Synthetic Paper from Plastic Waste: The Effect of $CaCO_3$ on Physical, Surface Properties and Printability

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Summary: This article is a description of recent work in the development of composite sheet materials from blends of recycled high-impact polystyrene (HIPS) and high-density polyethylene (HDPE), with a view to using them as synthetic paper for the printing trade. Four monolayer films of differing composition were characterized in terms of their physical and surface properties. They were further evaluated compared with each other and with commercial synthetic and cellulose papers, to discover relationships between $CaCO_3$ filler loadings, film structure and properties that could lead to improvements. In terms of their whiteness and water base inks printing properties, these sheets were generally inferior to the cellulose and synthetic papers. Notwithstanding this, in some tests they showed superior quality; thus, in offset printing, the high surface gloss, probably due to the HIPS content, made the colors brighter in some mono-oriented film samples.

Keywords: fillers; film surface properties; polystyrene blends; recycling; waste

Introduction

In recent years, the plastics component of municipal waste has expanded into a veritable 'plastic mountain', creating an urgent and growing problem for present-day society and future generations.[1,2] Any solution to this problem should, of necessity, include the development of the recycling techniques necessary for plastic waste to be used as a raw material in the fabrication of new goods. Although the processing of waste plastic has improved in several ways, in practice the poor mechanical properties and fluctuating economic value of the recycled products can limit their versatility. The production of synthetic paper from waste plastic helps to preserve the environment in two ways, by cutting the consumption of natural resources and by reducing the volume of used plastic thrown into the municipal garbage.

Manufacturing synthetic paper from used plastic allows conventional cellulose paper to be substituted in a variety of applications, reducing the worldwide growth in consumption of paper, which is traditionally made from wood pulp. The rising consumption of wood leads to the clearing of more and more native forest to make room for plantations of the tree varieties used in paper-making. Another issue is the large number and quantity of chemical additives needed in the traditional process – disposing of these additives can cause serious pollution problems.[3–6]

During the experiments carried out prior to these presented in here, it was observed that when HIPS was mixed into polypropylene (PP) film, some of its properties were enhanced, such as opaqueness, stiffness and surface polarity following corona treatment. This discovery motivated a study into the feasibility of making synthetic paper with HIPS as the base polymer, replacing the PP matrix.[8] We have then

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tested blends of post-consumer HIPS and HDPE in various proportions, with inorganic fillers and other additives. A variety of comparative tests were carried out on the films produced at each composition, using commercial cellulose and synthetic papers as standards, so as to identify the most suitable composition for fabrication of synthetic paper for graphic printing.

In this article, we report and analyze the results from tests of microscopic surface morphology, whiteness, surface energy and printing quality (for offset, silkscreen and ink-jet printing), carried out on films with one type of $CaCO_3$ filler used in different proportions.

Experimental

HDPE resin, with an average melt flow index (MFI) of 0.23g/10min, was obtained from urban plastic waste, consisting chiefly of post-consumer rigid bottles, collected at the selective waste depot located in the UFSCar campus. The used disposable HIPS cups, average MFI of 5.0 g/10min, were collected from commercial establishments in São Carlos city, and the $CaCO_3$ filler was Super-Micro KRVA from Imerys. The additives used were: styrene-butadiene multibloc compatibilizing agent (SBS, Basf); Dimodan internal antistatic agent (Danisco Ingredients Inc), and TiO_2 in the rutile crystal structure, donated by Indústria Cardinali S/A.

The HIPS cups were first ground in a primary grinder, MAK 250 (Kie), the resulting flakes being washed in clean water at room temperature, dried in a fanned oven at 50 °C and finally agglomerated in a Lombard 162 agglutinator. The HDPE bottles were initially ground to more easily cleanable pieces, then washed in clean water at room temperature, dried and shredded into flakes, as described in previous publications.[2,7] The additives were mixed into the resins in a *Drais* high-speed mixer (MH), in the proportions given in Table 1.

The composites were pressed into plates, ground and then extruded in a single-screw extruder (Gerst 24 × 25D), with a temperature program of 170/200/210 °C, to finally being chopped into pellets. To produce the films, the same extruder with a flat film die attached was used, and temperature profile of 170/200/210 °C and 210 °C in the die. The screw rotation speed was 30 rpm, the film being cooled with compressed air, at a pressure of 2 atm, on emerging from the die, and drawn at a speed of 14.5 m/min. Finally, all films were then subjected to electric corona discharge (ECD) treatment on both surfaces at the same and constant conditions.

Film surface morphology was analyzed with a Zeiss DSM 940A scanning electron microscope (SEM), with an energy-dispersive X-ray spectroscopy (EDS) attachment for micro-analysis. The surface energy (γ) of the films was measured as defined in the ASTM standard D-2578, which states that the surface energy of a film is equal to the surface tension of a liquid that just wets the film, spreading out without coalescing when a drop is placed on the surface. The solutions used in this test were made up from diethylene glycol and formamide, whose surface tensions are 36 and 54 dynes $\cdot$ cm^{-1}, respectively. Specifically for γ measurements, the samples were divided into two separate lots, which were treated with ECD at two different intensities, high

Table 1.
Proportions (wt%) of constituents of synthetic paper films.

Sample	HIPS (%)	HDPE (%)	SBS (%)	$CaCO_3$ (%)	Anti-static (%)	TiO_2 (%)
SM 0	76.0	19.0	4.8	–	0.2	–
SM10	67.7	16.9	4.2	10	0.2	1
SM20	60.0	15.0	3.8	20	0.2	1
SM30	52.4	13.1	3.3	30	0.2	1

(HV) and low (LV) voltage. The value of γ of the treated films was measured periodically to monitor its decay during storage. The albedo or whiteness index (w.i.) of each film was measured in conformity with ASTM E313, using an spectrophotometer *Spetroplus* designed for this purpose, calibrated with a black and a white standards.

Printing Tests

In all printing tests, the printability and the adherence of the ink to the synthetic paper samples were assessed qualitatively as excellent, good, regular or poor. To test adherence, a piece of adhesive tape (Adere, Brazil), 1.5 cm wide, was applied to the printed surface, the small bubbles that formed under the tape eliminated manually and a rolling weight was then passed over the tape. After which the tape was pulled off each sample and the smaller the amount of ink removed by the tape, the better was the assessment.

In offset tests, samples were printed in an Adast 725 automatic offset printer. First they were fixed to adhesive paper and placed in the printer as part of a routine print run. In screen test (*silkscreen*), the films were affixed to a screen of porous fabric that was blocked with a stencil, with a word or drawing cut out. Ink was passed through the screen to reproduce the image on the paper, and excess ink was removed. The serigraphic ink used was a water-based emulsion. For screen prints, the strip of tape was fixed at the side of the printed figure, after the test. In ink-jet test, square samples of 10 cm^2 were cut from film papers and glued in the center of an A4 cellulose paper. The printer was set to *normal* quality and used to print the same figure on every sample, to enable subsequent comparison of its printing quality.

Results and Discussion

SEM micrograph of the $CaCO_3$-loaded film SM20 (Table 1) is shown in Figure 1, together with its EDS microanalysis of the dispersion of Ca. The large, clear particles

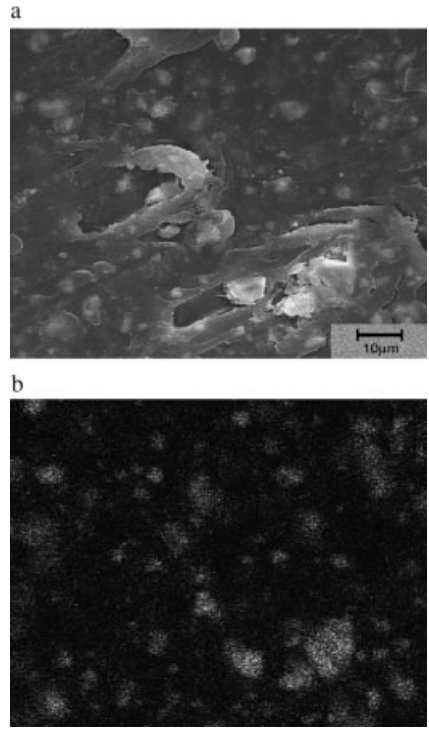

Figure 1.
SEM micrographs of film SM20 : (a) surface morphology; (b) microanalysis of Ca.

are of $CaCO_3$, as can be seen in more detail in the corresponding figure on the right. Note that these particles form few clumps, assuming an average size for single particles of about 3.0 μm, indicating that the filler is well dispersed in the polymer matrix of the blend. With the exception of SM10, the samples exhibited a rather homogeneous distribution of the inorganic filler, demonstrating that the additives have been incorporated efficiently into the blends.

By comparing Figures 1 and 2, and the micrographs of the other samples not shown here, with Figure 3, in which the micrograph of a commercial synthetic paper (*CsP*) is displayed, it is apparent that all the films have similar surface morphologies. However, small flaws were seen across the entire surface of the films under study, which were attributed to the formation of microcavities and die lip build-up during film extrusion. Material could be seen accumulating at the lips of the die,

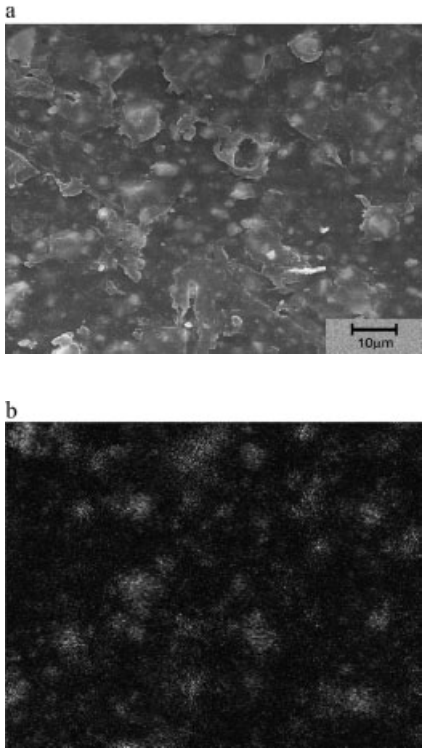

Figure 2.
SEM micrographs of film SM30: (a) surface morphology; (b) microanalysis of Ca.

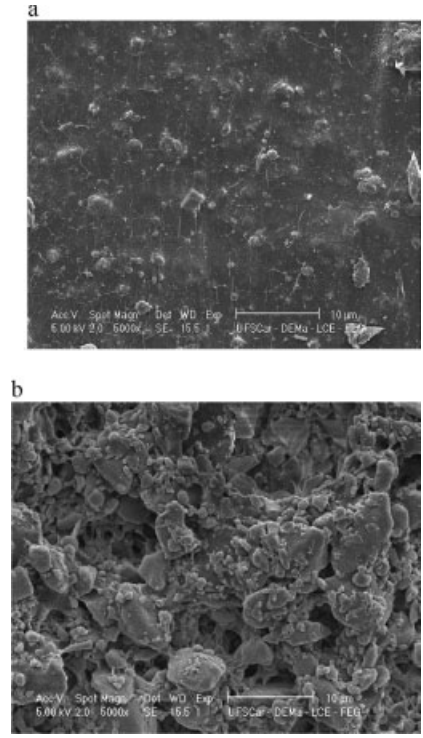

Figure 3.
SEM micrographs of *CsP*; (a) side A, (b) side B with coating.

which became detached from time to time, dragged along by the flow of the film. This process was observed macroscopically, and it is reasonable to suppose that the film surface also had microscopic flaws.

Some of the surface flaws could be seen to form at the interfaces of the polymer matrix with the filler particles, owing to the intense shear forces in those regions; i.e. microcavities. This is most evident in the film containing 20% $CaCO_3$ (Figure 1(a)), in which they were seen in greatest quantities. In contrast, in the *CsP* tested, no similar defects or microcavities were observed on either surface, A or B. In that sample, side B is coated with a layer that provides the surface with regular, uniformly distributed cavities, to act as a key for the ink.

Whiteness

The measured whiteness indices (w.i.) of the samples are displayed in Table 2, where all the films are seen to have similar values. This may be explained by the presence of 1% of the white pigment TiO_2 in all the $CaCO_3$-loaded samples, irrespective of the filler content. On the other hand, the lowest w.i. was shown by sample SM0, possibly because it contained neither filler nor pigment particles.

It was recognized that factors other than the presence or otherwise of inorganic particles in the film might be responsible for the variation in w.i, and the potential influence of film microstructure was analyzed. As mentioned above, larger numbers of microcavities were observed in SM20 than in the other films, and this could explain the slightly higher w.i. values of this film (with or without ECD). This hypothesis is strengthened by the observation that these films, and others consisting of PP with $CaCO_3$ filler and an antistatic additive, exhibited much larger numbers of

Table 2.
Measured whiteness and surface energy of samples and control papers.

Sample	Whiteness (w.i.)		Side	Surface energy γ (dynes/cm)				
	without ECD	1 day after (LV)		without ECD	time after LV		time after HV	
					1 day	7 months	30 days	8 months
SM0	28.1	24.6		31	43	41	—	—
SM10	28.7	27.4	int	33	47	45	49	49
			ext	33	39	39	45	45
SM20	29.8	28.5	int	33	41	39	53	47
			ext	33	37	41	45	41
SM30	28.2	27.1	int	33	41	41	47	—[a)]
			ext	33	37	37	47	—[a)]
CellP	105.4			45				
CsP	49.3		A	>50 < 54				
	77.6		B	>54 < 56				

[a)] test not done for lack of material.

microcavities and a marked increase in whiteness when they were subjected to a second orientation in the transverse direction (perpendicular to that in which they had been pulled).[8] On the other hand, it cannot be ignored that the samples were made from recycled material. This could contain a variety of impurities and degradation byproducts that would impart a variable degree of yellowing to the blend and thus contribute to the differences in whiteness from film to film as well as to the very lower values of w.i. compared to those of commercial cellulose and synthetic papers.

Surface Energy

The surface energy results are also presented in Table 2, for all the synthetic paper films, at various times after ECD treatment or untreated, plus those for the controls. All the paper films produced from the blends exhibited, although high energies when ECD treated, lower values of γ than *CsP*, with the only exception of SM20 treated with high voltage. Interestingly, samples that were not surface-treated with ECD gave practically identical results, irrespective of the filler load, indicating that putative variations in the surface roughness due to $CaCO_3$ particles had no significant influence on γ measurements in untreated films. By contrast, in the treated films, the mineral filler does seem to have affected γ, especially when the high values obtained with a small amount of filler (SM10) are compared with the somewhat lower energies of films with heavier inorganic particles loads (SM20, SM30).

It is worth noting that sample SM0, without $CaCO_3$ or TiO_2, exhibited the lowest surface energy of all when untreated, yet its value of γ was raised substantially by ECD treatment, making it equal to or greater than that of filled samples. However, the differences between the surface energy values of the various samples do not appear to have affected their printing properties, whereas the presence or otherwise of mineral particles had a profound effect, as will be discussed in the next section.

As already mentioned, the same surface energy test was repeated after a long period, to assess the capacity of the films to maintain the value of γ imparted by the ECD. Examination of the table shows that film surfaces that responded well to the treatment retained most of their energy after storage for 7–8 months. In the case of SM30 subjected to ECD (HV) treatment, the second test could not be performed as there was insufficient material, but from the general trend of results, good stability of γ may be expected here too. In Table 2, a general slight fall in γ can be observed over time; nonetheless, all samples retained their high surface energy (~40 dynes/cm). This is desirable in the printing trade, where in practice it is known that a paper whose

surface energy does not fall will retain its good printing quality.

Printing Tests

Offset Printing

As described above, print adherence was classified qualitatively (excellent, good, regular or poor) by observing the amount of ink removed by adhesive tape. In offset printing, all samples containing filler showed excellent adherence, including those not treated with corona discharge, irrespective of the amount of filler, in contrast to the results obtained in previous work.[9] Those studies involved films made from PP/HIPS/$CaCO_3$ composites, with lower proportions of HIPS in the blends (14, 25 and 33%) and another type of calcium carbonate filler (Carbital 700, which has larger particles), and the printing quality was poor in all samples not treated with ECD.

A few photographs of these printing tests are included, to give the reader a better idea of the results obtained. For offset, Figures 4 and 5 present results for samples SM30, *CsP* and SM0.

Figure 4 is representative of the excellent print quality and adherence of the solvent-based offset ink seen on all synthetic paper samples, surface-treated or not. It can be seen clearly that the tape has not removed any of the ink. The commercial synthetic paper (Figure 5(c)) showed excellent printability on both sides (A and B) and again the adhesive tape did not remove any ink. As expected, similar excellent print quality and ink adhesion were observed when plain A4 cellulose paper was tested in the same way.

On the other hand, the sample of film that contained no mineral filler particles, SM0, showed poor ink adherence, as can be seen in the photograph of this test in Figure 5. In this case, the surface treatment had some positive effect, but it was insufficient to entirely prevent the removal of ink by the tape. This indicates that the $CaCO_3$ filler is at least as important as corona treatment in producing a film with good offset printability.

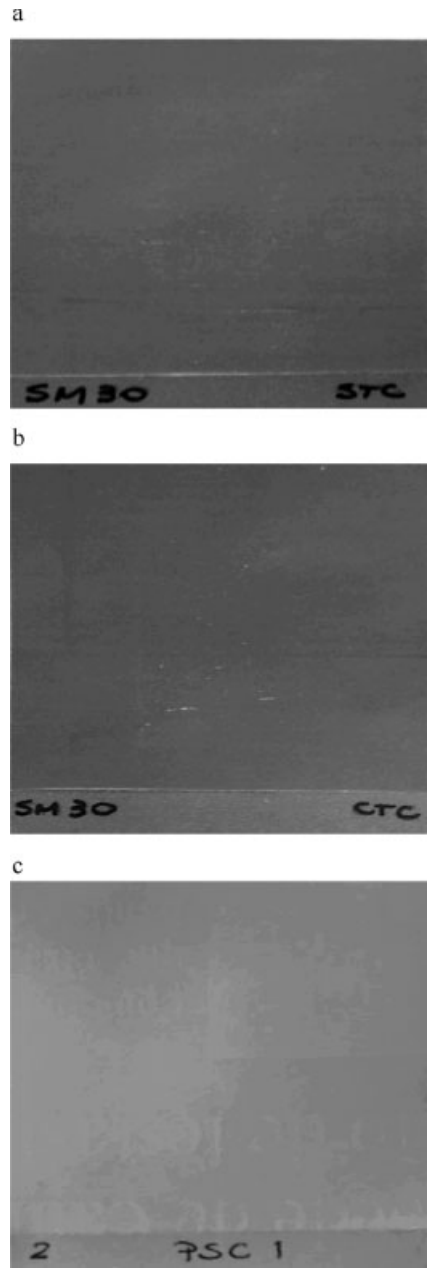

Figure 4.
Offset print on film sample SM30, (a) untreated and (b) surface-treated with ECD, and (c) commercial synthetic paper, coated side B.

Screen Printing (Silkscreen)

The screen printing results, illustrated in Figures 6 to 8, showed that once more an excellent printing quality and ink adhesive-

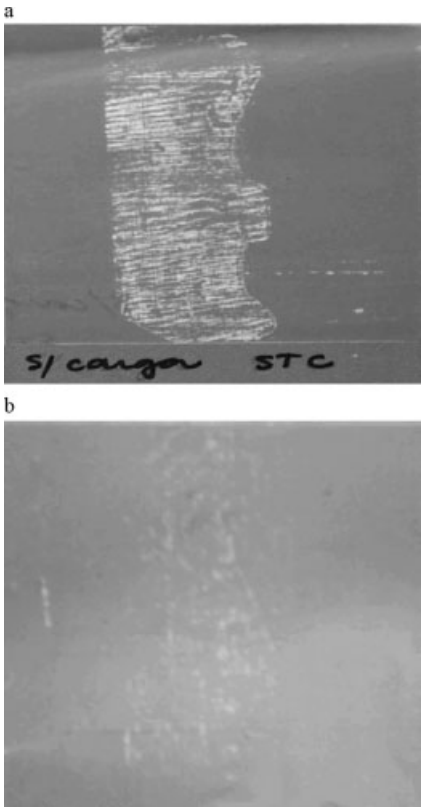

Figure 5.
Offset print on film sample SM0, (a) untreated and (b) surface-treated with ECD.

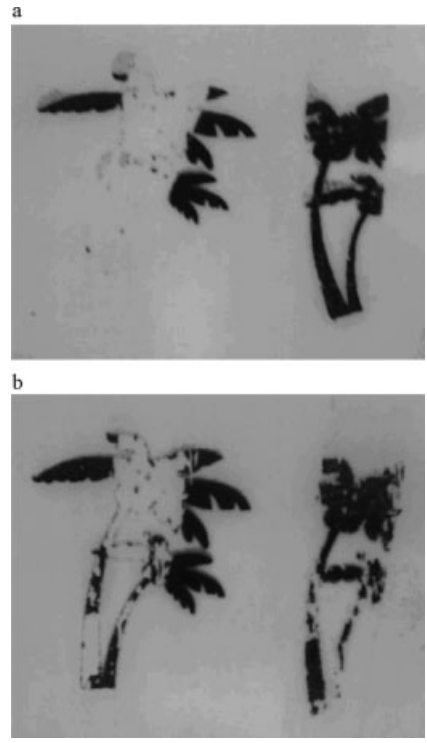

Figure 6.
Silk-screen printing on samples of SM0, (a) untreated and (b) ECD treated.

ness were achieved, not only on the commercial papers, *CellP* and *CsP*, but also on every synthetic paper with $CaCO_3$ filler, even without surface treatment. As the adhesive tapes glued at the side of the prints show, none of the ink was removed from any of these samples. This confirms that the presence of the type of filler employed here has a favorable influence on the printing characteristics of the film surface, with non-water-soluble inks, regardless of the filler content in the HIPS/HDPE blend.

That influence is evident when Figure 6, which shows the film without any inorganic filler, is compared with the other photographs. In this case, not even the corona treatment enabled the serigraphic ink to adhere well to the surface. The adhesive tape glued beside the print after the test, as described in the test protocol, shows quite clearly the poor adhesiveness of the ink.

Ink-jet Printing

The qualitative results of this test may be compared in Figures 9 and 10. Around 24 h after printing, some of the printed images still looked wet, the ink having a gel-like appearance. Thus, in these cases, the ink dried too slowly for these films to be suitable for this application.

Some samples were practically incapable of being printed, as can be seen for the SM10 film without ECD treatment in Figure 9(a). Indeed, this figure is representative of the poor ink-jet printing quality exhibited by all the samples not treated with ECD, whether or not they contained $CaCO_3$. The surface treatment significantly enhanced the printing on the synthetic paper samples with the water-soluble ink used for this process, but the quality remained poor, with the one exception of sample SM30, which is illustrated in Figure 9(c).

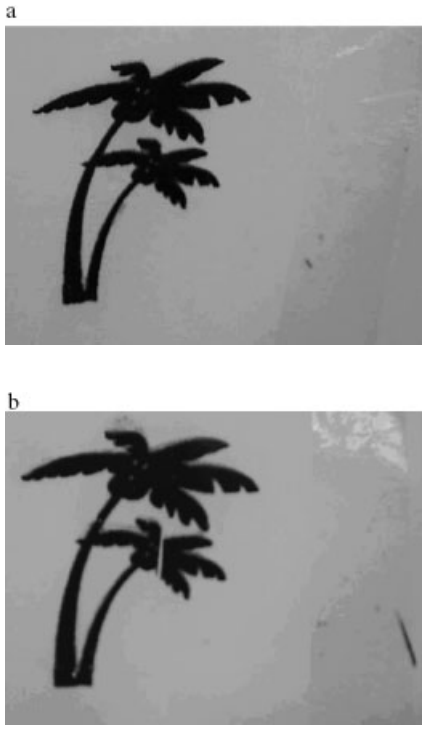

Figure 7.
Silk-screen printing on samples of SM10, (a) untreated and (b) ECD treated.

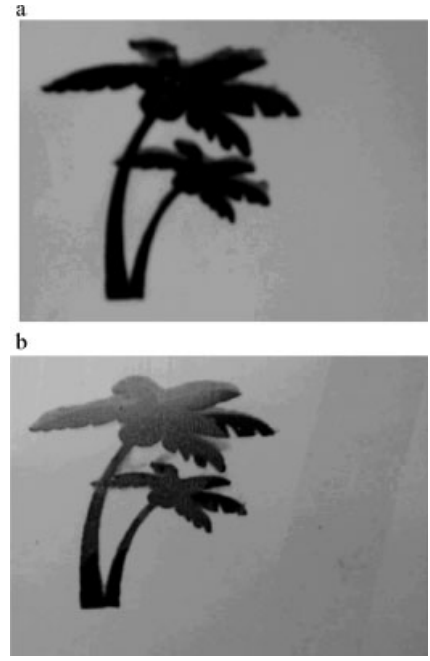

Figure 8.
Silk-screen printing on ECD-treated surfaces of samples, (a) SM20 and (b) SM30.

It was actually impossible to perform the adhesiveness test on the synthetic paper samples, including the control, *CsP* (see Figure 10), because of the ink-drying problem. Evidently, this particular commercial synthetic paper is not appropriate for ink-jet printing, since on side A of this sheet the ink failed to dry and smeared, while on side B there was an excess of ink, probably due to the coating on that side, which blurred the details of the printed image. As expected, the same test gave perfect results on *CellP*.

Conclusions

Surface examination by SEM of the synthetic paper samples prepared in this study revealed a morphology closely resembling that of the uncoated surface of a commercial variety of synthetic paper (*CsP*). Comparing the images, the inorganic filler content of *CsP* was closest to that of the HIPS/HDPE composites with the highest $CaCO_3$ content studied. The degree of dispersion and homogeneous distribution of the inorganic particles observed by micro-analysis indicated that the method used to incorporate the additives in the high-speed Drais mixer was highly effective.

The whiteness of the synthetic paper was practically uninfluenced by the mineral filler, in the range 10–30% by weight. This was attributed to the fact that the white pigment TiO_2, maintained at a constant content of 1% by weight, had much more effect on the whiteness index than did the $CaCO_3$ filler. The effect of surface imperfections, mainly microcavities, and the role of discoloration by degradation byproducts were also considered, but no definite conclusions can be drawn in this respect without a fuller analysis.

For ink-jet printing with a water-soluble ink, these films had very poor properties,

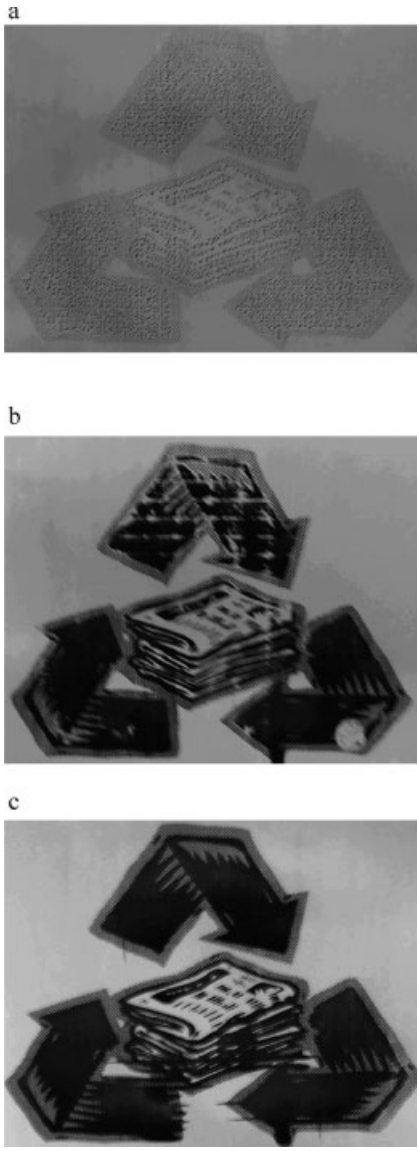

Figure 9.
Ink-jet printing on film SM20, (a) untreated and (b) ECD surface treated; (c) SM30 ECD surface treated.

every composition (SM10, SM20 and SM30) showing several faults, and even *CsP* was inadequate for this type of printing. By contrast, all these blends of recycled HIPS and HDPE, plus *Super Micro KRVA* $CaCO_3$, generated films with very good characteristics for offset and screen printing, irrespective of the $CaCO_3$ content and whether or not their

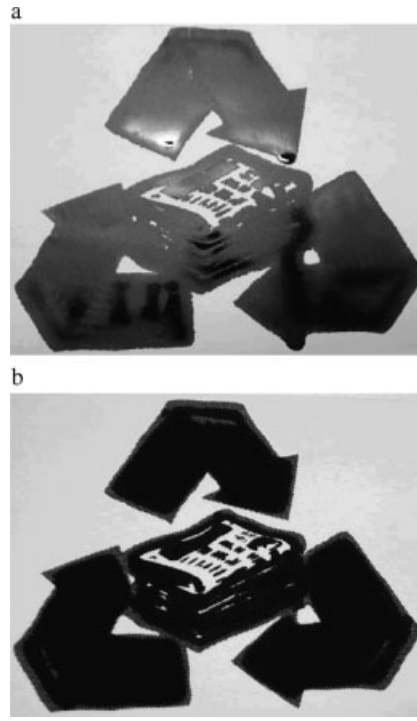

Figure 10.
Ink-jet printing on *CsP* samples, (a) side A and (b) side B, with coating.

surfaces were corona-treated. For these two printing processes, these films were comparable in printability and ink adhesiveness to the commercial papers used as standards, *CsP* and *CellP*, and could be used as substitutes for those commercial synthetic and cellulose products.

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