Compatibility Study of Recycled Poly(vinyl chloride)/Styrene-Acrylonitrile Blends

David Garcia, Rafael Balart, Francisco Parres, Juan López

Mechanical and Materials Engineering Department, Polytechnic University of Valencia, Paseo del Viaducto, 1 03801 Alcoy, Spain

ABSTRACT: The aim of the present study is to analyze the compatibility between recycled Poly(vinyl chloride) (PVC) and styrene-acrylonitrile copolymer (SAN). With this objective recycled PVC coming from credit cards have been blended with both virgin and recycled SAN with the aim of increase the benefits of recycled PVC. The compatibility of the components will be crucial for the final properties of the material. Furthermore, the recycled nature of some of the components will determine the compatibilization capability of the blend. The degradation level in the recycled materials was determined using Fourier transform infrared spectroscopy (FTIR). The compatibility between the PVC and the SAN was studied using differential scanning calorimetry and dynamic mechanical analysis. A greater compatibility was observed in mixtures of PVC and virgin SAN than in mixtures of PVC and recycled SAN. Finally, a morphological study of the fracture surface under cryogenic conditions was carried out using scanning electron microscopy. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 20–27, 2007

Key words: poly(vinyl chloride) (PVC); compatibility; recycling; blends; waste

INTRODUCTION

For over 70 years, Poly(vinyl chloride) (PVC) has been used in many types of applications (pipes, window frames, cable insulation, floor coverings, credit cards, etc), because of its specific properties, which make this polymer unique and unparalleled.[1,2] Over the past few years, enormous PVC consumption has led to an excessive growth in waste generation, which has created a problem for most countries, the solution of which is not easy. Depositing this waste in landfills is viewed as the last option, and incineration involves environmental problems because of the emission of hydrogen chloride during the thermal decomposition of PVC.[3,4] To address this problem, recycling has been highlighted as an efficient solution.

Recycling has become a matter of increasing interest over the past few years, partly due to the problem produced by the great amount of waste, and partly due to the appearance of new techniques for separating PVC from other materials which act as contaminants in the recycled material.[5,6] In several papers, the PVC recycling has been analyzed in depth.[7–9] Since PVC is a polymer which is particularly sensitive to thermal degradation, special attention should be paid to the recycling process, usually involving a decrease in the mechanical and thermal properties, thus requiring the use of stabilizers.[10]

The mixing of PVC with other polymers is carried out to improve its properties. This procedure acquires a greater relevance for recycled PVC, where the decrease of performance is more considerable. Thus, the incorporation of polymers which increase the benefits and, in particular, thermal stability is of vital importance.

As such, the styrene-acrylonitrile copolymer (SAN) copolymer, a material with excellent thermal properties, high stiffness and good dimensional stability, has acquired undeniable importance, since the incorporation of SAN with the PVC permits an increase in mechanical stability with the temperature and helps to reduce the melt fracture during the processing.[11] In addition, the PVC/SAN blend shows outdoor weatherability and improved flame retardancy.[12] This has allowed this type of blend to acquire irrefutable importance within the commercial blends.

For this type of blend, when it comes to determining its benefits, the study of compatibility between the components of the blend becomes vital. There are several studies which refer to the compatibility of PVC with SAN, although most of these deal with blending through solution casting.[13–16] However, melt mixing plays a significant role in the blends of plastics

at an industrial level, and in particular, with regards to recycled plastics. A significant factor which should be taken into account in the blends where copolymers are present is that miscibility is significantly influenced by the composition of copolymers. In the case of SAN, the amount of acylonitrile (AN) is an important factor. Several studies have demonstrated the existence of partial miscibility between PVC and SAN for concentrations between 11.5 and 26 AN wt %.[14]

In the present article, the partial compatibility between recycled PVC coming from credit cards and virgin SAN and recycled SAN coming from Waste Electrical and Electronic Equipment (WEEE) has been studied, with the aim of improving the benefits of recycled PVC. Since recycled polymers are used, it was necessary to analyze the level of degradation suffered during service life and the reprocessing. This was carried out using the Fourier transform infrared spectroscopy (FTIR). In addition, the compatibility of the samples was analyzed using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). This technique also facilitated the study of the mechanical stability of the blends with regard to temperature. Finally, the morphology of the fracture surfaces under cryogenic conditions was analyzed using scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The materials used in this study are shown below. Main properties of these materials are shown in Table I.

1. Recycled PVC (R-PVC) coming from credit card waste (K value = 62). This PVC was supplied in pellet form by Crearplast, S.L. (Ibi, Spain). The PVC waste was washed to remove any contaminants and crushed in a granulator. Subsequently, it was extruded and was added 1 p.h.r. of CaZn stabilizer to limit the thermal dehydrochlorination of PVC, 0.5 p.h.r. calcium stearate for lubrication and 2.5 p.h.r. of $CaCO_3$.
2. Virgin SAN POLIDUX S-580 supplied by Repsol Química, S.A. (Madrid, Spain) in pellet form.
3. Recycled SAN supplied by Crearplast, S.L. (Ibi, Spain) in pellet form coming from WEEE.

Preparation of blends

Blending of PVC with SAN was carried out using a two-roll mill (Dupra, S.L., Alicante, Spain) at 30 rpm rotor speed with a front roll temperature of 180–190°C and a rear roll temperature of 170–180°C. The blending process was conducted with different amounts of virgin and recycled SAN. The blend time was about 5 min to limit thermal dehydrochlorination of PVC.

Infrared spectroscopy analysis

Fourier transformed infrared spectroscopy (FTIR) measurements were carried out using Perkin–Elmer Spectrum BX infrared spectrometer (Perkin–Elmer España, S.L., Madrid Spain). For its completion, films with sufficient transparency were obtained through dissolution with tetrahydrofuran (THF) and subsequently dried to remove all solvent traces. Hundred scans at a resolution of 4 cm^{-1} were carried out for each sample.

Scanning differential calorimetry studies

The calorimetric analysis was carried out using DSC Mettler-Toledo 821 equipment (Mettler-Toledo, Schwerzenbach, Switzerland). Samples ranging between 6 and 7 mg in weight were used. A first heating (30–120°C at 10°C/min) was completed, followed by a cooling process (120–30°C at 10°C/min) to remove the thermal history, and was finished with a second heating (30–200°C at 10°C/min). The T_g values were determined from the second heating process. Tests were performed in a nitrogen environment (flow rate 30 mL/min).

Dynamic mechanical analysis

The measurements of dynamic mechanical properties were determined using an ARES N2 (TA Instruments, New Castle). Tests were carried out in torsion deformation mode, at frequency of 1 Hz. The strain amplitude was kept constant at 5% and the temperature programs were run from 30 to 150°C at a heat-

TABLE I
Main Properties of Materials Used

	AN content (wt %)	MFI (g/10 min)	Tensile strength (MPa)	Strain at break (%)	Tensile modulus (MPa)	Charpy impact (KJ/m^2)
Recycled PVC	–	–	32.16	4.18	1831	4.05
Virgin SAN	20	10.1	58.2	2.50	2788	0.78
Recycled SAN	20	11.5	31.4	1.56	2456	0.64
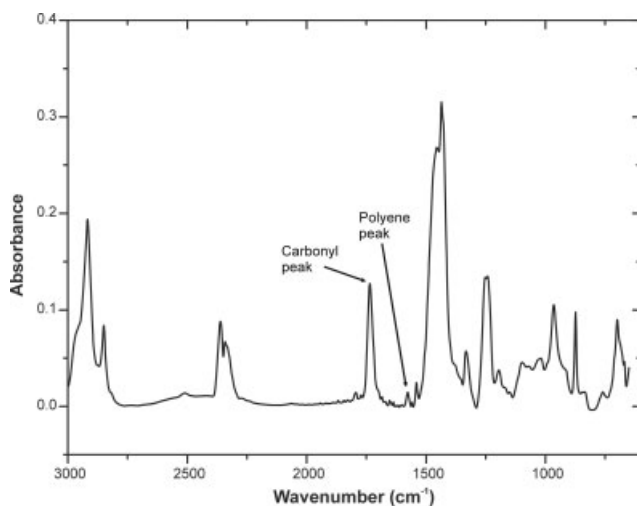
Figure 1 FTIR spectrum of recycled PVC.

ing rate of 5°C/min. The dimensions of the sample were 13 × 11 × 3 mm.

Scanning electron microscopy analysis

SEM photographs of different samples were carried out by a SEM JEOL 6300 (JEOL, Peabody, USA). Samples were previously coated with gold; the coating process was performed in vacuum conditions. The fracture surfaces observed were obtained in cryogenic conditions using liquid nitrogen.

RESULTS AND DISCUSSION

### Determination of the degradation level in recycled polymers

The level of degradation in recycled polymers can have a decisive influence on compatibility with respect to other polymers. The determination of this degradation was the first stage in the development of the present study. The possible degradation existing in the materials used was analyzed by means of the FTIR. In Figure 1, the IR spectrum of recycled PVC is shown. It can be observed a peak at 1602 cm^{-1}, associated with the presence of polyene sequences, which are representative of certain thermal degradation of the PVC, because of to the rupture of chains, and the subsequent liberation of hydrogen chloride.[17] A peak at 1735 cm^{-1}, corresponding to carbonyl groups, can also be seen. The carbonyl groups can also be associated to certain level of degradation. However, when considering the use of the PVC from the credit card during its service life, a material rarely exposed to high temperatures or solar radiation, and the nature of PVC itself, the presence of carbonyl groups is probably the consequence of the

addition of vinyl acetate or even a plasticizer like DOP.[18] Regarding to this, vinyl acetate is frequently used as an additive in formulations for credit cards to increase their flexibility. Finally, it is remarkable the existence of a peak at 700 cm^{-1}, which can be attributed to the presence of stearate type stabilizers normally used in PVC.[19]

With regard to the SAN copolymer, as can be observed in Figure 2, no significant differences can be identified between virgin and recycled SAN. The presence of the peak corresponding to the bond CN (around 2239 cm^{-1}), which is indicative of the amount of AN present, is higher in the recycled SAN that in the virgin one. With regard to the possible degradation of recycled SAN, the IR spectrum of this material does not indicates traces of degradation because of the absence of carbonyl groups (around 1750 cm^{-1}) and hydroxyl groups (around 3250 cm^{-1}), which are the main groups present in thermooxidative degradation.[20]

Compatibility of PVC/SAN systems

The study of the compatibility of PVC blends with virgin and recycled SAN was conducted using the study of the changes in the glass transition temperature (T_g). Recycled PVC presents a T_g of 77.9°C. This value is slightly inferior to the normal value for rigid
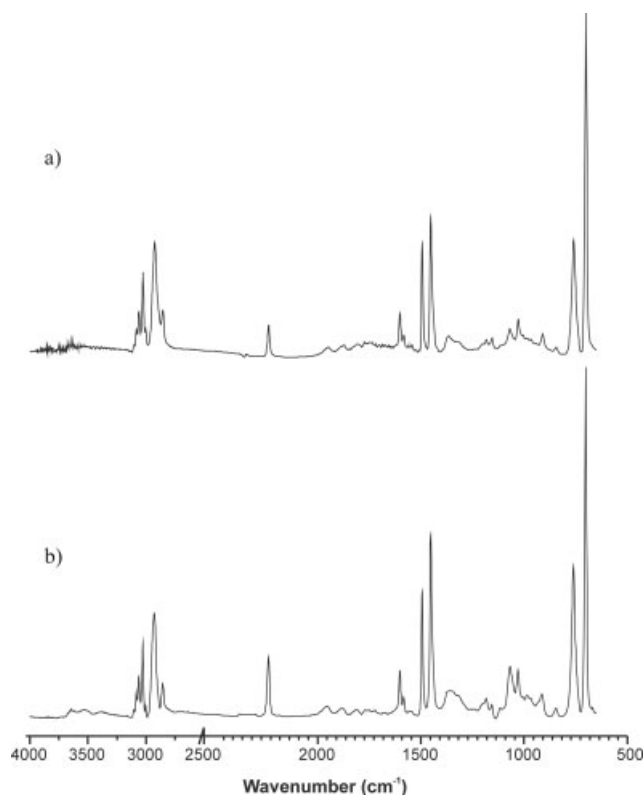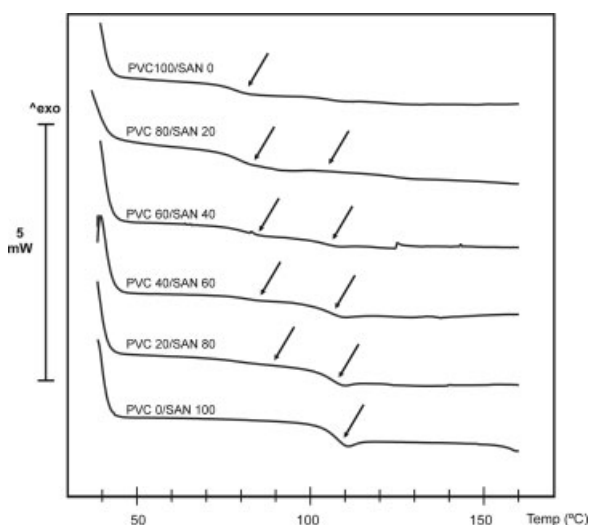

Figure 2 FTIR spectrum of: (a) virgin SAN; (b) recycled SAN.
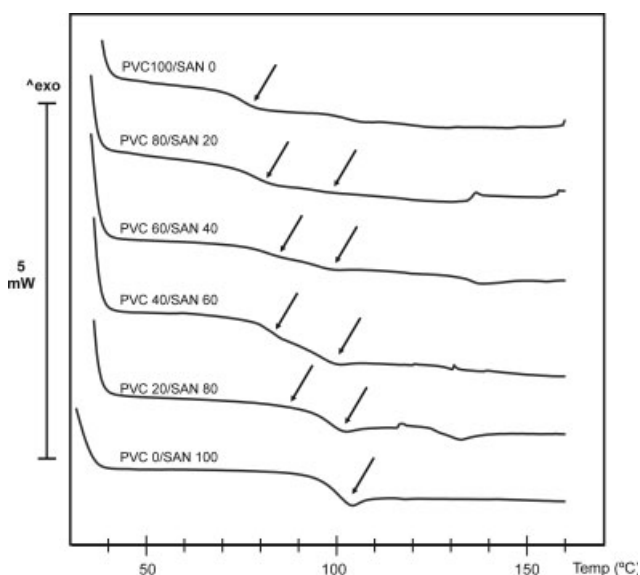
Figure 3 DSC scans of recycled PVC/virgin SAN blends with different compositions.

Figure 4 DSC scans of recycled PVC/recycled SAN blends with different compositions.

PVC. This reduction in the T_g value corroborates the addition of vinyl acetate or DOP to PVC or even certain degradation of polymer matrix, with the consequent decrease in the T_g. However, it should be noted that the processing conditions can influence the plasticizer effect. Thus, the processing of PVC on a rank of temperatures of 160–180°C followed by a slow cooling can reduce its plasticizing effects.[19,21] Furthermore, virgin and recycled SAN display T_g values of 104.6 and 105.9 respectively, the usual values for this type of polymer.

Figures 3 and 4 show DSC curves relative to the second heating scan, for the blends of recycled PVC with virgin and recycled SAN respectively. The existence of two clearly differentiated transitions can be observed in all range of compositions studied. The first of these corresponds to the T_g of the PVC phase present in the blend, whereas the second corresponds to the T_g of the SAN phase. For the recycled PVC, as for the virgin and recycled SAN without blend, only a T_g characteristic of an amorphous polymer can be observed. On the other hand, a significant variation in the T_g of the PVC and SAN phases, determined by the influence of one phase on the other can be observed (Table II). This phenomenon is indicative of the existence of partial miscibility, because of the interaction between the polar groups of the SAN phase with the polar groups of the PVC phase.[13] This variation in the T_g is a consequence of the migration of species of low molecular weight present in the PVC towards the SAN, forming a SAN-rich phase with a certain amount of dissolved PVC. This situation causes a reduction in the T_g in this SAN-rich phase, since the dissolved PVC acts as an internal plasticizer. Similarly, the migration of the

species of low molecular weight in the PVC towards SAN dominions causes a PVC-rich phase, but with reduced mobility, contributing to an increase in the T_g.

To relate the variation in the T_g in the function of the composition of the blend, several theoretical equations have been proposed.[22–25] One of the most commonly-used is the Fox equation:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{1}$$

where w_1 and w_2 are the weight fractions of polymers 1 and 2; T_{g1} and T_{g2} are the glass transition temperatures of polymers 1 and 2 respectively. This equation can be employed to determine the weight fraction of each blend component and their respec-

TABLE II
T_g **Values (K) of Recycled PVC, Virgin SAN, and Recycled SAN-Rich Phase for Blends of Recycled PVC with Virgin and Recycled SAN**

Recycled PVC (wt %)	Recycled PVC/ virgin SAN blend		Recycled PVC/ recycled SAN blend	
	T_g (K) SAN-rich phase	T_g (K) PVC-rich phase	T_g (K) SAN-rich phase	T_g (K) PVC-rich phase
100	–	350.9	–	350.9
90	372.3	354.1	376.6	351.01
80	372.1	354.9	376.8	351.5
70	371.8	356.4	376.9	351.8
60	372.9	357.8	376.9	352.2
50	373.3	357.5	377.3	352.8
40	373.3	357.9	378	352.8
30	374.2	357.8	378.8	352.8
20	374.9	359.1	378.8	352.9
10	377.1	360.2	379.3	353.9
0	377.6	–	379.9	–
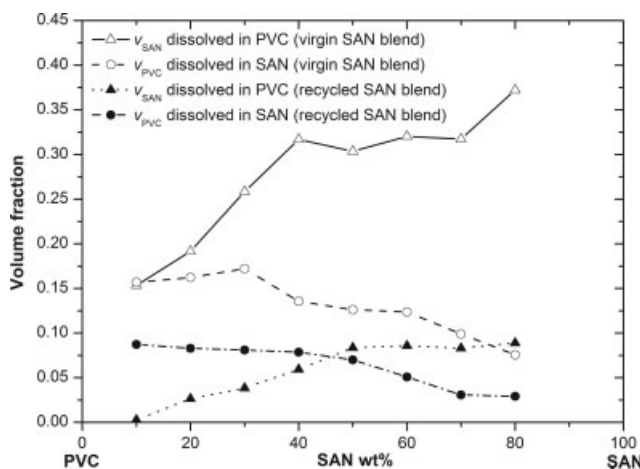
Figure 5 Plots of volume fraction of PVC and SAN dissolved in SAN and PVC respectively, for blends of recycled PVC with virgin and recycled SAN.

tive T_g. For blends with partial compatibility, when using a modified Fox equation, it is also possible to determine the compositions of the combined phases. As a result, the following equations are obtained:

$$w_2' = \frac{T_{g2}\,(T_{g1} - T_g')}{T_g'\,(T_{g1} - T_{g2})} \qquad (2)$$

$$w_1'' = \frac{T_{g1}\,(T_g'' - T_{g2})}{T_g''\,(T_{g1} - T_{g2})} \qquad (3)$$

where w is the weight fraction; 1 is the subscript referred to SAN; 2 is the subscript referred to PVC; ' is the superscript referred to SAN-rich phase and " is the superscript referred to PVC-rich phase. (e.g., v_1'' refers to the fraction in volume of SAN existing in the PVC-rich phase and v_2'' refers to the fraction in volume of PVC existing in the SAN-rich phase).

The T_g values of the PVC-rich and SAN-rich phases allow to determine the weight or volume fractions of each phase of the miscible components, according to eqs. (2) and (3). The volume fractions of PVC and SAN dissolved in the SAN-rich phase and PVC-rich phase respectively, with respect to the blend systems studied, can be observed in Figure 5.

It can be observed that there is a greater compatibility between the components of the blend with virgin SAN than in the blends with recycled SAN. It may be due to the different AN content existing in the virgin and recycled SAN. The recycled SAN has a higher AN content that causes a decrease in the compatibility with the recycled PVC. Besides to the different AN content, the incorporation of virgin SAN allows a better compatibilization of the chains in the blending process, making it possible for a greater number of short chains, probably with cer-

tain level of degradation, to migrate from the recycled PVC towards the SAN. As such, the T_g of the PVC increases more significantly, whereas the SAN, since it incorporates these chains, obtains greater plasticization, and, as a consequence, its T_g decreases to a greater degree.

In blends with high SAN content, the quantity of PVC is very low, by this way the SAN make a matrix where the PVC is completely surrounded by SAN. This fact causes an effect of higher compatibilization, as reveal the higher values of T_g. Experimentally there is a difficulty in determining the T_g of the PVC-rich phase since it is in a very low quantity. However the T_g of SAN-rich phase is easily identified and it shows a T_g value close to pure SAN. This fact corroborates the total compatibilization for percentages lower than a determined value.

For the blend with virgin SAN, a greater difference in the dissolution capability between the PVC and the SAN can be observed. Thus, the dissolution capability of the SAN chains within the PVC chains is slightly greater than the admission capability of SAN by the PVC. This fact proves the existence of a greater capability of compatibilization in the virgin materials with regard to recycled one, since the light degradation of SAN acts as obstacle for improve the compatibility with recycled PVC with certain level of degradation too.

Dynamic mechanical analysis

As previously mentioned, one of the main disadvantages in using recycled PVC is the decrease in mechanical properties as a function of temperature. The incorporation of SAN with PVC will improve their mechanical stability with the temperature. In Figures 6 and 7 the DMA curves are given, expressed through the variation of the storage shear modulus (G') as a function of the temperature, for the different concentrations of the blends of recycled PVC with virgin and recycled SAN respectively. As predicted, at room temperature, where the behavior of the material is hard and vitreous,[26] the recycled PVC shows a value of G' notably inferior to that of the SAN. As the temperature increases, a progressive decrease in G' is produced. In the case of the PVC, this decrease occurs starting from 40°C (around 70°C, the PVC displays a soft and gummy behavior), whereas for the SAN this decrease is produced from 90°C onwards. With regards to virgin and recycled SAN, the DMA curve illustrates that the virgin SAN has a higher G' at room temperature.
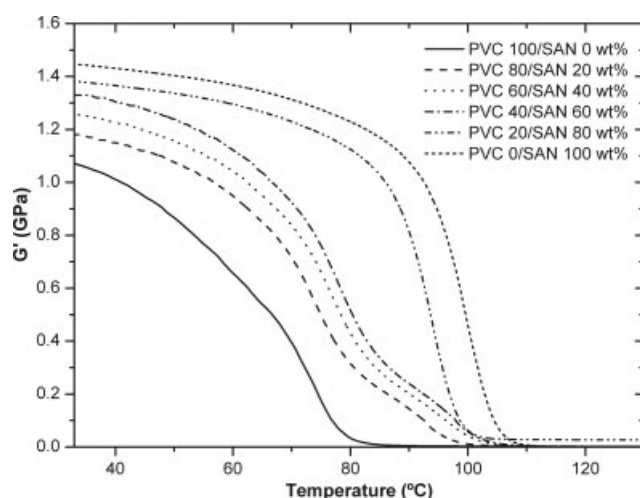
With respect to the blends, as the temperature rises, the mechanical stability of the blend increases with the concentration of SAN. As a result, for concentrations of SAN close to 60 wt %, there is no sudden decrease of G' until temperatures approach
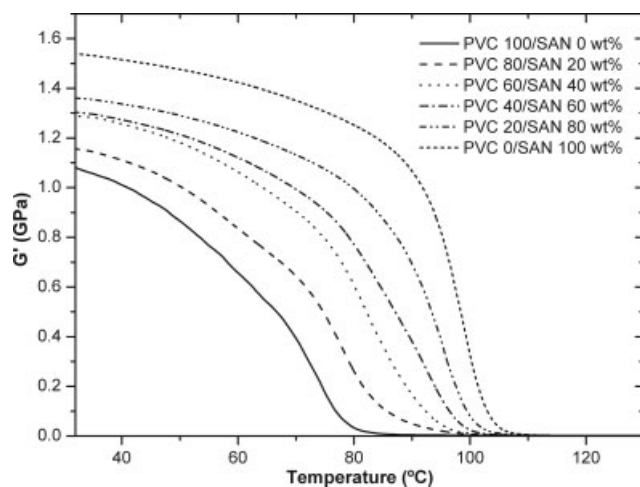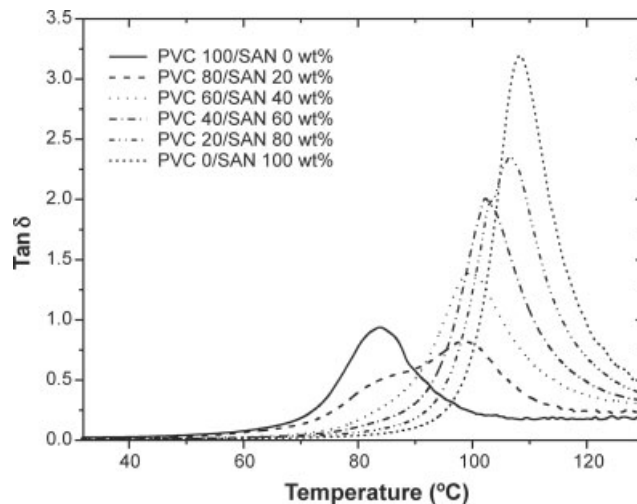
Figure 6 Variation of storage shear modulus as a function of temperature for recycled PVC/virgin SAN blends with different compositions.

Figure 8 Variation of loss modulus as a function of temperature for recycled PVC/virgin SAN blends with different compositions.

90°C. Similar behavior can be observed for PVC blends with recycled SAN, although in this type of blend, the increase of stability is lower in all the range of compositions.

Figure 8 shows the loss modulus (G″) as a function of the temperature for different blend compositions of recycled PVC with virgin SAN. A peak of G″ can be observed for both recycled PVC and virgin SAN. As the concentration of SAN increases, the separation of the peaks decreases until these overlap. This behavior corroborates the existence of an interaction between the two polymers integrating the blend,[13] which corroborate the results obtained by the calorimetric analysis, and verifies the presence of a certain concentration of SAN in the PVC than *vice versa*. In the recycled PVC and recycled SAN blends. Regarding to the blends with recycled SAN

(Fig. 9), two different peaks, corresponding to the PVC-rich phase and the SAN-rich phase of the blend can be observed; also these peaks have shifted with the initial peaks of pure PVC and SAN respectively. The identification of two peaks in a greater range of concentrations is revealed, which indicates a lower compatibility with this type of blend. However, the results obtained both virgin and recycled SAN do not let identify clearly the two peaks of PVC-rich phase and SAN-rich phase for all range of compositions.

Morphology study of blends

The morphology of the fracture surfaces of the blends of PVC with SAN was investigated using SEM under cryogenic conditions. The recycled PVC

Figure 7 Variation of storage shear modulus as a function of temperature for recycled PVC/recycled SAN blends with different compositions.
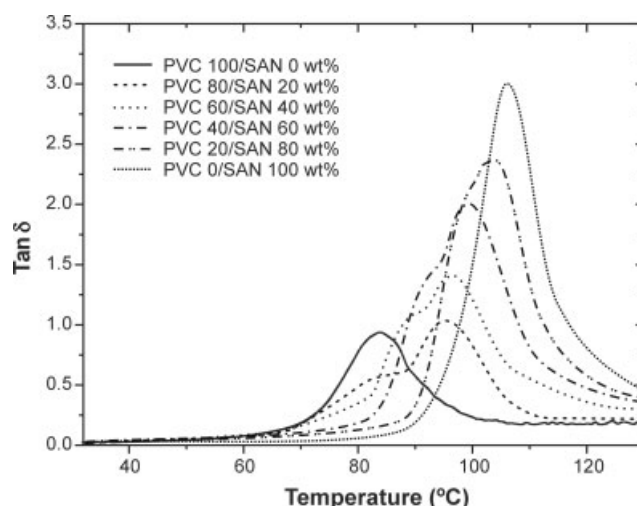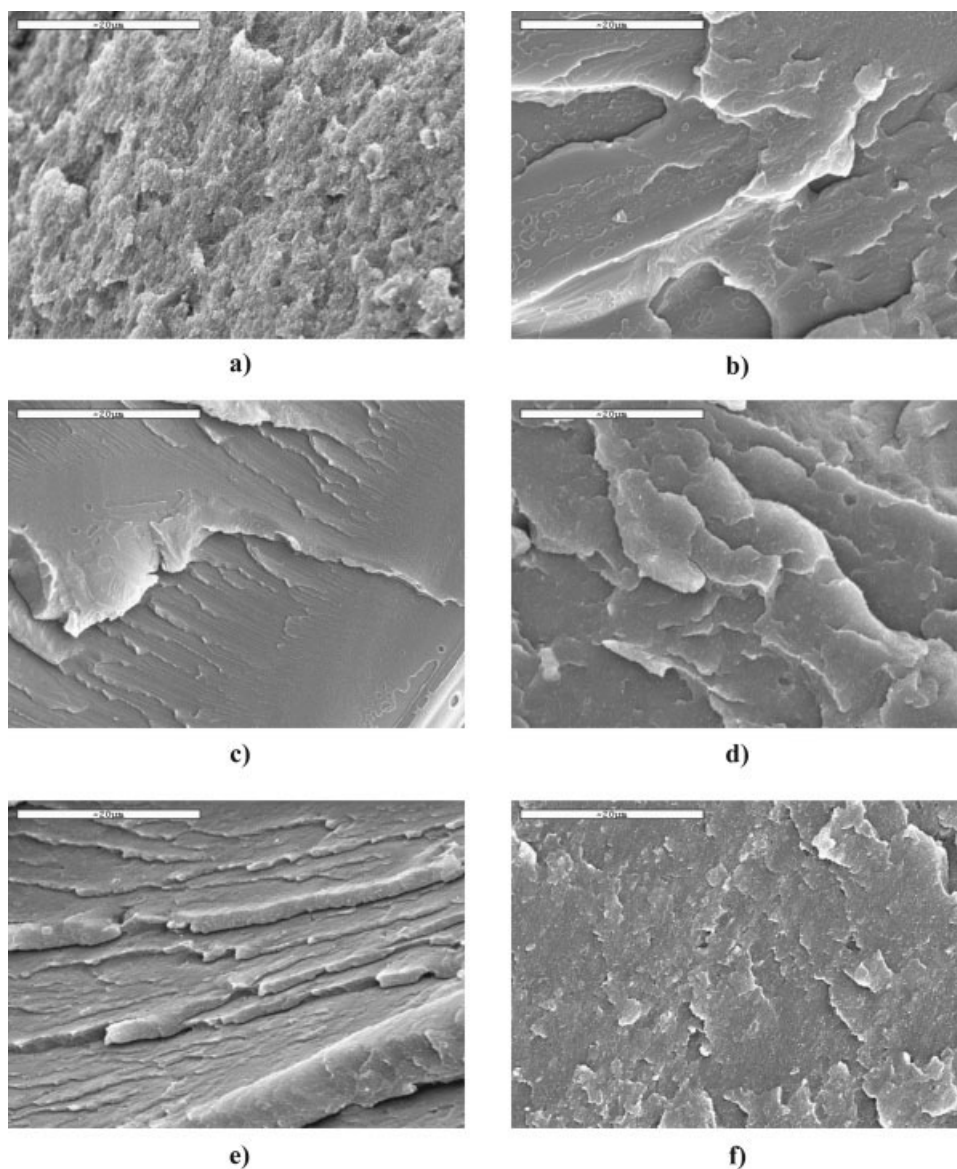

Figure 9 Variation of loss modulus as a function of temperature for recycled PVC/recycled SAN blends with different compositions.

Figure 10 Scanning electron micrograph of fractured surfaces of recycled PVC blends with different compositions: (a) recycled PVC 80/virgin SAN 20; (b) recycled PVC 40/recycled SAN 60; (c) recycled PVC 40/Virgin SAN 60; (d) recycled PVC 50/virgin SAN 50.

shows a brittle and scaly fracture surface [Fig. 10(a)], characteristic of a fragile behavior.[26] Conversely, the virgin SAN [Fig. 10(b)] shows a layered and smooth surface, whereas the recycled SAN [Fig. 10(c)] displays a fracture characteristic of a mirror zone where the fractures are preceded by craze formation and subsequent breakdown. No type of impurity has been identified as the cause of the fracture in the recycled materials.

With regard to PVC/virgin SAN blends, the fracture surface is mainly composed of separate tiny platelets with hardly any roughness [Fig. 10(d)]. The size of the platelets increases with the content in SAN, in such a way that the platelets overlap [Fig. 10(e)]. In general, a satisfactory interfacial adhesion can be observed, since no type of agglomeration,

which would prove the complete lack of compatibility, can be seen. In the blends with recycled SAN, the morphology of the fracture surfaces is also mainly formed by tiny platelets. However, these present a rougher surface than in the previous samples [Fig. 10(f)], with some areas where some hollows can be observed, which suggest a lack of interfacial adhesion in the blend. These results are supported with those obtained using the calorimetric analysis.

CONCLUSIONS

As a general conclusion, this work has shown that recycled PVC blends obtained from credit cards with virgin SAN and recycled SAN derived from WEEE

are partially compatible. The study of the variation of the two glass transition temperatures (T_g) identified in the calorimetric curves obtained using DSC with respect to the composition of the blend, has permitted the quantification of the compatibility of the blends. This compatibility can be attributed to the interaction between the polar groups of the SAN phase and the polar groups of the PVC together with a migration of species of low molecular weight. Higher levels of compatibility were obtained for the PVC blends with virgin SAN, since the levels of degradation in the recycled SAN interfered negatively in this aspect. For low percentages of PVC in SAN, the T_g related to SAN shows higher values to expected ones. These results were corroborated using DMA curves. The incorporation of SAN increased the mechanical stability with reference to the temperature of the blends. The blends which presented better compatibility were those which offered better results. As a result of their inherent environmental benefits and their low cost, the use of blends incorporating recycled materials is recommendable and advantageous for their production at an industrial level.

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