

# A Study of the Recycling and Stability of Flexographic Photopolymer Plates

Cristina C. Cordeiro,<sup>1</sup> Adriano M. Bernardin,<sup>2</sup> Luciano Da Silva,<sup>1</sup> Márcio A. Fiori,<sup>1</sup> R. Benavides,<sup>3</sup> Leonardo W. Oenning,<sup>1</sup> Marcos M. S. Paula<sup>1</sup>

<sup>1</sup>Laboratório de Síntese de Complexos Multifuncionais, Universidade do Extremo Sul Catarinense, Criciúma 88806-000, Santa Catarina, Brazil

<sup>2</sup>Departamento de Engenharia de Materiais, Universidade do Extremo Sul Catarinense, Criciúma 88806-000, Santa Catarina, Brazil

<sup>3</sup>Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna H. 140, Saltillo, Coahuila, México

Received 25 March 2009; accepted 9 March 2010

DOI 10.1002/app.32406

Published online 3 June 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Flexographic photopolymer plates have a wide range of commercial applications despite the fact that recycling of such materials is difficult. In consequence, there is a large bulk of leftover material around the world. In this research, the photopolymer plate waste products, identified as styrene-butadiene rubber (SBR)/polyester are blended into common polypropylene (PP) and ethylenevinylacetate (EVA) resins at different loading percentages. PP and EVA are used as the polymer matrix and the recovered styrene-butadiene rubber (SBR) material as the filler. Evaluation of the mechanical, spectroscopic, thermal and chemical properties, as well as morphology, is done by means of scanning electron microscopy (SEM).

Mechanical results show that elongation strongly depends on the matrix polymer: the greater the amount of solid-sheet photopolymer (SSP), the smaller the elongation. No specific interactions were detected; however, thermal degradation and transitions were displaced, suggesting some miscibility. More homogeneity is seen for EVA blends, with no significant chemical attack detected. It is possible to reuse these recycled materials in blends with PP and EVA resins. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1436–1441, 2010

**Key words:** blends; recycling; thermal stability; flexographic photopolymer plate; waste

## INTRODUCTION

The recycling of polymeric materials is a problem that has not been solved adequately. Only 30% of polymeric waste is recycled as potential sources of chemicals and energy.<sup>1–3</sup> In Brazil, it is estimated that 1150 thousand tons of plastics are consumed each year, but only 17.5% is reinserted into the production chain as input material.<sup>4</sup>

With increasing plastics consumption, the main challenge is to keep pace in waste recovery. Chemical recycling, via thermal and/or catalytic conversion, has been recognized as an ideal approach that could significantly reduce the net cost of disposal of industrial plastic wastes.<sup>2,3</sup> Simple mechanical blending works as well.<sup>5</sup>

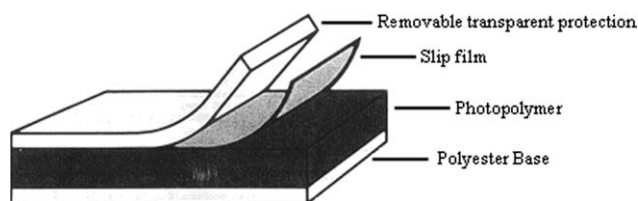
The flexographic printing plate industry uses large amounts of photopolymerized materials. These are used as cover sheets that protect the virgin surface of the plates, a curable layer composed of an elastomeric and photosensitive copolymer, styrene/butadi-

ene, and other additives.<sup>6</sup> Properties of photopolymeric plates depend largely on processing conditions<sup>7</sup> and material composition.<sup>8</sup> Figure 1 shows a schematic representation of a solid-sheet photopolymer (SSP) material.

Despite great demand for industrial use of these materials, there are no relevant publications in the open literature regarding recycling or post consumption of flexographic printing plates. However, it is known that reused SBR, when added to another resin in small quantities, behaves as a filler to increase stiffness and make the material more brittle.<sup>9,10</sup> The physical and mechanical properties of blended SBR are sensitive to small variations in the amount of individual components.<sup>11</sup> EVA copolymers constitute good counterparts for blends with unsaturated elastomers such as SBR because of their excellent mechanical properties, as mentioned by Soares et al.<sup>12</sup>

On the other hand, ethylene propylene diene (EPDM) has been reinforced with PP, which has a significant effect on the rigidity of the material, especially after addition of compatibilizers.<sup>13</sup> In this case, PP has also been modified by addition of 5–10% of epoxidized natural rubber.<sup>14</sup> Moreover, the properties of cracks, analyzed during mechanical evaluations,

Correspondence to: M. M. S. Paula (mms@unesoc.net).



**Figure 1** Schematic structure of a typical solid-sheet photopolymer plate.

were also modified when nonmetal fibers from thermosetting recycled plastics were used with PP.<sup>15</sup>

In the present work, we report the recycling of waste products based on SSP/EVA and SSP/PP blends. The mechanical, thermal, and chemical properties were evaluated, as well as the samples morphology via scanning electron microscopy (SEM).

## EXPERIMENTAL

### Materials

Solid-sheet photopolymer plates (SSPs) were collected from local industry and used in their unmodified form. The SSPs were cut into small pieces and micronized cryogenically in liquid nitrogen at  $-180^{\circ}\text{C}$  to obtain a powder with particle size less than 24 mesh ( $\sim 0.5$  mm). Particles were dried to constant weight at  $90^{\circ}\text{C}$  before preparation for use in blends.

### Blends preparation

Blends were prepared by adding the dried micronized polymer plates to EVA (from Plásticos União S.A., Brazil) or PP (Braskem, Brazil) at different percentage rates according to Table I.

Pellets were created using a single spindle extruder (OZ-E-EX-L-22, Orizon). The processing parameters, such as temperature and spindle speed, were adjusted in accordance with the blend compositions and kept constant for each blend. Spindle rotation ranged between 80 and 120 rpm. Temperature varied between  $140^{\circ}\text{C}$  and  $155^{\circ}\text{C}$  with  $5^{\circ}\text{C}$  increments along the four heating zones. Extruded blends were pelletized and used to prepare molded test probes in a HIMACO LH model 150–80 (80 tons) molding machine at  $180^{\circ}\text{C}$ . The procedure for sample preparation was carried out according to ASTM D 638.

### Characterization of samples

Tensile mechanical properties were studied on standard polymer probes using dumbbell-shaped tensile-test specimens cut from the composite sheets. The stress–strain data were obtained with an EMIC model DL 10,000 tensile-testing instrument. The

equipment was maintained under the same conditions for all blend films and operated at an extension rate of 3 mm/min. The values of yield stress, tensile strength, and elongation at break (plastic deformation) were determined according to ASTM D 638. At least five specimens were tested for each sample, and the average values were reported.

The FTIR spectra were recorded in a Varian 3100 Excalibur series instrument using an attenuated total reflectance (ATR) accessory in the interval of  $400\text{--}4000$   $\text{cm}^{-1}$  and a resolution of  $4$   $\text{cm}^{-1}$ .

Thermal analysis was performed using a differential scanning calorimeter (DSC-50) and a thermogravimetric system (TGA-50), both from Shimadzu. The evaluations were carried out under a nitrogen atmosphere. DSC traces were collected after the second heating cycle (ambient to  $300^{\circ}\text{C}$  with heating and cooling ramps of  $15^{\circ}\text{C}/\text{min}$ ) to eliminate the thermal history of the probes. TGA evaluations were obtained from heating procedures of ambient to  $600^{\circ}\text{C}$  in ramps of  $20^{\circ}\text{C}/\text{min}$ . Finally, morphological and microstructural analyses were performed by means of SEM in a JEOL JSM 6390. Fractured samples, taken from mechanical evaluations, were gold coated prior to the SEM evaluations.

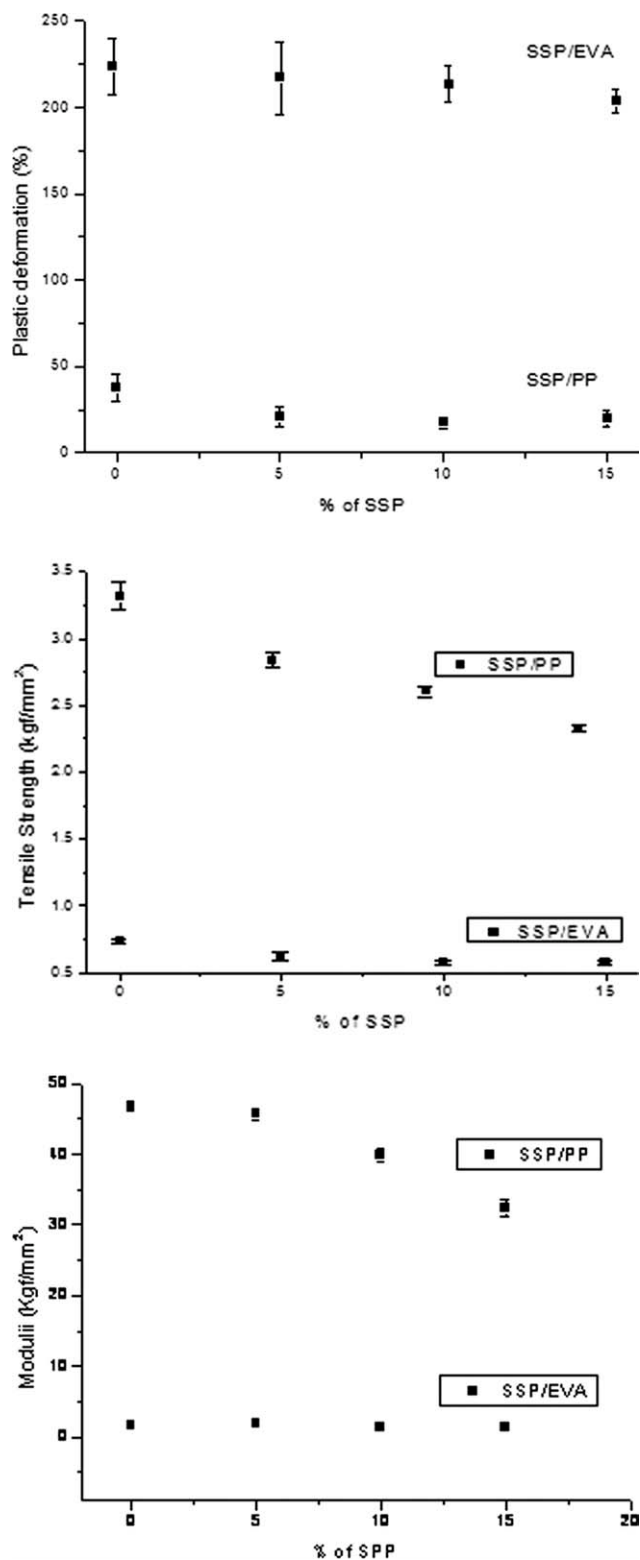
Blends were also evaluated in their resistance to chemical attack when in contact with various chemicals. The procedure was carried out following ASTM D543 directions. Three specimens of each sample were immersed in corresponding solvents at  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$  with magnetic stirring for 24 h. The chemical products used were: NaOH 10%, HCl,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , acetone, acetic acid, methanol, ethanol, *N,N*-dimethylformamide (DMF) and toluene.

## RESULTS AND DISCUSSION

Figure 2 shows the mechanical properties of each of the blends. An important difference in deformation percentage [Fig. 2(A)] can be seen between PP and EVA materials. EVA can be elongated by more than 200%, whereas PP sustains just less than 50% of deformation under stress. The tensile strength and moduli traces show similar behavior [Fig. 2(B,C)]. Moreover, the plates affect such mechanical

**TABLE I**  
Composition of Blends SSP/PP and SSP/EVA

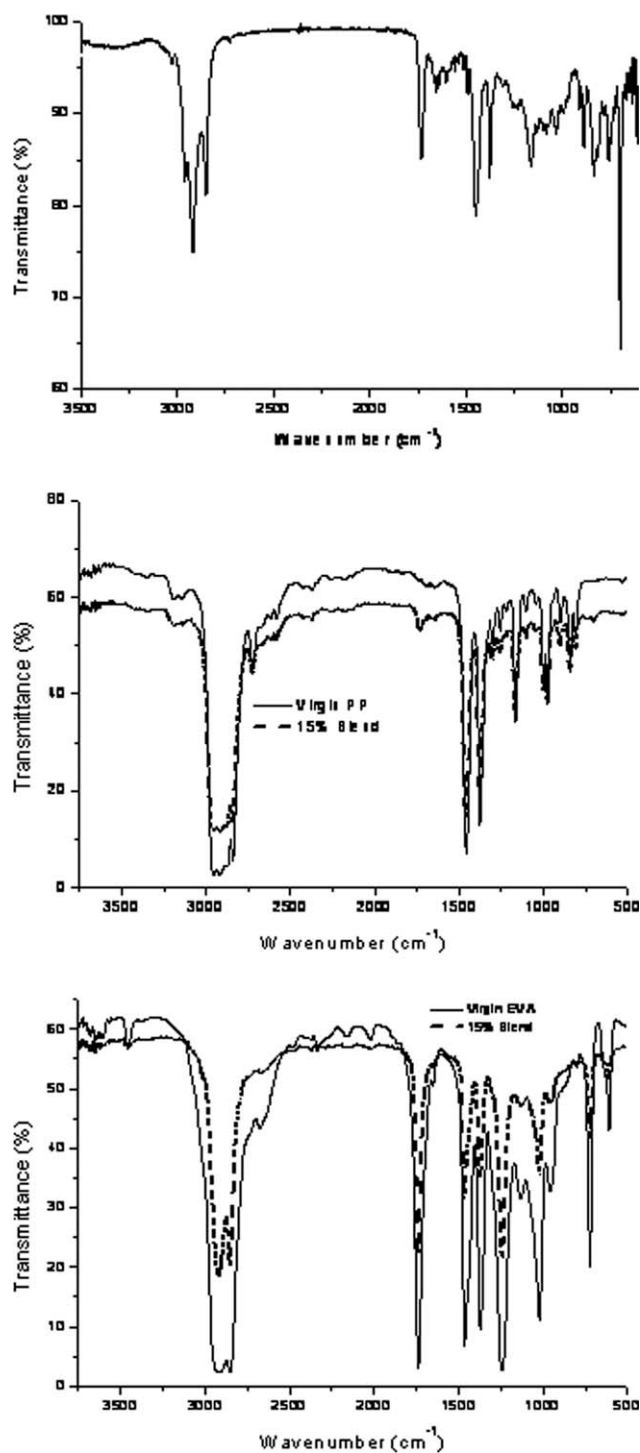
Blend	Composition (wt %)		
	SSP	PP	EVA
1a	5	95	–
1b	10	90	–
1c	15	85	–
2a	5	–	95
2b	10	–	90
2c	15	–	85



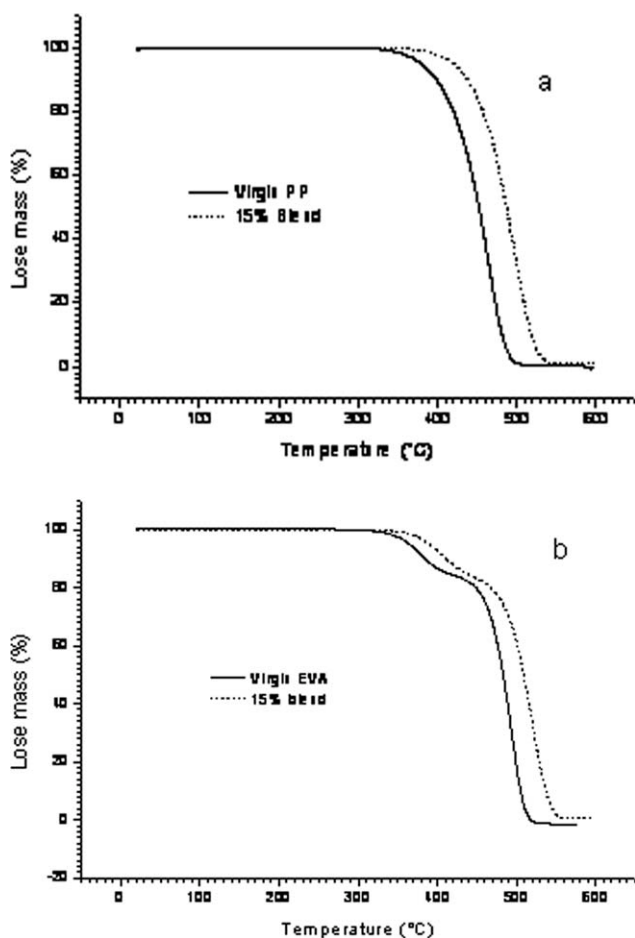
**Figure 2** Mechanical properties of blends as a function of the amount of SSP added.

properties. Although the effect is not very large, it is noticeable, especially for higher loads and reducing them for PP, but lightly enhancing them for EVA. This means that plate particles behave as an inorganic load even with crystalline PP.

The occurrence of specific interactions between the blend components has been analyzed by FTIR spectroscopy. Figure 3 gives the FTIR spectra of pure SSP [Fig. 3(a)] and both pure PP and its blend as well as pure EVA and its blend. There are no important differences between the original and blended materials. The PP blend [Fig. 3(b)] shows a small signal about  $1700\text{ cm}^{-1}$  corresponding to carbonyl



**Figure 3** FTIR spectra of (a) pure SSP; (b) 15% SSP blends with PP and (c) EVA.



**Figure 4** Thermogravimetric curves of 15% blends with PP and EVA.

species, which could come from the plates. Another small signal at  $3300\text{--}3400\text{ cm}^{-1}$  from both materials can be attributed to the presence of peroxides coming from a small oxidation process in the polymer chain. The rest of the signals from both spectra correspond to the proposed structures.

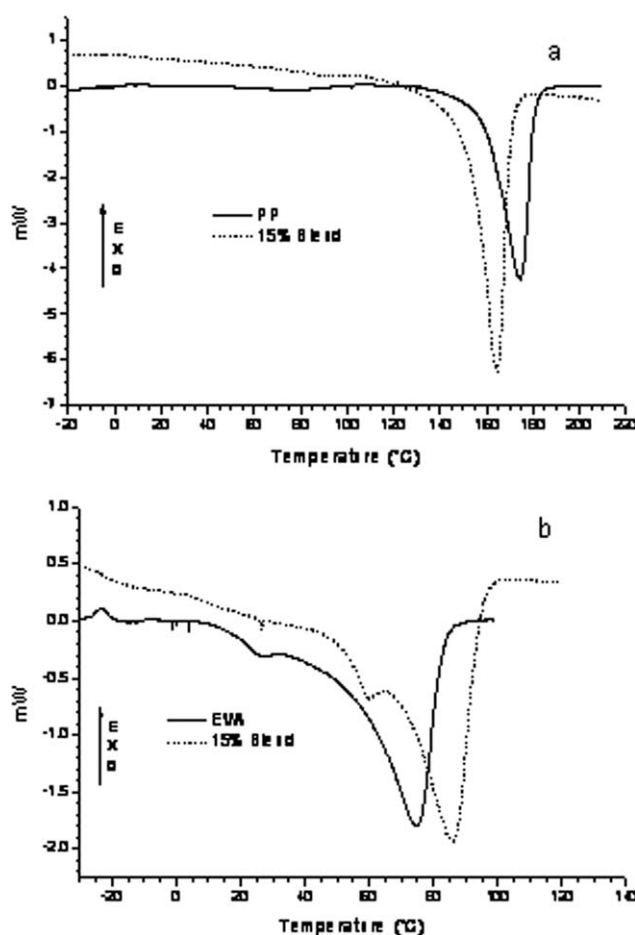
Figure 3(c) corresponds to EVA materials and also shows no difference between the pure and blend. In this case, the strong signal below  $1750\text{ cm}^{-1}$  corresponds specifically to the carbonyl from the acetate group from the EVA which covers the small one coming from the plate. The rest of the signals from both spectra correspond to the proposed structures.

Figure 4 shows the thermogravimetric traces for both materials before and after blending with the plates. Figure 4(a) shows the TGA curves of virgin PP and its higher loaded blend (15% SSP). PP by itself has a one step decomposition involving evolution of volatiles due to thermal degradation, starting at  $330^\circ\text{C}$ . Blended PP shows the same step of thermal degradation but at a higher temperature ( $350^\circ\text{C}$ ). These results indicate that addition of SSP improves thermal stability of the resin due to some miscibility between materials. It has to be mentioned

that polyester plates degrade at around  $400^\circ\text{C}$  and as such enhances the stability being mixed with the PP. Blends with 5% and 10% SSP have traces of volatiles evolving at temperatures in a corresponding sequence between the 0% and 15% (not shown here).

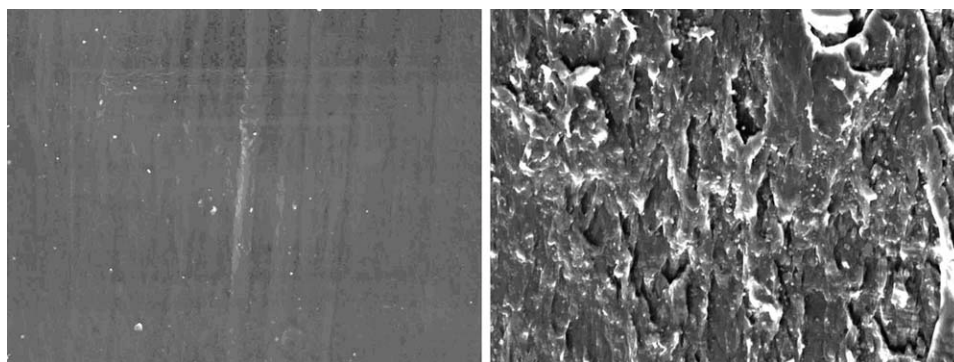
Figure 4(b) shows the TGA curve of virgin EVA resin and its blend, which contains the highest amount of SSP prepared (15% w). In the virgin EVA, two thermal degradations are observed; the first is at  $320^\circ\text{C}$ , corresponding to the acetic acid evolved from the vinyl acetate (VA) decomposition, and the second thermal degradation is at  $440^\circ\text{C}$ , from the hydrocarbonated chains. It is clear that the blended sample shows a similar trend; however, the evolution of volatiles displaces measurements by  $\sim 20^\circ\text{C}$  ( $320\text{--}340^\circ\text{C}$  and  $440\text{--}463^\circ\text{C}$ , respectively). This supports the idea that addition of SSP improves thermal stability, as seen with PP. Again, the 5% and 10% SSP give expected trends in PP blends, like those seen in EVA–SSP.

Figure 5 shows the DSC thermograms for PP and EVA and their corresponding blends. In the case of PP, which has higher melting temperature ( $T_m = 175^\circ\text{C}$ ), a reduction effect of  $10^\circ\text{C}$  in the transition



**Figure 5** Differential scanning calorimetry thermograms of 15% SSP blends with PP and EVA.





**Figure 6** SEM micrographs of 15% SSP blends with PP (a) and EVA (b) (magnification, 600 $\times$ ).

temperature is observed [Fig. 5(a)]. This indicates some miscibility between the components of the blend. It must be mentioned that the plates are composed mainly of SBR and polyester,<sup>16</sup> with the former in higher amounts. The polyester component has a melting temperature of 80°C and is the reason for the reduction of the PP melting transition.

Two details can be observed for EVA blends [Fig. 5(b)]. Melting temperature is, in this case, increased by more than 10°C, and a signal near 60°C appears for the 15% blend. The former means there is a change in the thermal properties due to the reinforcement of EVA with the polyester–SBR mixture from the plate. Moreover, the new signal corresponds to the  $T_g$  of the polyester from the recycled plates according to the characterization of raw materials.<sup>16</sup> The  $T_g$  signal of the SBR rubber at –20°C is also noticeable. Intermediate effects were seen for the blends consisting of 10% and 15% of the plate matter for both materials.

An important feature of SSP recycled material blends is a reduction of thermal properties of rigid materials such as PP but incrementation of thermal properties for soft resins such as EVA. These changes in the transition temperatures also confirm

the results of TGA and indicate that the mechanism of accelerated thermal decomposition is different in each polymer when the SSP is present.

SEM studies give an idea of miscibility between blends. Figure 6 depicts a view of (a) PP/plate and (b) EVA/plate. It can be seen that a smoother, better dispersion of the recycled photopolymer can be achieved with the PP matrix in comparison to the EVA blend. These observations may be due to a higher dispersion in values of the mechanical evaluation for the latter material. There is no strong indication of miscibility between components of the blends; however, evidence of changes in mechanical and thermal properties, as well as the lack of specific interactions by FTIR, indicates that there is compatibility between recycled plates and PP or EVA resins.

The resistance to chemical attack was determined using the ASTM D543 standard and the results are summarized in Table II. It is clear that all materials increase mass after immersion in the used reagents, with percentages as low as 0.03% or as high as 66.3%.

The inorganic reagents have the lowest interaction with blends; the EVA materials gained the highest percentages after contact with strong acids (nitric

**TABLE II**  
**Mass Variation of Blends After Chemical Attack**

Reagent	Mass variation							
	Weight of SSP in PP (%)				Weight of SSP in EVA (%)			
	0	5	10	15	0	5	10	15
NaOH (10%)	0.07	0.08	0.04	0.03	0.40	0.10	0.20	0.30
HCl	0.10	0.40	0.30	0.30	0.10	0.10	0.20	0.20
HNO <sub>3</sub>	0.20	0.20	0.30	1.00	9.30	13.60	15.40	16.50
H <sub>2</sub> SO <sub>4</sub>	0.30	0.30	0.40	0.40	16.40	13.70	14.90	30.60
CH <sub>3</sub> COOH	0.10	0.06	0.10	0.20	6.20	6.70	6.60	7.10
Acetone	0.40	0.40	0.06	0.07	7.20	3.10	7.20	30.30
MeOH	0.20	0.10	0.10	0.10	1.40	1.40	1.50	1.50
EtOH	0.20	0.04	0.06	0.20	1.80	1.70	1.60	1.50
DMF	0.20	0.40	0.50	0.60	2.00	2.00	1.30	0.30
Toluene	5.60	14.50	15.70	20.60	66.10	70.00	78.50	66.30

and sulfuric). The blends interact more with organic reagents than inorganic reagents. In addition, the EVA materials sustain the greatest increase in mass percentage after the treatment. Toluene is the only organic reagent that had an important interaction with the polypropylene blends. It is obvious that the differences are mainly due to the functionality of EVA, with a minor effect from the amount of recycled plates used in the blends.

In general, the blends have a high level of resistance to chemicals, as seen by low interaction with most reagents. After 24 h of treatment, no visual or optical alterations in the blends were detected that would indicate a chemical attack.

### CONCLUSIONS

The mechanical properties of PP and EVA are little affected by the addition of the photopolymer plates as a common filler. No difference in chemical functionality was detected by means of FTIR; however, the temperature of degradation was delayed. The effects on thermal transitions of matrix resins indicate miscibility with recycled photopolymer plates, especially with EVA, as shown by a more homogeneous microscopic structure. Chemical resistance of blends is high for most of the reagents tested, especially the inorganic ones. EVA was the most affected without sustaining serious visual damage. In general, such photopolymeric plates can be recycled by adding them to common resins, such as PP and EVA. Such blends can be easily prepared by common processing methods.

The authors thank the Brazilian institutions: Fapesc (Fundação de Amparo a Pesquisa do Estado de Santa Catarina) and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and the financial support from CONACyT-Mexico for the sabbatical stay.

### References

1. Bismarck, A.; Baltazar-Y-Jimenez, A.; Sarikakis, K. *Environ Dev Sustain* 2006, 8, 445.
2. Salmiation, A.; Garforth, A. *Waste Manage* 2007, 12, 1891.
3. Lin, Y.-H.; Yang, M.-H. *Polym Degrad Stabil* 2007, 92, 813.
4. Gomes, C. F. S.; Nunes, K. R. A.; Xavier, L. H.; Cardoso, R.; Valle, R. *Omega Int J Manage S* 2008, 36, 395.
5. Paula, M. M. S.; Rodrigues, F. B. B. M.; Bernardin, A. M.; Fiori, M. A.; Angioletto, E. *Mat Sci Eng C Bio S* 2005, 403, 37.
6. Liu, X.; Guthrie, J. T. *Surf Coat Int Pt B C* 2003, 86, 91.
7. Liu, X.; Guthrie, J. T.; Bryant, C. *Surf Coat Int Pt B C* 2002, 85, 313.
8. Liu, X.; Guthrie, J. T.; Bryant, C. *Surf Coat Int Pt B C* 2004, 87, 167.
9. Santos, W. N.; Agnelli, J. A. M.; Mummery, P.; Wallwork, A. *Polym test* 2007, 26, 216.
10. Martínez-Barrera, G.; López, H.; Castaño, V. M.; Rodríguez, R. *Radiat Phys Chem* 2004, 69, 155.
11. Fernández-Berridi, M. J.; González, N.; Mugica, A.; Bernicot, C. *Thermochim Acta* 2006, 444, 65.
12. Soares, B. G.; Alves, F. F.; Oliveira, M. G.; Moreira, A. C. F.; Garcia, F. G.; Lopes, M. F. S. *Eur Polym J* 2001, 37, 1577.
13. Bouchart, V.; Bhatnagar, N.; Brieu, M.; Ghosh, A. K.; Kondo, D. *CR Mecanique* 2008, 336, 714.
14. Senna, M. M. H.; Abdel-Fattah, A. A.; Abdel-Monem, Y. K. *Nucl Instrum Meth B* 2008, 266, 2599.
15. Zheng, Y.; Shen, Z.; Cai, C.; Ma, S.; Xing, Y. *Mater Des* 2009, 30, 958.
16. Cordeiro, C. C. MSc Thesis, Universidade do Extremo Sul Catarinense: 1v. Criciúma: Brazil, 2008; 110 p.