desirable value is considered as 38 dyn/cm or more). Similar to a recent argument⁴ against using liquid surface tensions as representing the surface energy of solids in relation to the critical contact angle concept, it is questionable whether the surface tensions of the mixtures used in the wetting tension test directly represent the surface energy of the polymer. The ethanol-octane spreading test clearly demonstrates this point. The surface tension of ethanol is 22.8 dyn/cm at 20°, while that of *n*-octane is 21.8 dyn/cm at the same temperature. The difference between the various mixtures is thus caused by the varying interaction with the solid surface, owing to the changes in the polarity of the mixture, in spite of the fact that the surface tensions of the liquids involved are very similar. Also noticeable is the fact that the surface tensions of ethanol and octane are much lower than the value that is considered characteristic in the wetting tension test.

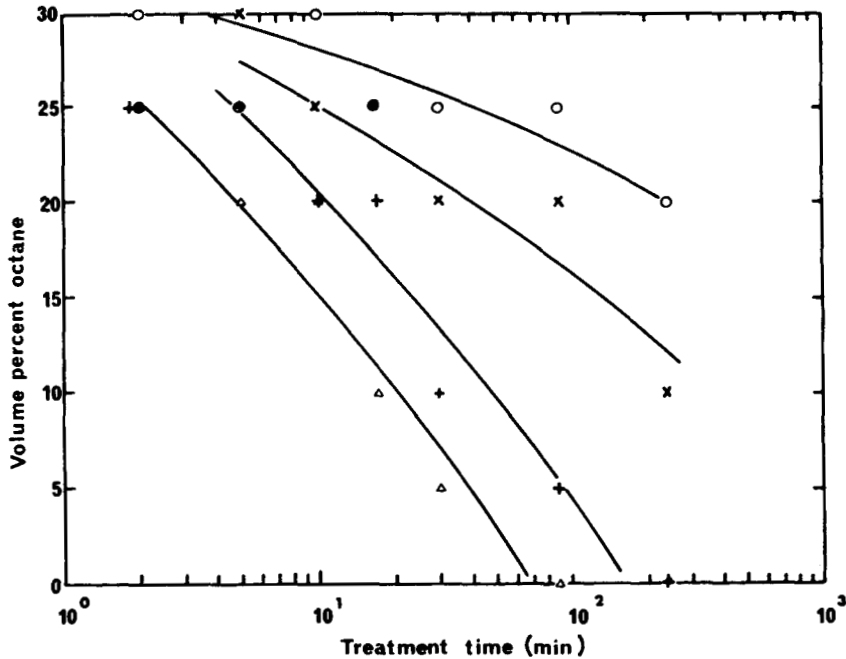


Fig. 3. Concentrations of mixtures which undergo continuous spreading on films formed from LDPE powder treated with chromic acid. See Fig. 1 for legend.

In conclusion, the alcohol-hydrocarbon spreading test has been shown to be much more sensitive than contact angle measurements for the characterization of chromic acid-treated polyethylene. In addition, this test avoids some of the pitfalls involved in the wetting tension test.

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