Synthetic Paper from Plastic Waste: Influence of a Surface Treatment with Corona Discharge

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ABSTRACT: Polymers generally have a chemically inert surface, are nonporous, and have low surface energy, which is characterized by their relatively weak adhesion to other materials. Numerous methods have been developed to modify polymer surfaces chemically. This study was an investigation of how the surface energy of synthetic paper (composite film) could be altered after treatment by corona discharge and of the stability of the surface energy of a film produced from postconsumer polypropylene (PP). A PP/filler (70/30 w/w) composite film was processed in a single-screw extruder with a flat-film dye. In this study, the film stretching rate and electric charge potential of the film surface treatment were the process parameters analyzed. The results showed that the conditions of the surface treatment by corona discharge and the presence of a filler (calcium carbonate) influenced some surface properties: the contact angle, surface energy, and ink adhesion. The surface energy of the composite film increased from 38.7×10^{-3} N/m^2 without treatment to 52.3×10^{-3} N/m^2 with treatment. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3420–3427, 2009

Key words: composites; films; poly(propylene); (PP); recycling; surfaces

INTRODUCTION

The pulp and paper industry uses thousands of tons of water a day and creates considerable effluent problems during the manufacture of paper products. It is also responsible for deforestation through logging. On the other hand, the plastics industry has a lower environmental impact than the pulp and paper industry. In many situations, plastics are considered attractive materials because they can be produced to satisfy the requirement of resistance to weather, water, acids, and corrosion; thus, they are increasingly replacing paper and other materials in a number of areas.[1,2]

The increase in the consumption of plastic products has led to an increased volume of municipal plastic waste (MPW), particularly from food packaging. Their final elimination is considered a serious ecological problem because of difficulties encountered in (1) reducing the volume to allow economic disposal, (2) breaking down the polymeric material to a condition in which the mechanisms of natural decomposition can operate, and (3) reducing the use of raw materials from nonrenewable sources.[1,2]

Polyolefins represent a high proportion of MPW, and polypropylene (PP) is one of the commonest polyolefins found there, being used to produce many products ranging from plastic bags to food and beverage product packaging. On the other hand, the market for products that require surface printing is enormous, and composite PP films, already known as synthetic paper, offer a way to obtain a film capable of receiving inks, provided that some kind of surface treatment is applied.[1,3–8] Therefore, the fabrication of synthetic paper with plastic from MPW would be an interesting way to reduce the environmental impact.

The various processing conditions used to obtain paper-like plastic films produced by extrusion from virgin resins are described in several patents.[3–10] These composite films contain inorganic fillers and additives, which improve their rigidity, tensile resistance, opacity, and ink receptivity.[5,9–11] The presence of calcium carbonate (CaCO$_3$) in a film leads to the formation of microvoids, which first provide a reduction in density and second make the film more opaque as they diffract the rays of light.[1,5,12] On the other hand, the quality of the film depends on the volume fraction, size, dispersion, and shape of the voids. For instance, large voids reduce the strength and impair printability. Moreover, the way in which voids form can affect productivity.[13,14]

Generally, the surface of these composite films is treated by corona discharge (CD). The mechanism of CD involves generating a plasma of ionized gas and other reactive species, and the required apparatus is easily installed at a step in the film-making process. The plasma, containing electrons, ions, and free radicals, interacts with the polymer surface and modifies its chemical and physical properties. Surface modification consists mainly of forming functional groups on the surface and etching the surface, thereby improving its printability. In the case of polyolefin-based synthetic paper for printed applications, the polymers must adhere well to other substances such as inks.

Adhesion to polymers is a manifestation of the attractive forces that exist between all atoms, and they fall into three broad categories: primary (covalent), quasichemical (hydrogen bonds), and secondary (van der Waals) forces.[15] It is generally agreed in theory that attraction generated by secondary forces and hydrogen bonding alone is sufficient to produce adhesive bonds between polymer molecules of a strength equal to that of bonds within the molecules themselves, without the need for covalent bonds. Thus, surface modification with CD has proved to be effective and has been applied widely to produce the necessary adhesive bonds in synthetic paper products based on polyolefins.

In the printing and writing paper market, it is to be expected that the use of synthetic paper will grow because these products possess important properties that are superior to those of pulp-based products. In addition to the advertising market, which is typified by outdoor posters and timetables in railway and bus stations, some other potential markets exist for synthetic paper in which it could have a great impact as a novel material, particularly when printed products, such as calendars or catalogues, need to be durable.[8–10] In book printing, synthetic paper also offers higher durability and greater tear, water, grease, and oil resistance, which should lead to its application in children's books, factory manuals, materials used outdoors, music scores, and so on.

Published work on the preparation of composite films from plastic waste is very scarce, except for that of this research group.[1,14,16–20] The influence of various postconsumer polymer matrices on the processing of polymer mixtures filled with $CaCO_3$ has been studied, as well as the effects of the type of process and thermochemical surface treatment on the physicomechanical and surface properties of the composite films produced.[1,16–20] Extending this work, this study examined the influence of surface treatment by CD on composite films of postconsumer PP, which was investigated by an analysis of the physicochemical and morphological properties and an assessment of the stability of the film surface energy during prolonged storage.

EXPERIMENTAL

The postconsumer PP used to produce the recycled composite film was mineral water bottle residue selectively collected from plastic waste at the Federal University of São Carlos (São Carlos, Brazil). The inorganic additives were $CaCO_3$ [Inacarb 700, Quimbarra Group (now Imerys, SP, Brazil)], which was used as a filler (30 wt %), rutile TiO_2, which was used as a white pigment (3 wt %), SiO_2 (Sylobloc 44, Grace Davison, SP, Brazil), which was used as an antiblocking agent (1 wt %), and Irganox B215 (Ciba Especialidades Químicas, SP, Brazil), which was used as a stabilizing agent (0.2 wt %).

Postconsumer PP was precut with a MAK 250 knife mill (KIE Máquinas e Plásticos, Ltd., SP, Brazil), washed with plain water at room temperature (23°C), dried in a rotating chamber with air flow at 50°C, and finally chopped into the form of flakes with the same MAK 250 knife mill. The inorganic filler and additives were manually premixed. The PP was compounded with these particulates in a Werner Pfleiderer twin-screw extruder (Frankfurt, Germany) at 150 rpm with a temperature profile of 225, 235, 235, 240, 240, and 240°C. The flow rate of the premixed compound was controlled with an automatic feeding–dosage apparatus located immediately after the resin melting zone of the extruder.

The PP composite film was processed in a Gerst model $25\times24D$ single-screw extruder (Gerst Ind. e.Com. de Máquinas, São Paulo-SP, Brazil) with a flat-film die running at 100 rpm with a temperature profile of 180, 200, 220, and 220°C. A compressed air system mounted just at the die output was used to cool the emerging film, which was pulled only in the machine direction through a CD system (Contreat, SP, Brazil). This system, provided with parallel rollers with variable pulling (stretching) rates and varying electrical discharge potentials, enabled the effects of various oxidative treatment conditions on the film surface properties to be assessed. In this study, the following parameters were analyzed: (1) stretching rate (R_s) values of 5 and 9 rpm and (2) three different applied electrical potentials, as shown in Table I.

The surface morphology of the $PP/CaCO_3$ composite films, which were stretched at two different rates and then treated at three discharge potentials, was subjected to comparative analysis based on images obtained with a Stereoscan 440 LO scanning electron microscope (FEI Europe B.V., Eindhoven, Netherlands). Samples were covered with gold in a Balzers SCD 004 (Liechtenstein, Switzerland) sputter coater before being examined under the microscope at an acceleration voltage of 20 kV.

The surface tension of the composite films was determined. Because the attractive forces for adhesion decrease with the inverse sixth power of the

TABLE I
Treatment Conditions for CD on Composite Films

Sample	Treatment conditions for CD	
	R_s (rpm)	Electrical potential (kV)
1	0	0
2	5 (1.7 m/min)	12
3	5 (1.7 m/min)	18
4	5 (1.7 m/min)	24
5	9 (3.4 m/min)	12
6	9 (3.4 m/min)	18
7	9 (3.4 m/min)	24

distance between the molecules of two distinct surfaces, it is apparent that the surfaces to be adhered must come into close, wetting contact. Wetting contact is related to the contact angle of liquid droplets on the substrate surface and is related through Young's equations to the surface energy (tension) of the substrate. The total surface energy (γ_t) is composed of a nonpolar or dispersion component (γ_d) and a polar component (γ_p), as represented in eq. (1). Measuring the contact angles against two or more liquids whose surface tensions and respective polar and dispersion components are known and applying the harmonic mean formula, which is described elsewhere,[1,15,21] we can calculate the total surface tension and component energies of the polymer substrate:

$$\gamma_t = \gamma_p + \gamma_d \tag{1}$$

Here, γ_t, γ_p, and γ_d of film substrates were calculated by the measurement of the contact angle by the pendant drop method, as specified in ASTM D 724-89, in a Tantec CAM-Micro goniometer (Lunderskov, Denmark) with two liquids: water ($\gamma_t = 72.8 \times 10^{-3}$ N/m) and methylene iodide (CH_2I_2; $\gamma_t = 50.8 \times 10^{-3}$ N/m).[15] Because the composite film surfaces were heterogeneous, contact-angle measurements were taken at seven different points on each test sample surface.

The stability of the surface tension of one of the composite films (stretched at 5 rpm and corona-treated at 24 kV) was tested over a total period of 11 months by monitoring of the water and CH_2I_2 contact angles of the film at defined time intervals. The samples were stored in the laboratory under mild environmental conditions at a temperature of $25 \pm 5°C$ and at a relative humidity of $60 \pm 10\%$.

Offset ink adhesion was determined as recommended in the ASTM D 3359 standard with a specific adhesive tape (1.5 cm wide; 3M; São Paulo, Brazil). A length of tape was fixed across the film with a roller and then peeled off the film rapidly, removing a quantity of printing ink. Because the force applied over the tape was constant for all the samples, it was possible to analyze comparatively

the degree of adherence of the printing ink by a qualitative visual evaluation of the amount of ink removed by the tape.

RESULTS AND DISCUSSION

Surface morphology analysis

Scanning electron microscopy (SEM) micrographs of the PP/CaCO₃ composite film (70 : 30), with and without surface treatment, are shown in Figure 1. A
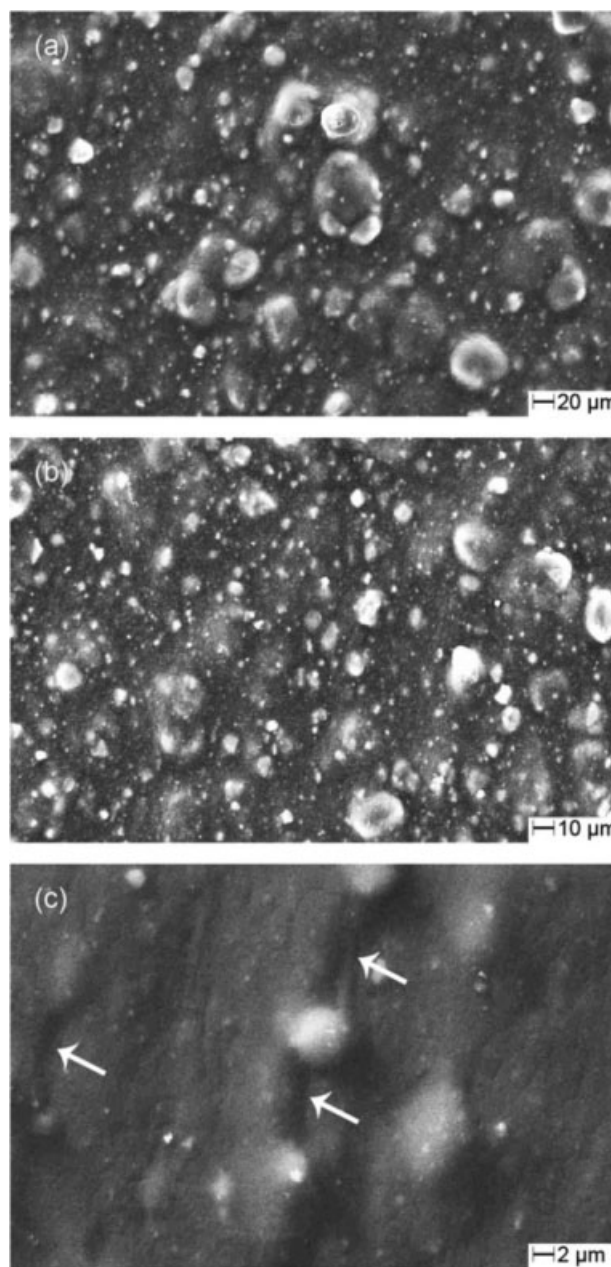
Figure 1 SEM micrographs of the composite film surface pulled at $R_s = 5$ rpm: (a) 1000× magnification without surface treatment, (b) 1000× magnification with CD surface treatment, and (c) 6000× magnification with CD surface treatment.

rough surface with an aggregation of filler particles in the PP matrix can be observed in Figure 1(a,b), and a wide range of filler sizes is shown in both micrographs. Significant morphological changes with respect to the filler dispersion at the surface of the composite films were not observed in the SEM analysis after treatment by CD. However, the treated film had a slightly higher concentration of particles of the filler at the film surface, as shown in Figure 1(b), and some of these particles appeared to be not covered by the polymer. This result indicates that the CD treatment had an active effect on the filled film surface.

A micrograph of the CD-treated composite film surface, at a magnification of 6000×, is shown in Figure 1(c). Here, microvoids or surface depressions, 4 to 6 μm in size, can be observed on the film surface, originating from the film stretching process. The presence of the filler in the film led to the formation of these microvoids[3,4] when the film was subjected to stretching in a uniaxial orientation process. Different kinds of microcavities have also been observed in $CaCO_3$-filled uniaxial films made from recycled PP, as reported elsewhere.[14] The presence of such voids/cavities increases the opacity of a composite film,[4,5,8] and this property is very important for its application in synthetic paper.

Surface energy analysis

As described in the Experimental section, γ_t is the sum of γ_d and γ_p, both of which were determined in the comparative characterization of the PP composite films. Figure 2(a,b) shows the results of this analysis for films with and without surface treatment by CD at three different applied discharge voltages and at R_s values of 5 and 9 rpm. The values of γ_t, γ_p, and γ_d plotted at 0 kV in both graphs refer to untreated films.

As expected, the CD-treated composite films had a higher γ_t value (from 42 to 52×10^{-3} N/m) than the untreated films (38.8×10^{-3} N/m) at both R_s values and at the three CD voltages (12, 18, and 24 kV). The low surface energy of the untreated composite films was due to the fact that the intermolecular forces of cohesion acting on the polymeric films were mainly dispersion forces, which led to low surface energy and therefore poor adhesion.

γ_p was considerably higher after the CD treatment, being 11–35 times the value for the untreated films. These results confirm that during the corona treatment, some of the nonpolar groups of PP, such as C—H and C—C, reacted with air molecules (O_2 and N_2) converted by CD into ions and free radicals, giving rise to polar functional groups on the film surface, such as hydroxyl (OH), carbonyl (CO), and nitrogen-containing groups.[13] A similar reaction was

(a)

(b)
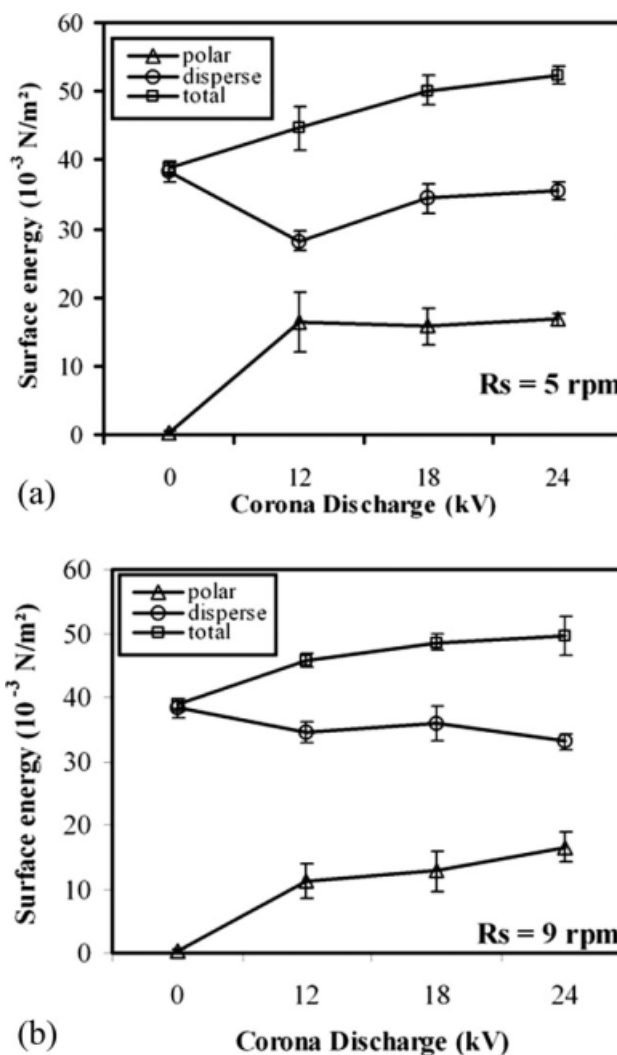
Figure 2 Surface energy of the composite films, without and with CD treatment, processed at (a) $Rs = 5$ ppm and (b) $Rs = 9$ rpm.

observed by Clark and Feast[22] in the CD treatment of PP films; infrared spectra showed absorption bands of CO and OH species formed during the treatment. They also found nitrogen-containing groups such as —ONO_2 and NO_3 and thus concluded that the PP film contained amide slip agents.

The value of R_s was observed to have a significant influence on γ_p. Figure 2(a) shows that γ_p for the composite film with $R_s = 5$ rpm (1.7 m/min) reached a stable value already at an applied potential of 12 kV. Further increases in the exposure voltage had no significant influence on the polar component of the surface energy (16.8×10^{-3} N/m) because of the saturation of polar species such as the CO group on the treated film surface. According to Harth and Hibist,[23] the modification of a PP film by plasma treatment can result in changes in the wettability of the composite film due to the formation of surface functional species containing oxygen and

nitrogen; however, it is saturated after a short time and then is not affected by higher exposures.

In Figure 2(b), γ_p of the composite films stretched at a higher rate ($R_s = 9$ rpm) is shown. In this case, γ_p rose with the exposure dose, but it was lower than that of films stretched at $R_s = 5$ rpm (11 and 12.8×10^{-3} N/m for CD of 12 and 18 kV, respectively). This is readily explained by the high R_s value of the film, as the film had a lower residence time in the CD treatment. This result indicates that at $R_s = 9$ rpm, the composite film surface was not saturated with polar functional species at a CD potential of 12 kV.

As for γ_d, it decreased after exposure to the CD treatment, as can be seen in Figure 2 by a comparison of the results for the treated composite films with those for the untreated ones. However, this change in γ_d was less marked than the change in γ_p. This result thus agrees with the reports of other authors who found that a change in the surface energy is due not only to γ_p but also to the dispersion forces, which contribute to a lesser extent than γ_p.[24,25] Although γ_p is related to chemical groups found on the surface after CD treatment, γ_d may be related to the surface topography.

The topographical changes induced in the films by CD were analyzed only by observation of the surface micromorphology, by SEM, of treated and untreated films. The CD treatment appears to have roughened the surface, leaving more of the filler particles exposed, without polymer covering, as already discussed. This would theoretically result in a bigger value of γ_d in treated films, which is the opposite of what was observed.

However, it must be kept in mind that the contact-angle measurements were made over an area several orders of magnitude larger than that used in the SEM analysis. Furthermore, apart from the chemical reactions with activated molecules, the films were subjected to heat during the CD treatment. This certainly led to changes on a scale too large to be observed in the micrographs, such as smoother and more uniform macrotopography, which resulted in lower measured values of γ_d in treated films versus untreated films.

The composite films treated by CD showed rising values of the total surface tension as the CD potential increased, especially at the lower film R_s value, as can be seen in Figure 3(a). These results show that films stretched at 5 rpm were exposed for a longer time to CD, thus exhibiting a higher γ_t value than the composite film treated at 9 rpm. However, the average total surface tension of the composite films treated at 5 rpm and 12 kV ($\gamma_t = 44.6 \pm 3.2 \times 10^{-3}$ N/m) was slightly lower than that at 9 rpm ($\gamma_t = 45.7 \pm 1.2 \times 10^{-3}$ N/m).
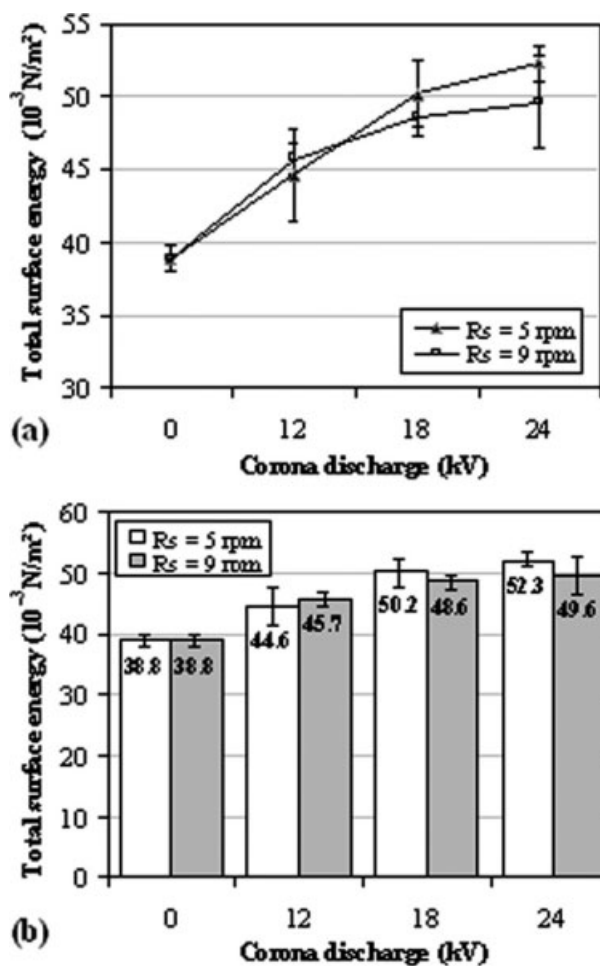
Figure 3 γ_t of the composite films, without and with CD treatment, at $Rs = 5$ rpm and $Rs = 9$ rpm: (a) graph and (b) bar chart.

When these data are plotted in a bar chart, as in Figure 3(b), it becomes clear that, although the average γ_t value for the 5 rpm sample treated at 12 kV was lower than that for the 9 rpm one, the corresponding error bars were wider for the former. They were also the widest among all the CD intensities. Also, the possibility should be considered that, at this relatively low voltage (12 kV) in comparison with 18 and 24 kV, the difference in the treatment residence time at 5 and 9 rpm did not significantly affect γ_t of the composite films. This idea is supported by the trend at higher voltages, at which the difference in the effect of R_s on γ_t increased with the discharge voltage, as can be seen in Figure 3(a).

The stability of the surface energy of the composite film following CD treatment was monitored with the aim of assessing the rate of decline of this property as a function of the storage time because not all the substrates were printed immediately after surface modification. A simple way to study the stability of surface energy is monitoring of the change in
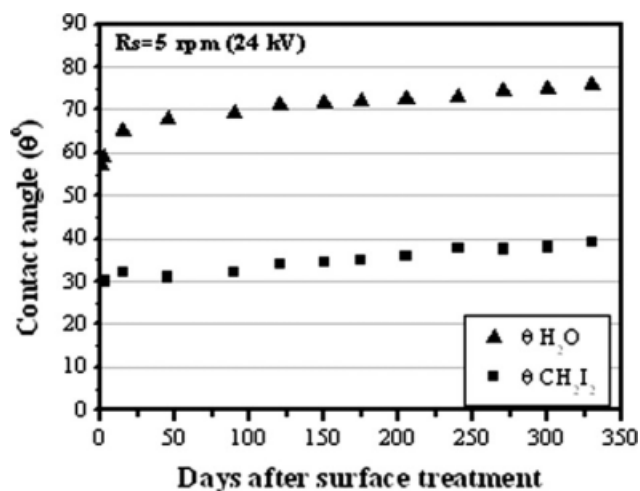
Figure 4 Stability of the contact angles of water and CH_2I_2 on the CD-treated composite films after treatment by CD during storage under environmental conditions.

the wettability of the film surface, as described in the Experimental section.

Figure 4 shows the contact angles of the composite film stretched at $R_s = 5$ rpm and treated with a 24-kV electrical discharge versus the storage time up to 11 months. The values obtained with CH_2I_2 were lower than those with water, as the film was more easily wetted with CH_2I_2 because its surface energy is lower than that of water.

The contact angles for both liquids increased similarly as a function of the storage time. However, the contact angles obtained with water on the film surface showed a more significant increase (33%) between the first day after the CD treatment (contact angle = 58°) and the last day of the experiment (330 days after the CD treatment) when the contact angle was 77°. This shows clearly that the decay in the number of polar species on the surface was more pronounced than the decay in the number of species contributing mainly dispersion forces.

The γ_t values for the composite film treated by CD ($R_s = 5$ rpm and electrical potential = 24 kV) are plotted against the storage time for 11 months under environmental conditions in Figure 5. The surface energy of the treated composite film showed a decrease from 52×10^{-3} (zero storage time) to 44×10^{-3} N/m (storage time = 11 months), that is, a decrease of 18%, the greatest reduction occurring in the first 2 weeks, during which the γ_t value fell from 52 to 48×10^{-3} N/m. The surface energy remained almost constant over the next 3 months, changing from 48 to 47×10^{-3} N/m, and then decreased very slowly over the remaining 9 months, as can be seen in Figure 5.

These results indicate that the environmental conditions during storage influenced this property, although the ambient temperature had no influence on the physicochemical changes on the film surface. On the other hand, the absorption of water into a composite film from humid air can cause a volume expansion, and according to Jacques,[26] a wet period followed by a dry period can cause a volume contraction of the surface layers, setting up higher mechanical stresses within the material. Cycling of the conditions can eventually result in fatigue, setting the stage for further chemical and mechanical changes or degradation.

Analysis of ink adhesion

Figure 6 shows the composite films produced with and without treatment by CD (with applied voltages of 18 and 24 kV) at R_s values of 5 and 9 rpm after the offset ink adhesion or peeling test.

The offset ink had a darker tone when applied to the composite film treated at $R_s = 5$ rpm [Fig. 6(a)], and this indicated its greater absorption capacity versus that of the film treated at $R_s = 9$ rpm [Fig. 6(b)]. This result confirms those obtained by Danella et al.,[27] who observed greater ink absorption on films with high surface energy and irregularities detected through the coefficient of friction.

According to the qualitative peeling test of offset ink adhesion to the composite films (ASTM D 3354), the CD treatment at the lower R_s value (5 rpm) led to stronger adhesion than that at 9 rpm. This can be seen in the sample in Figure 6(a), which showed fewer white sites of removed ink in the test region, whereas the transparent tape that was peeled off showed a smaller amount of ink removed than that in Figure 6(b). The improved adhesion can be attributed to the higher surface energy observed on the
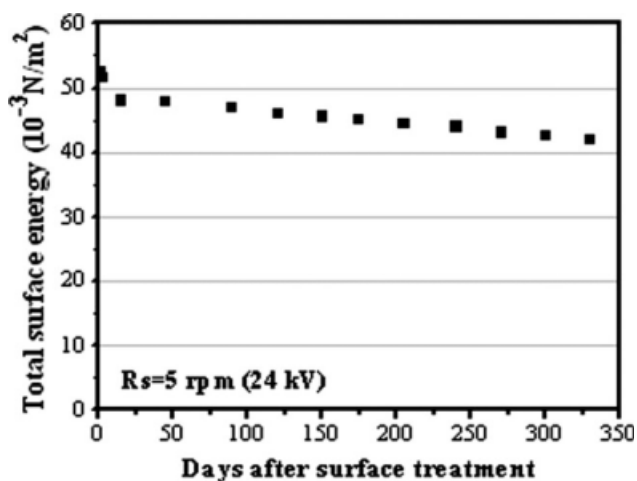
Figure 5 Stability of γ_t of the composite films after treatment by CD during storage under environmental conditions.
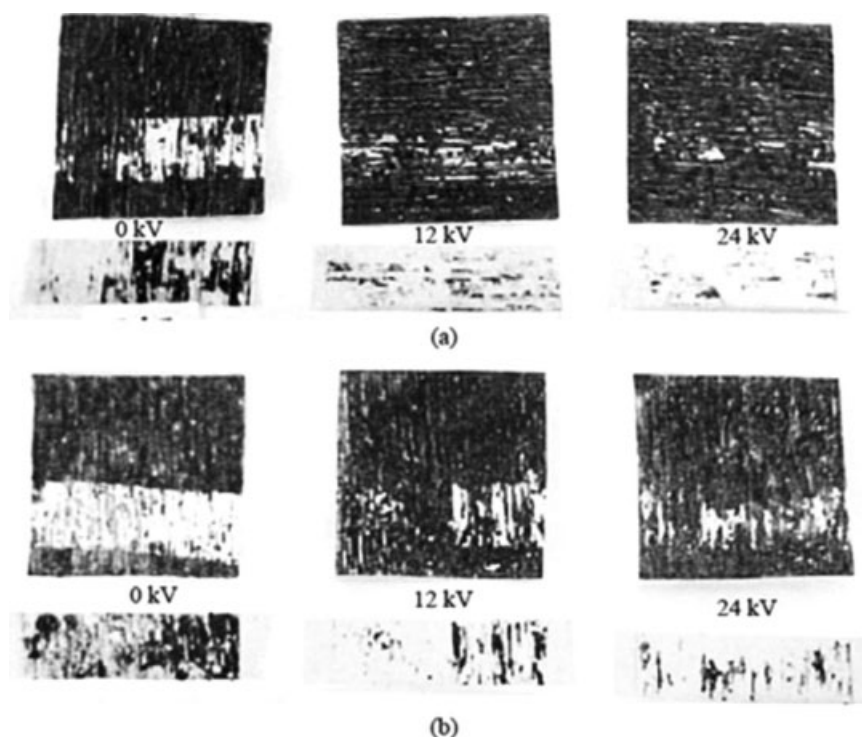
Figure 6 Tests of the adhesion of offset ink onto composite films with and without CD treatment at (a) 5 rpm and (b) 9 rpm.

film treated at 5 rpm; this is related mainly to the higher polarity of the surface groups.

In addition, the peeling test showed that films treated by CD adhered strongly to offset ink, and the untreated films adhered only very weakly, the ink peeling from the printed surface.[4,6] These results were again consistent with the low surface energy of the untreated films.

CONCLUSIONS

Greater irregularity, manifested as roughness and a variety of nonuniform features, was observed by SEM in the microtopography of the surfaces of PP composite films after surface treatment by CD. $CaCO_3$ filler particles appeared more concentrated and not covered with polymer at the surface of the treated films, and this indicates that this treatment exerts an active influence on this mineral filler.

A composite film treated at $R_s = 5$ rpm with applied voltages of 18 and 24 kV showed a higher γ_t value than a similar film pulled at 9 rpm and, therefore, adhered more strongly to offset ink. At both R_s values, all the treated samples showed higher γ_t values than the untreated samples, and this was essentially due to the sharp increase in γ_p because γ_d decreased with the CD treatment.

As for the stability of the improved surface tension, prolonged storage of composite films resulted in a γ_t loss of 18% in treated films, which was clearly demonstrated by an increase in the water contact

angle on the composite film from 57° immediately after treatment to 77° after 11 months of storage; this indicated a loss of wettability.

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