

A Comparative Study of Plasma-State and Plasma-Induced Polymerization of Acrylonitrile for Modification of Cellophane Surfaces.

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Cellophane was grafted with polyacrylonitrile using both plasma-induced and plasma-state polymerization techniques. The plasma-induced technique requires a two-stage reaction procedure: 1) first, the substrate is activated with a radio-frequency cold plasma; 2) second, a monomer is introduced into the vacuum chamber to graft to the activated surface. The plasma-state technique involves use of the monomer as the activated plasma gas for direct grafting. The plasma modified surfaces were characterized by ESCA, AFM, wetting measurements, and t-peel tests. Both plasma polymerized substrates appear more smooth than cellophane by AFM and show higher peel strength with polypropylene than untreated cellophane. The plasma-state polyacrylonitrile grafted cellophane displays peel strength fifteen times better than untreated cellophane; whereas, plasma-induced polyacrylonitrile grafted cellophane has an adhesion strength seven times better than untreated cellophane.

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1. Introduction

An increasing environmental concern over the volume of non-degradable waste in landfills has lead researchers to study bio-based composite materials as replacements for plastics. These materials consist of natural fibers or wood flour embedded in a synthetic polymer matrix. Bio-based composites are lightweight and inexpensive and are used for molded automotive applications such as trunk and hood linings, and into door components. Paper-polyethylene laminates are used for photographic paper and food packaging. These materials rely upon good adhesion between the two components for adequate stress transfer to the matrix to provide good strength properties in the composite and to avoid delamination in the other products.

However, the hydrophobic plastic matrix is inherently incompatible with the hydrophilic natural polymer. Therefore, a surface treatment of either component is necessary to provide adhesion across the interface. Surface modification for adhesion has been performed by chemical methods [1-3], corona treatment [4,5], and plasma modification [3,6-8]. Plasma activation and polymerization are useful methods to tailor surface properties of a material [9, 10]. Plasma treatment has been used mainly for modification of synthetic materials, however, natural materials have also been plasma treated [11, 12].

We have studied two types of plasma polymerization procedures to graft a vinyl monomer to cellophane: plasma-induced polymerization and plasma-state polymerization. Plasma-induced polymerization is a two step procedure: 1) first, a substrate surface is activated with a radio-frequency inert cold plasma under vacuum; 2) second, a monomer is introduced into the vacuum chamber to graft to the activated surface. Since this is a free radical polymerization, the chemical structure of the polymer should be similar to conventional polymers formed by this method. Plasma-state polymerization is a one-step procedure where the monomer is used as the plasma gas and directly grafts to the substrate surface. The resulting polymer from plasma-state polymerization is made of primary stable fragments which deposit and graft to the surface of the substrate. Therefore, the chemical structure is quite different from conventional polymers. These plasma techniques are advantageous over chemical grafting reactions because the bulk of the substrate is not hindered and, since the monomer is introduced in the gas phase, less monomer is used and less homopolymer is formed, which reduces waste, cleanup, and environmental hazards.

Cellophane, which is regenerated cellulose, was chosen as the natural polymer substrate. By using cellophane, we study a uniform material and avoid unnecessary variables encountered when using lignocellulosic substrates. Acrylonitrile was chosen as the vinyl monomer. It forms a more hydrophobic polymer which should provide better compatibility with a synthetic matrix; also, it contains nitrile groups which have been proven to enhance adhesion to polypropylene [13,14]. The chemical and physical characteristics of the grafted surfaces were analyzed by electron spectroscopy for chemical analysis, dynamic contact angle analysis, and atomic force microscopy. The peel strength between the plasma grafted substrates and polypropylene was measured by a t-peel test.

2. Experimental

2.1 Materials

Cellophane, containing no additives was supplied by Flexel for this study. The cellophane was not further purified prior to reaction. Acrylonitrile (Aldrich, 99+%) was used as received. High purity argon (Liquid Carbonic) was used for surface activation in plasma-induced polymerization and for washing the plasma chamber in both procedures. Polypropylene films were donated by Solvay for adhesion tests.

2.2 Methods

A capacitively coupled radio frequency reactor (Technics) was used for the plasma procedures. The reactor has been described in a previous publication [15].

For the plasma-induced polymerization procedure, the cellophane films were placed on the lower (grounded) electrode and held in place with an aluminum ring around the outside. The reactor was evacuated to base pressure of 50 mTorr. A pyrex monomer bulb was filled with 3 mL of acrylonitrile; the monomer was frozen with liquid nitrogen and the air was evacuated; then the monomer was thawed. Argon was flowed into the chamber for washing. The lower electrode was cooled with liquid nitrogen circulation to -30°C . Argon was then introduced until the chamber pressure reached the desired pressure. An argon plasma was initiated at a desired power for a designated time. After the reaction, the chamber was evacuated to base pressure and isolated; then the acrylonitrile was flooded into the chamber. Argon was flooded in to atmospheric pressure; then the substrate was left to warm for 4-1/2 hours. The treated substrate was removed from the chamber; sealed in a polyester bag; and placed in the oven to graft copolymerize acrylonitrile at 62°C for 40 minutes. The grafted cellophane was washed with dimethylformamide and rinsed with acetone to remove any homopolymer. The argon plasma conditions for the results reported here were 100 W power, 275 mTorr pressure, and 6 minute treatment time.

For the plasma-state polymerization procedure, the cellophane film was placed on the upper (powered) electrode of the reactor and secured with an aluminum ring. The chamber was evacuate to a base pressure of 50 mTorr. Acrylonitrile was put into a long steel column attached to the chamber. The monomer was frozen with liquid nitrogen; oxygen was evacuated from the tube; and the monomer was thawed. The chamber was washed with argon. The monomer was flowed in at a rate of 7 sccm; the vacuum was partially closed off to maintain the desired pressure. The plasma was then initiated at the desired power for a designated time. Argon was flowed in to clean the residual monomer from the chamber for 10 minutes. The samples were removed from the chamber; then washed with dimethylformamide to remove ungrafted molecules; and rinsed with acetone. The experimental conditions used for the results reported here were 25 W power, 250 mTorr pressure, and 2.5 minute treatment time.

T-peel tests were performed with 2 cm wide samples using a T.C. Scott CRE tensile tester with a 10 lb load cell and peeled at a rate of 0.20 cm/sec. Laminates for the peel tests were made of polypropylene film between two cellophane sheets and pressed under 140 psi at 132°C for 6 minutes.

A Perkin Elmer Physical Electronics 5400 Small Area Electron Spectrometer (Mg source; 15 kV and 300 W) was used to detect atomic concentrations at the surface of the substrates. A Cahn Dynamic Contact Angle Analyzer was used for contact angle measurements. A Digital Instruments Nanoscope III Atomic Force Microscope was used to image the surface. Image areas scanned were $5\ \mu\text{m}$ and $750\ \text{nm}$.

3 Results and Discussion

3.1 Electron Spectroscopy for Chemical Analysis

Electron spectroscopy for chemical analysis (ESCA) was used to determine the surface atomic composition. ESCA spectra of plasma treated samples show a nitrogen peak. The N/C ratio was 0.23 for plasma-state polyacrylonitrile (PSPAN) grafted cellophane and is 0.11 for plasma-induced polyacrylonitrile (PIPAN) grafted cellophane. These ratios are lower than the N/C ratio of conventional polyacrylonitrile of 0.33. The lower N/C ratio determined for PIPAN is a consequence of incomplete coverage of the cellophane film; only 33% of the surface was covered. The PSPAN ratio was lower due to the fragmentation of the acrylonitrile and reformation into a different chemical structure containing a lower N/C ratio than conventional polyacrylonitrile. Munro and Grünwald [16] found a similar ratio for PSPAN on aluminum foil.

3.2 Dynamic Contact Angle Analysis

Fig. 3.1 shows a comparison of contact angles for untreated and plasma treated cellophane. The plasma polymerization treatments reduce the wettability of the cellophane film. Young and Nguyen [17] determined a contact angle similar to PIPAN (61.5°) for polyacrylonitrile grafted to thermomechanical pulp by the xanthate method (65.5°). The contact angle for PSPAN (49.6°) was slightly lower than that of PIPAN, possibly due to the higher nitrogen content of PSPAN. The ratio of the receding to advancing wettability of a substrate is the hysteresis. The plasma polymer-grafted cellophane exhibited significantly larger hystereses than untreated cellophane, thus, indicating the modified surfaces are less chemically homogeneous than the unmodified surface.

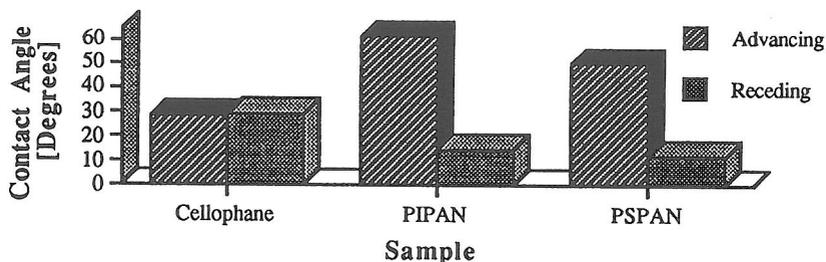


Fig. 3.1 Water wettability comparison between untreated cellophane and plasma polymerized samples.

3.3 Atomic Force Microscopy

Atomic force microscopy (AFM) is a particularly useful technique to analyze polymeric surfaces by measuring interatomic forces as a cantilever tip is scanned over a sample. It has the advantages that the sample does not have to be put into a vacuum or be conductive, and it shows more surface dimensionality than SEM [18]. The primary disadvantages are that the minute deflections of the tip are difficult to reproduce and the image resolution is limited by the atomic size of the cantilever tip, which may cause rounding of peaks [19]. Fig. 3.2 shows AFM images of the untreated and plasma

modified surfaces in the deflection mode where the sample height is held constant while the deflection of the tip is measured. An orientation is apparent in the untreated sample. The image of PSPAN is similar to the untreated cellophane where it appears that the polymer is grafting along the lines of the orientation in the cellophane. In contrast, the PIPAN grafted surface has a granular appearance. The grafted polymer also seems to have an orientation, which may be related to the number of initiation sites available on the cellulose for the induced polymerization..

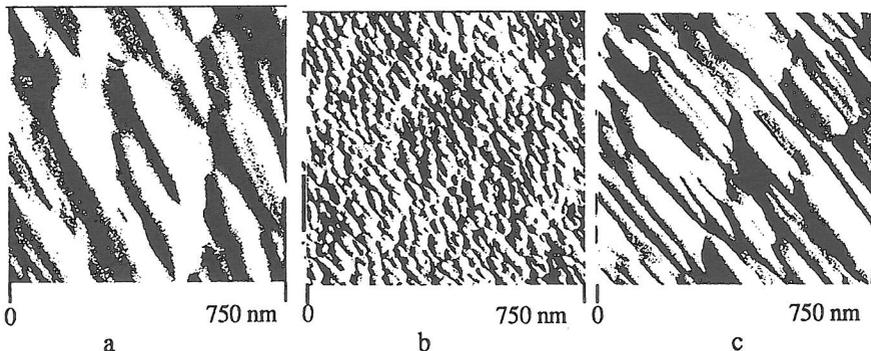


Fig. 3.2 AFM images of a) untreated cellophane, b) PIPAN-cell, and c) PSPAN-cell.

3.4 Peel Strength

Fig. 3.3 shows the peel strength comparison of untreated and plasma grafted cellophane to polypropylene. The plasma treated samples are significantly more adherent to polypropylene. Although PIPAN adheres more than six times better to polypropylene than untreated cellophane, PSPAN displays the greatest adhesion (129.6 mN/20 mm), which is fifteen times greater than untreated cellophane (8.4 mN/20 mm). This shows the improvement in adhesion, possibly due to the increased nitrogen content.

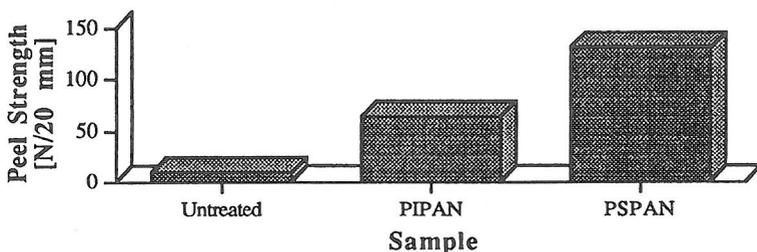


Fig. 3.3 Comparison of peel strengths between untreated and plasma polymerized samples with polypropylene.

4 Conclusions

Acrylonitrile was successfully grafted to cellophane by the plasma-induced and plasma-state polymerization techniques. Both plasma polymers enhanced adhesion of cellophane to polypropylene. The greatest adhesion was obtained with PSPAN, probably due to bonding through the nitrogen groups at the surface. Hydrophobicity also increased upon grafting the plasma polymers, which enhanced the compatibility between the cellophane and polypropylene. AFM images of the plasma surfaces show that the morphology is quite different between the two plasma polymers, indicating the mechanism of grafting is different with the two techniques. A more comprehensive analysis of the change in plasma polymer chemistry and morphology with variation in plasma conditions will give a better indication of the mechanisms of plasma polymer formation with the two techniques.

5 References

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