Mechanical Properties of Recycled PVC Blends with Styrenic Polymers

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ABSTRACT: The aim of this study is to improve the performance of blends made from recycled polyvinyl chloride (PVC), coming from credit card waste, so that these blends can be used for those applications that must fulfil some requirements with regard to mechanical properties and stability with temperature alterations. With this aim in mind, two polymers of styrenic origin have been combined: styrene acrylonitrile (SAN) and acrylonitrile butadiene styrene (ABS). These polymers are characterized by a satisfactory balance of mechanical properties and thermal stability. PVC blends with both virgin and recycled styrenic polymers have been studied throughout the entire range of compositions. The prior degradation of the recycled materials has been studied by means of Fourier transformed infrared spectroscopy (FTIR). The behavior of the observed T_g values has been analyzed using differential scanning calorimetry (DSC), and the existence of partial miscibility between the different components has been studied. The mechanical properties have been determined using tensile and Charpy impact tests. The thermal stability of the PVC blends with temperature changes has been determined using the Vicat softening temperature (VST). Finally, the fracture surface of the various blends has been analyzed using scanning electron microscopy (SEM). © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2464–2471, 2006

Key words: recycling; poly(vinyl chloride) (PVC); mechanical properties; blends; thermal properties

INTRODUCTION

Polyvinyl chloride (PVC) is one of the most commonly used plastics in the current market; with a production level exceeding 30 million tons per year,[1] with regards to volume, it is rated second only after polyolefins, the top thermoplastic, and before styrenic polymers. This significant volume of production can be attributed to the particular properties inherent in PVC[2,3] because of its low cost and versatility in processing, combined with its satisfactory physical and chemical properties. For this reason, PVC serves a wide variety of applications, such as pipes, window frames, cable insulation, floor coverings, credit cards, etc.[4]

The enormous consumption of PVC irreversibly produces a great amount of waste. The treatment of this waste and its acknowledgment is a matter that has increasingly captured the interest of researchers during recent years, mainly because of the problem of suitable locations that has arisen as a result of the rapid increase in plastic waste during the past few years.[5] Landfill sites are limited in most countries, and the deposition of PVC waste is only considered as a last option.[6] Additionally, the acquisition of energy through incineration[7,8] is currently facing significant environmental problems, such as the emission of toxic gases due to the use of inappropriate equipment or the lack of suitable conditions that facilitate correct incineration. To confront this situation and provide a solution, mechanical recycling is being increasingly used, facilitated by the new technologies for waste separation.[9–12]

On the other hand, PVC and, in particular, recycled PVC, unlike other thermoplastics, has a low thermal stability, which, in most cases, requires the use of stabilizers.[13] A possible degradation produced by inappropriate or excessive processing produces a reduction in properties with temperature alterations.[14,15] The element of using recycled material that has undergone some degree of degradation during its service life increases this phenomenon, thereby considerably reducing the mechanical properties[16,17] and, in particular, causes a diminution in the thermal stability of the material.

One of the methods of improving PVC is to combine it with other plastics. Many research papers have been developed in relation to this aimed at enhancing the performance of PVC through combining it with polymers intended for industrial use.[18–20]

TABLE I
Main Properties of Materials Used

	Density (g/cm^3)	MFI (g/10 min)	Tensile strength (MPa)	% Strain at break	Elastic modulus (MPa)	Charpy impact (KJ/m^2)
R-PVC	1.35	–	32.16	4.18	1831	4.05
V-SAN	1.08	10.1	58.2	2.50	2788	0.78
R-SAN	1.08	11.5	31.4	1.56	2456	0.64
V-ABS	1.05	8.9	32.9	20.9	1786	35.0
R-ABS	1.06	10.4	30.9	3.3	1370	15.4

The present study looks at the incorporation of styrenic polymers as a possible way of improving recycled PVC coming from credit cards to obtain a material with a high industrial applicability, specifically for those sectors where the fulfilment of mechanical and thermal requirements is necessary and where the demand for recycled PVC is important for cost reasons. In particular, the hydrosanitary sector normally uses recycled PVC, the application of which is conditioned by the fulfilment of the thermal stability requirements quantified by means of the measurement of the Vicat softening temperature (VST). To maintain a low cost, the use of recycled materials is more appropriate for the finalization of the blends. In such a way, in this study, both virgin and recycled styrenic polymers (styrene acrylonitrile (SAN) and acrylonitrile butadiene styrene (ABS)) have been used. Although the SAN can offer better results *a priori* for the blends, it is important to take into account that its consumption is notably lower than that of the ABS. As such, in this study, blends with ABS have been considered, since these offer greater availability mainly with regards to recycled material.

EXPERIMENTAL

Materials

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

i. Recycled PVC (R-PVC) in pellet form supplied by Crearplast, S.L. (Ibi, Spain), coming from credit card waste (K value = 62). The PVC waste was washed to remove any contaminants and crushed in a granulator. Subsequently, it was extruded and 1 phr of CaZn stabilizer, 0.5 phr calcium stearate and 2.5 phr of $CaCO_3$ were added.
ii. Recycled SAN (R-SAN) and recycled ABS (R-ABS) in pellet form supplied by Crearplast, S.L. (Ibi, Spain) coming from wastes from electrical and electronic industry (WEE).
iii. Virgin POLIDUX SAN *S*-580 (V-SAN) and virgin ABS POLIDUX A-164 (V-ABS) in pellet form

supplied by Repsol Química, S.A. (Madrid, Spain).

Blends and sample preparation

The blends were carried out using a two-roll mill. The blending process was conducted at a temperature of 180°C with different amounts of ABS and SAN both virgin and recycled (10, 20, 30, 40, 50, 60, 70, 80, 90, 100 wt %). The blend time never exceeded 5 min. Once the blend was obtained, a sheet was prepared on a hot plate press with a pressure of 3 MPa, applying a temperature of 110°C over 5 min, followed by a cooling period of 10 min until the temperature dropped to 40°C. Samples for tensile and Charpy impact tests were shaped using a universal clipper with the dimensions, according ISO 527–2. The samples that, due to their high brittleness, could not be shaped were machined.

Infrared spectroscopy (FTIR) analysis

Fourier transformed infrared spectroscopy (FTIR) measurements were carried out using Perkin–Elmer Spectrum BX infrared equipment (Perkin–Elmer España, S.L., Madrid, Spain). For its completion, films with sufficient transparency were obtained through dissolution with tetrahydrofuran. The films with solvent were kept in an air-circulating oven set at 90°C for 10 min to remove all solvent traces.

Thermal characterization

The calorimetric analysis was carried out using DSC Mettler-Toledo 821 equipment (Mettler-Toledo, Schwerzenbach, Switzerland). Samples of weight between 6 and 7 mg have been 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 eliminate the thermal history, and was finished with a second heating (30–200°C at 10°C/min). The T_g values have been determined from the second heating process. Tests were performed in a nitrogen environment (flow rate 30 mL/min).
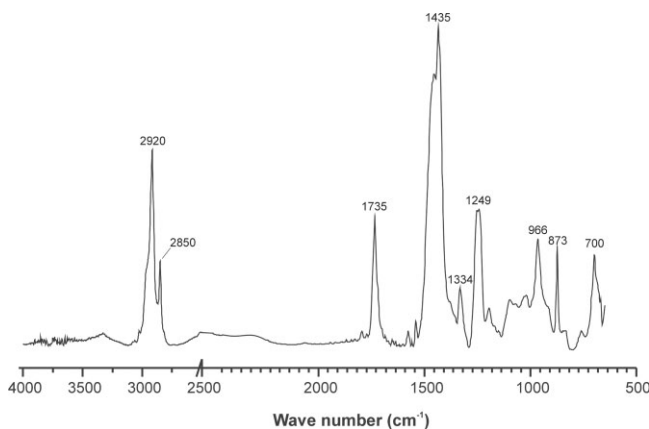
Figure 1   FTIR spectrum of R-PVC.

To determine the VST, a Vicat/HDT equipment of model Deflex 687-A2 (Metrotec, S.A, San Sebastián, Spain) was used. The oil used for the softening was silicon DOW Corning 200 Fluid 100 CS. The development of the test was carried out according to the guidelines of ISO 306. Melt flow index measurements were obtained with an extrusion plastometer (Ats Faar S.p.A, Vignate, Italy), according to the guidelines of ISO 1133.

Mechanical characterization

The tensile tests were carried out using a universal tensile test machine ELIB 30 (S.A.E. Ibertest, Madrid, Spain), following ISO 527. A 10 mm/min cross-head speed was used to determine the elongation at break, tensile strength, and elastic modulus starting from the tensile graph. All specimens were tested at room temperature. Impact energy was determined by using the Charpy impact machine (S.A.E. Ibertest, Madrid, Spain), according to the guidelines of ISO 179. A minimum of 5 samples was analyzed to obtain every result

Scanning electron microscopy (SEM) analysis

SEM photographs of different samples were carried out by a scanning electron microscopy JEOL 6300 (JEOL USA, Peabody). Samples were previously coated with gold; the coating process was performed in vacuum conditions. The fracture surfaces observed were obtained in the different tensile tests at room temperature.

RESULTS AND DISCUSSION

Determination of the degradation levels of the recycled materials

With recycled materials, prior to any study, it is of great importance to establish the existing levels of

degradation, which result from the processing or conditions of use of such materials. In particular, PVC is a material that is sensitive to thermal degradation. For this reason, it is particularly important to establish the levels of accumulated degradation in this material. The IR spectra of the different recycled materials used have been analyzed. In the case of R-PVC, a peak (Fig. 1), which corresponds to the carbonyl group at 1735 cm^{-1}, can be observed. Carbonyl groups are present in the stabilizers used in PVC.[21] However, because of the nature of the credit card, it can be presumed that the presence of vinyl acetate is the main cause of the appearance of the carbonyl group, since this is added to increase flexibility. Conversely, no evident signs of degradation in the R-PVC have been found. With regard to the R-SAN and R-ABS styrenic polymers (Fig. 2), no significant signs of degradation have been found in the spectrum, because of the absence of carbonyl groups (around 1750 cm^{-1}) and hydroxyl groups (around 3250 cm^{-1}) and the main groups that appear as a consequence of the thermal oxidative degradation.

Miscibility of R-PVC/styrenic polymer systems

The curves obtained using differential scanning calorimetry (DSC) of the R-PVC blends with the different styrenic polymers show the existence of two different
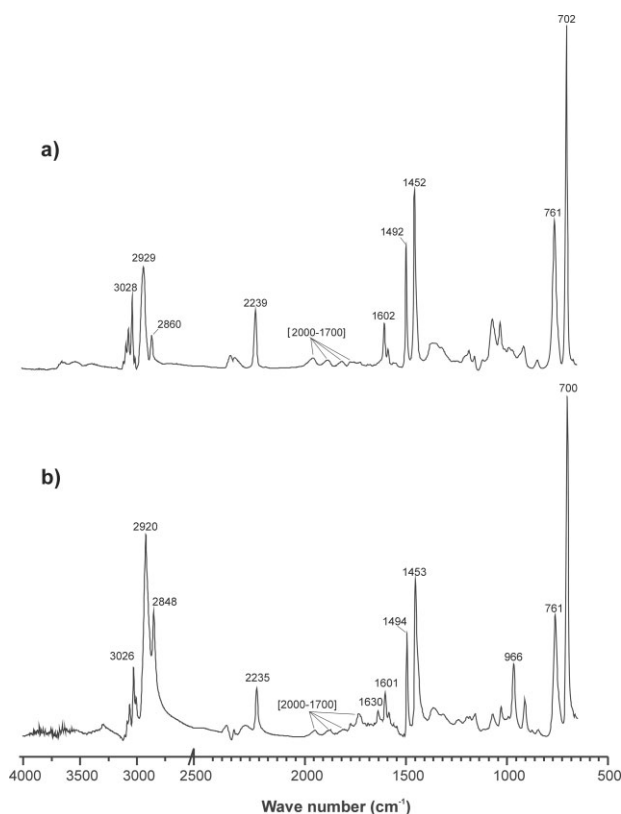

Figure 2   FTIR spectra of: (a) R-SAN; (b) R-ABS.

TABLE II
T_g **Values [°C] of R-PVC Rich Phase and Different Styrenic Polymer Phases**

RPVC (wt %)	RPVC/RSAN		RPVC/VSAN		RPVC/RABS		RPVC/VABS	
	R-SAN	R-PVC	V-SAN	R-PVC	R-ABS	R-PVC	V-ABS	R-PVC
100	–	77.9	–	77.9	–	77.9	–	77.9
90	103.6	78.01	99.3	81.1	100.8	78.5	101.9	81.1
80	103.8	78.5	99.1	81.9	101.0	80.4	102.8	82.6
70	103.9	78.8	98.8	83.4	101.1	80.9	103.8	82.7
60	103.9	79.2	99.9	84.8	102.6	81.6	105.1	82.9
50	104.3	79.8	100.3	84.5	103.8	81.8	105.7	83.1
40	105	79.8	100.3	84.9	104.9	83.6	106.0	83.1
30	105.8	79.8	101.2	84.8	105.6	84.0	105.9	84.4
20	105.8	79.9	101.9	86.1	105.8	84.6	106.0	84.9
10	106.3	80.9	104.1	87.2	105.9	85.7	106.1	85.1
0	106.9	–	104.6	–	105.9	–	106.2	–

glass-transition temperatures (T_g) throughout the range of compositions and for all the blends studied (Table II). The presence of two T_g is characteristic of blends that present partial miscibility or immiscibility. However, in all the cases, a variation of the two T_g of the blends as a function of their concentration can be observed. This fact is an indicator of the existence of a partial miscibility between the polymers.[22–24]

Throughout all the blends compositions, it can be seen that the T_g of the phase rich in PVC progressively increases with the amount of styrenic polymers. In addition, the T_g of the phase rich in SAN diminishes as the concentration in PVC increases. This characteristic is produced by the migration of PVC low molecular weight species with a possible slight degradation toward the SAN, which causes its plasticization and diminishes the T_g. On the other hand, the loss of these chains of low molecular weight permits an increase in the rigidity of the PVC, which is complemented by an increase in its T_g. It is important to point out that the presence of butadiene in the ABS, which has been

introduced in the SAN by means of a physical blend, causes a reduction in the variation of the T_g with regard to the blends with SAN; thereby, indicating lower miscibility in the system, which can be due to the fact that the butadiene itself interferes negatively in the interaction of the phases constituting the blend. On the other hand, the miscibility of the system will have a definitive effect on the mechanical properties of the blends, and therefore, worse mechanical performances should be expected for blends with ABS than for blends with SAN.

Vicat softening temperature

The thermal stability of the R-PVC blends with the styrenic polymers has been established by means of the VST. The results obtained for all the blends analyzed (Fig. 3) show a linear correspondence between the VST and the composition of the blend. Thus, in the system R-PVC/styrenic polymer, an increase in the VST, proportional to the concentration of added polymer, is produced. The parameters of the linear adjustment for the different styrenic polymers incorporated into the R-PVC are shown in Table III. As can be observed, the higher values of "b" parameter are obtained by incorporation of SAN polymers because of their higher thermal stability. Also for small percentages of styrenic polymer, a greater influence on the nature of the material than their origin is observed.
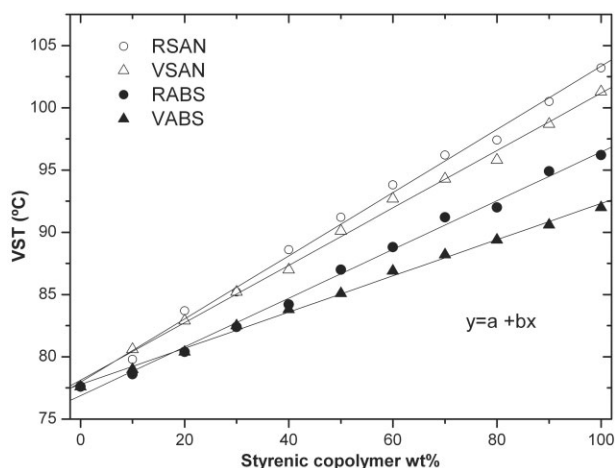

Figure 3 Plot of VST temperature versus different styrenic polymers wt %.

TABLE III
Linear Fit Parameters and R^2 of VST Variation with wt % of Different Styrenic Polymers ($y = a + bx$)

Styrenic polymer	a	b	R^2
R-SAN	77.93	0.25	0.996
V-SAN	78.10	0.23	0.997
R-ABS	76.86	0.19	0.995
V-ABS	77.78	0.14	0.997

Figure 4   Variation of tensile strength versus styrenic polymers wt % incorporated to R-PVC.
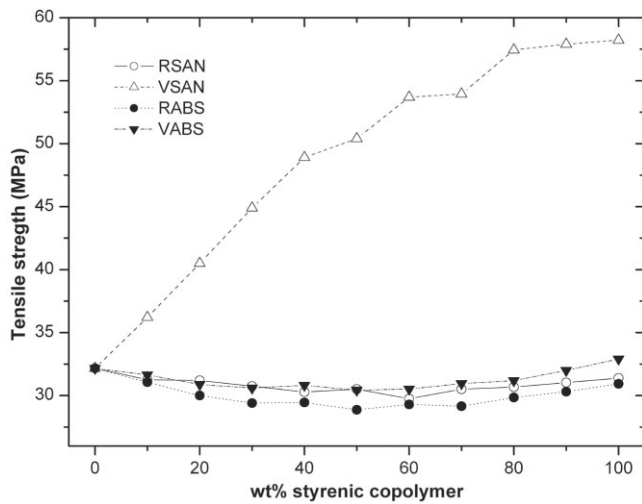

Figure 5   Variation of strain at break versus styrenic polymers wt % incorporated to R-PVC.

Thus, a higher increase is obtained with the blends containing SAN than with those containing ABS, whereas there is barely any difference between materials of the same nature of both recycled and virgin origin. This fact is important when determining the composition required to obtain the necessary VST for applying the R-PVC in certain specific sectors.

According to the results, it is possible to establish an empirical relation capable of predicting the VST of a specific composition given that the VST of the materials that integrate the blend (eq. (1)).

$$VST = w(VST(x) - VST(PVC)) + VST(PVC) \quad (1)$$

where $VST(x)$ is the VST of the styrenic polymer, $VST(PVC)$ is the VST of the R-PVC, and w is the fraction in weight of the incorporated styrenic polymer. This proportionality between the VST and the composition of the blends reinforces the fact that these blends comply with the "mixture law," despite the absence of total miscibility. This fact can be attributed to the markedly macroscopic nature of the VST temperature with regard to other property types, such as the mechanical properties, in which the levels of interaction in the interface of the components integrating the blend play a decisive role.

Mechanical characterization

In Figure 4, the evolution of the tensile strength with regard to the composition of the blends can be observed. A considerable increase in the tensile strength is produced as the concentration of V-SAN increases. However, the incorporation of other styrenic polymers results in the diminution of this property. Despite all this, the decrease in the tensile strength is not
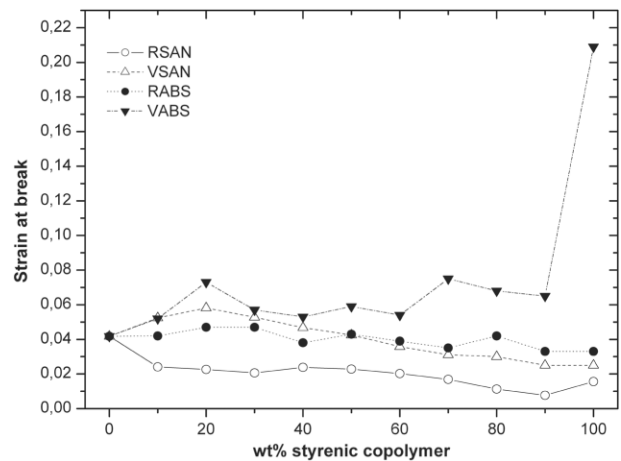
sufficiently significant to cause an important reduction in benefits, which would discourage the use of these blends for industrial purposes. This diminution is the consequence of the lack of interaction in the interface of the components of the blend. However, in the blend with V-SAN, the levels of interaction are reasonably higher causing an improvement in the tensile strength.

With regard to the elongation at break (Fig. 5), as it was expected, the incorporation of SAN causes a reduction in the strain at break, since it is a material with low ductility. This diminution is less significant in the blend with V-SAN compared with blend with R-SAN, because of its higher brittleness. However, it should be highlighted that for concentrations up to 20 wt % of V-SAN not only does the strain at break fail to diminish, but it actually shows an increase. With the incorporation of ABS, the results obtained show a markedly different nature, depending on its origin. The incorporation of V-ABS improves the elongation of the
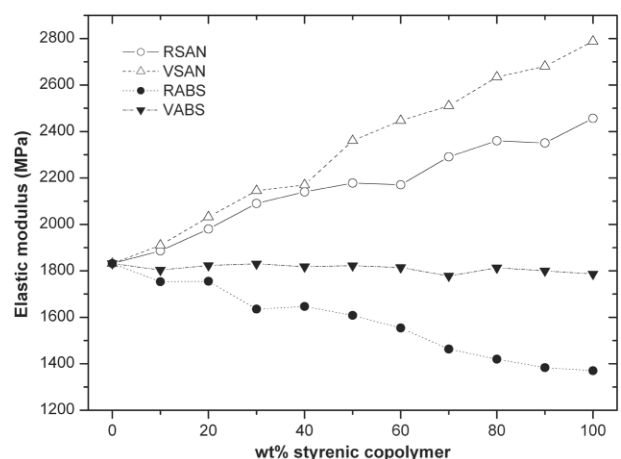

Figure 6   Variation of elastic modulus versus styrenic polymers wt % incorporated to R-PVC.
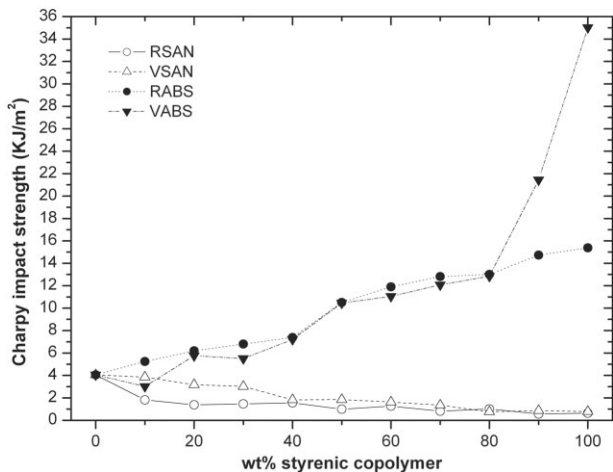
Figure 7 Variation of Charpy impact strength versus styrenic polymers wt % incorporated to R-PVC.

R-PVC. However, the incorporation of R-ABS causes its diminution, mainly because of the low capacity for deformation that this material possesses. The large reduction in strain at break, which the V-ABS represents with the incorporation of small amounts of R-PVC, probably caused by the interference between the butadiene present in the V-ABS with the R-PVC, should be emphasized. In blends with R-ABS, this

aspect is less obvious, because of the lower elongation capacity that this type of blend presents.

The elastic modulus increases throughout the concentrations with the incorporation of SAN (Fig. 6), adopting higher values with V-SAN, since this material has a higher elastic modulus. In the blends with ABS, a diminishing for the blends with R-ABS can be observed, whereas in the blends with V-ABS, the values are similar throughout the concentrations.

With regard to impact strength, (Fig. 7), as the concentration of SAN increases, there is a reduction, which is more significant in blends with R-SAN. Conversely, the incorporation of ABS increases the impact strength of the blend as its concentration increases because a dissipative deformation processes occur, such as multiple crazing. However, for a concentration close to 10 wt %, this increase is not significant and can even imply a slight decrease. In this case, as in the case of the strain at break, a significant decrease in impact strength in blends of V-ABS with small percentages of R-PVC can be seen, because of, as in the previous case, the interference of the butadiene phase of the V-ABS with the R-PVC.

Morphology study of the fracture surfaces

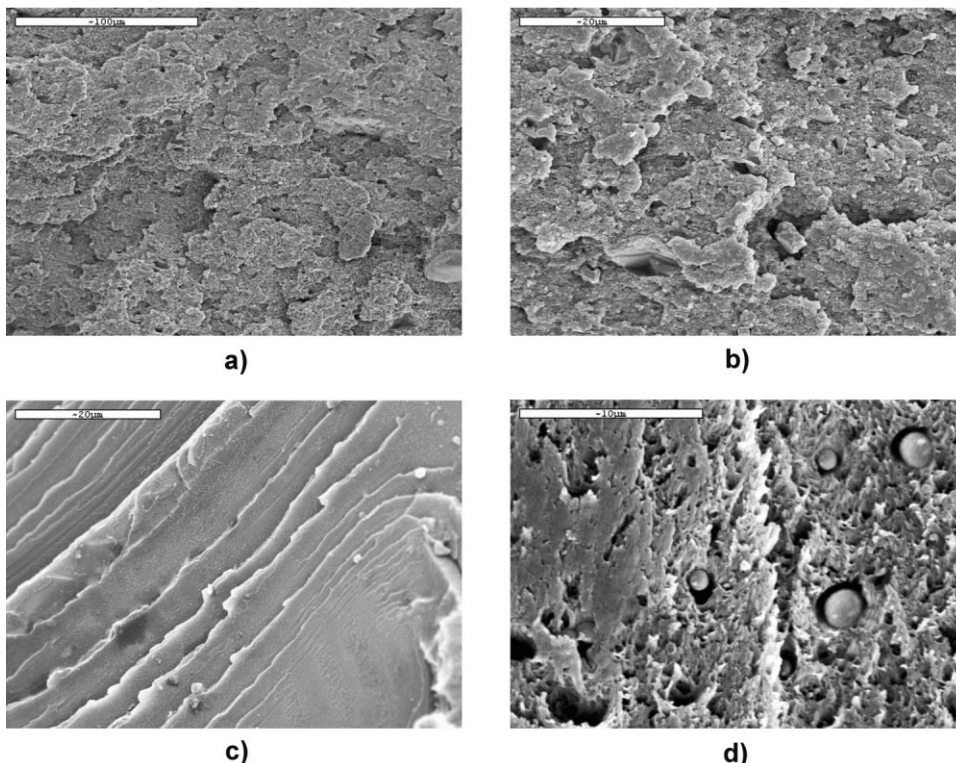The study of the morphology of the fracture surfaces using the SEM technique was carried out to identify

Figure 8 SEM micrograph of fractured surfaces of recycled materials: (a) R-PVC ×500; (b) R-PVC ×2000; (c) R-SAN ×2000; (d) R-ABS ×5000.
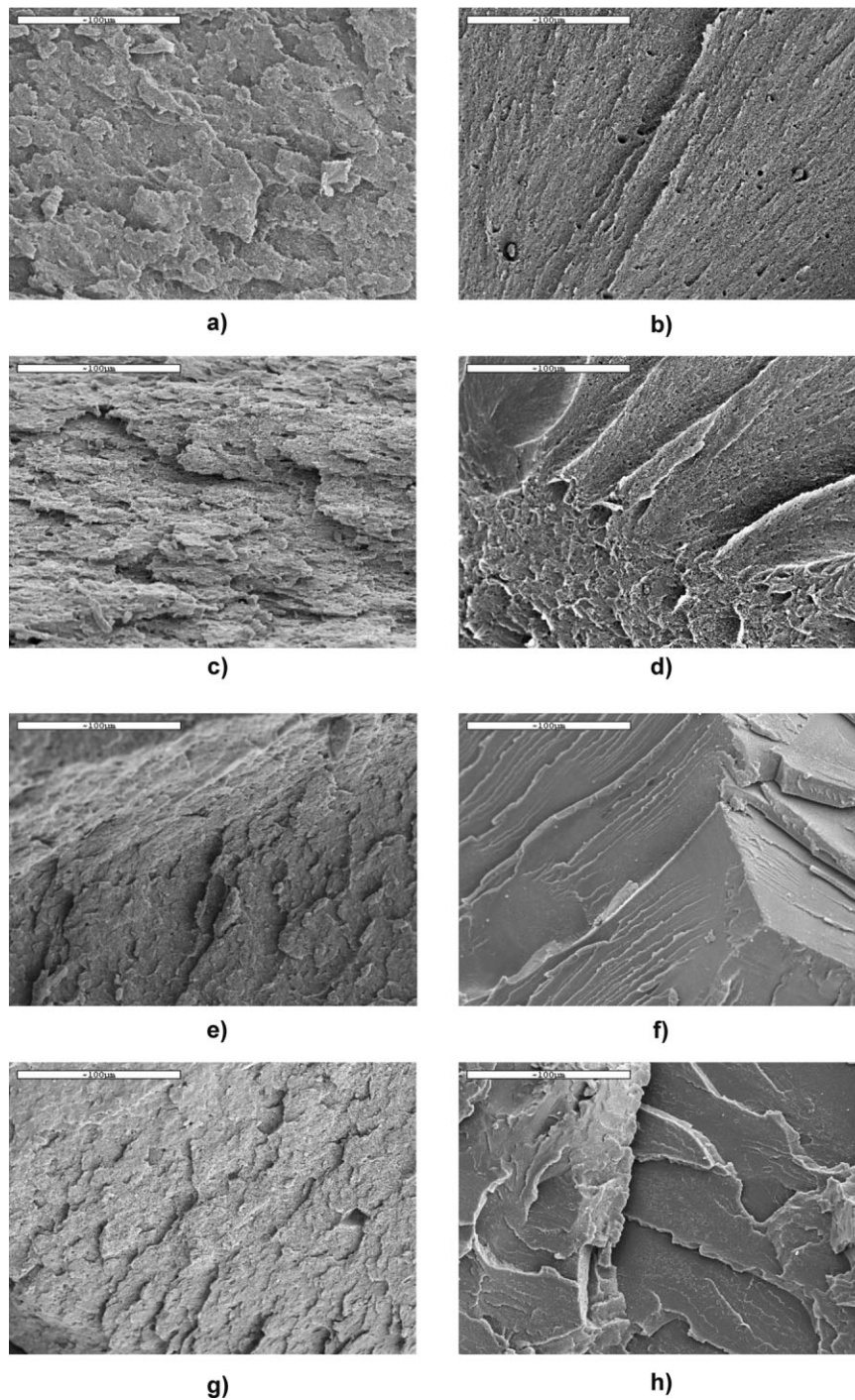
Figure 9 SEM micrograph of fractured surfaces of *R*-PVC blends with different compositions ×500: (a) R-PVC 60/R-ABS 40 wt %; (b) R-PVC 0/R-ABS 100%wt; (c) R-PVC 60/V-ABS 40% wt; (d) R-PVC 0/V-ABS 100 wt %; (e) R-PVC 60/R-SAN 40 wt %; (f) R-PVC 0/R-SAN 100 wt %; (g) R-PVC 60/V-SAN 40 wt %; (h) R-PVC 0/V-SAN 100 wt %.

any sort of impurity that would be able to act as stress concentrator, thus facilitating the fracture. In addition, the SEM technique permits the corroboration of the results obtained through the mechanical characterization and the establishment of a relationship between fracture surface and mechanical properties. As can be observed in Figure 8, the fracture surfaces obtained for recycled materials, after the tensile test, do not display

any indications of impurities that may lead to the fracture of the material. However, in the case of R-ABS, a lack of interaction between the butadiene phase, identifiable as randomly dispersed spheres with dimensions between 1 μm and 3 μm, and the SAN matrix can be observed. This lack of interaction existing in the R-ABS may be the cause of a strong reduction in the mechanical properties, which is the

case for the blends with R-PVC. On the other hand, the fracture surface of the R-PVC shows low levels of roughness, which are representative of the low ductility of the material.[25]

With regard to the morphology of the blends, in Figure 9, it can be observed that in the blends with R-SAN and V-SAN, fracture surfaces characteristic of fragile materials are obtained as the concentration of SAN increases in each case. On the contrary, in the blends with V-ABS blends, the surfaces obtained are distinguished by morphologies characteristic of ductile fractures. In the blends with R-ABS, it can be observed that the presence of butadiene spheres with a lack of interaction in the matrix phase of SAN provides fracture surfaces of barely roughness and fragile character.[26] In this sense, the butadiene acts as a stress concentrator, which encourages the fracture of the material.

CONCLUSIONS

The elaboration of blends made of R-PVC coming from credit cards with styrenic polymers is a feasible solution for the improvement of its mechanical and thermal properties. Thus, it enables the use of these types of blends in sectors where compliance with specific requirements related to mechanical properties and thermal stability is necessary.

The levels of degradation observed in R-PVC from credit cards are not significant. Similarly, in the recycled styrenic polymers analyzed, no significant levels of degradation have been observed.

The use of the DSC technique has permitted the identification of two clearly different glass-transition temperatures (T_g) in the R-PVC blends with styrenic polymers studied, displaced with regard to the T_g values of the materials without blending, which proves the existence of partial miscibility between the components. This miscibility, in turn, has a decisive repercussion on the mechanical properties of the different blends.

The incorporation of the styrenic polymers facilitates an increase in the thermal stability of the R-PVC, determined by the VST, which reveals a linear relation between the amount of incorporated styrenic agent and the VST. The blends with SAN show the best results in comparison with those for ABS.

The incorporation of styrenic polymers with the R-PVC causes a strong variation in the mechanical properties, although the results obtained show a strong relation to the type of styrenic polymer added, both as a result of its nature (SAN or ABS) and origin (recycled or virgin). The two virgin materials offered the best results, although, from an economic point of view, the low cost of the recycled materials makes this the most feasible solution.

The incorporation of SAN into the R-PVC improves the resistant mechanical properties, and a significant reduction in the ductile properties, which can be caused by the fragile nature of the SAN, and the absence of miscibility between the components can be noted. With regard to the ABS blends, the improvement in the ductile qualities, which can be a result of the butadiene content present in this material, should be highlighted.

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