

Characterization of blends of poly(vinyl chloride) waste for building applications

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Abstract In the present article we study the improvement of the performance of recycled poly(vinyl chloride) (PVC) coming from credit cards for its use in the fabrication of pipes and fittings in the hydrosanitary sector, in order to meet the requirements established in the international standards. With this purpose, styrene polymers from both virgin and recycled origin have been added to recycled PVC in different concentrations. Since these are recycled materials, the previous degradation of the recycled materials used has been taken into consideration. On the other hand, the compatibilization between polymers considered, which is the influential factor in the final properties of the blend, has been analysed by differential scanning calorimetry. The mechanical properties of the blends have been determined by tensile and impact test, and the thermal properties by Vicat softening temperature and dynamic mechanical analysis. Finally, fracture surfaces of the different blends have been analysed by scanning electron microscopy. The results obtained show a generalized improvement in the properties for small quantities added from styrene polymers, which makes the use of these blends in the building industry a feasible option.

Introduction

Over the last decades, the use of thermoplastics in buildings has notably increased. With regards to this, one of the

plastics which has been most widely used is poly(vinyl chloride) due to its low cost and its unique features, which have permitted its use in a wide range of applications [1], such as water distribution piping, home plumbing, drain wastage, window frames, skylights, floor coverings, credit card, packaging, cable insulation, etc.

The enormous consumption of PVC generates enormous quantities of waste, mainly of PVC derived from applications in which the products have a short-term life. In most cases, landfill sites are saturated, and incineration is a measure that poses significant risks to the public and the environment, due to the fact that during the incineration process, the PVC releases hydrogen chloride [2, 3]. Thus, mechanical recycling, aided by the new techniques of waste separation [4–7], is considered to be the best solution.

The main application of recycled PVC is the fabrication of pipes and fittings in the building sector. Apart from this, the main source of recycled PVC is that coming from credit cards. Subsequently, there are many enterprises dedicated to the selling and distribution of credit card waste. However, recycled PVC derived from credit cards cannot be used in the building sector, since, due to its flexible nature, it fails to meet the existing European standards related to thermal stability.

In this article, the possibility of improving recycled PVC derived from credit cards by means of incorporating styrene polymers, characterized by an excellent thermal stability, is studied. For this purpose, the styrene-acrylonitrile (SAN) and acrylonitrile-butadiene-styrene (ABS) copolymers have been used. Also, since the cost of the final product is a determining factor in establishing its market competitiveness, recycled SAN and ABS coming from waste electrical and electronic equipment (WEEE), with lower cost than virgin ones, have been taken into account.

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With regards to PVC/ABS blends, they are used in a wide variety of applications, their most relevant property being their high impact strength and satisfactory thermal stability [8]. In addition PVC/SAN blends show outdoor weatherability and improved flame retardancy.

The level of degradation of the recycled materials used in this study has been analysed using Fourier transform infrared spectroscopy (FTIR). In addition, the PVC blends with styrene polymers have been analysed using differential scanning calorimetry (DSC) in order to study their compatibility. The mechanical properties of the blends have been determined by means of the tensile and impact tests. In addition, with the aim of meeting the requirements established in the respective standards with regard to thermal stability, the Vicat softening point (VST) of the different blends have been measured, and the mechanical behaviour as a function of the temperature has been analysed using the dynamic mechanical analysis (DMA). Finally, the morphology of the surfaces of the blends fractured in cryogenic conditions has been analysed using scanning electron microscopy (SEM).

Experimental

Materials

The main properties of these materials are shown in Table 1. The materials used in this work are shown below.

- Recycled PVC (R-PVC) coming from credit card waste with a K -value = 62 (K -value is the viscosity measurement correlated with molecular weight according to ISO 1628-2 standard). 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 1 p.h.r. of CaZn stabilizer, 0.5 p.h.r. calcium stearate and 2.5 p.h.r. of CaCO_3 were added to limit the thermal dehydrochlorination of PVC.
- Virgin PVC ETINOX EF-0140 with (K -value = 60) in pellet form supplied by Aiscondel, S.A. (Barcelona, Spain).

- Recycled SAN supplied by Crearplast, S.L. (Ibi, Spain) in pellet form coming from wastes from electrical and electronic industry (WEEE).
- Virgin SAN POLIDUX S-580 supplied by Repsol Química, S.A. (Madrid, Spain) in pellet form.
- Recycled ABS in pellet form supplied by Crearplast, S.L. (Ibi, Spain) coming from WEEE.
- Virgin ABS POLIDUX A-164 in pellet form supplied by Repsol Química, S.A. (Madrid, Spain).

Sample preparation

The blends were prepared using a two-roll mill (front roll 180–190 °C; rear roll 170–180 °C). The blending process was conducted with different amounts of ABS and SAN both virgin and recycled. The blend time never exceeded 5 min to limit thermal dehydrochlorination of PVC. Once the blend was obtained, sheets with a thickness around $4 \cdot 10^{-3}$ m were 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 die-cutting machine with the dimensions according to ISO 527–2. The samples which, due to their high brittleness, could not be shaped were machined.

Characterization

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. In total, 100 scans at a resolution of 4 cm^{-1} were carried out for each sample.

The calorimetric analysis was carried out using DSC Mettler-Toledo 821 equipment (Mettler-Toledo Inc., Schwerzenbach, Switzerland). Samples ranging between 6 and

Table 1 Main properties of materials used

	Density (kg/m^3)	MFI ($\text{kg}/10 \text{ min}$)	Tensile strength (MPa)	% Elongation at break	Tensile modulus (MPa)	Impact strength (kJ/m^2)	VST (°C)
Recycled PVC	1,350	–	32.2	4.18	1,831	4.05	77.6
Virgin SAN	1,080	0.0101	58.2	2.50	2,788	0.78	101.3
Recycled SAN	1,080	0.0115	31.4	1.56	2,456	0.64	103.2
Virgin ABS	1,050	0.0089	32.9	20.9	1,786	35.0	92.0
Recycled ABS	1,060	0.0104	30.9	3.3	1,370	15.4	96.2

7 mg in weight were used. A first heating (30 °C–120 °C at 10 °C/min) was completed, followed by a cooling process (120 °C–30 °C at 10 °C/min) to eliminate the thermal history, and was finished with a second heating (30 °C–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).

To determine the Vicat softening temperature, 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 ISO 306.

Melt flow index (MFI) measurements were obtained with an extrusion plastometer (Ats Faar S.p.A, Vignate, Italy) according to the guidelines of ISO 1133.

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 crosshead 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 ISO 179. A minimum of five samples was analysed in order to obtain every result.

The measurements of dynamic mechanical properties were determined using an ARES N2 (TA Instruments, New Castle, USA). Tests were carried out in torsion deformation mode, at a frequency of 1 Hz and the temperature programmes were run from 30 to 150 °C at a heating rate of 5 °C/min. The dimensions of the test specimens were 13 × 11 × 3 mm.

SEM photographs of different samples were carried out by a scanning electron microscopy JEOL 6300 (JEOL USA Inc., Peabody, USA). 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 and also in cryogenic conditions using liquid nitrogen.

Results and discussion

Preliminary tests

One of the main requirements of the European standards regarding the construction of pipes and fittings for the building sector is the obtainment of a specific thermal stability in terms of the Vicat softening point (VST). In particular, it is necessary to have a VST above 79 °C. However, due to its flexible nature, the recycled PVC derived from credit cards has a lower value of VST

(77.6 °C). Thus, an increase in the VST is presented as the first objective to be met. With this in mind, some preliminary tests were carried out by blending recycled PVC with virgin PVC usually used in the fabrication of pipes. The results obtained showed an increase in the VST (Fig. 1), also it can be observed that the amount of virgin PVC needed to reach the required VST value to meet the standard, is close to 50 wt%. From the economic perspective this solution is not viable. For this reason, another type of work involving the PVC is required. The incorporation of other polymers with high thermal stability, such as styrene polymer appears to be the main alternative.

Level of degradation of recycled materials

The level of degradation accumulated in recycled polymers can have a decisive influence on compatibility with regards to other polymers and consequently, on the performance of the blend [9, 10]. In order to evaluate the existing level of degradation for the recycled polymers employed in the present study, the Fourier transform infrared spectroscopy (FTIR) has been used. The IR spectrum obtained for the recycled PVC shows the presence of polyene sequences. These sequences are identified in the IR spectrum by a peak which absorbs an infrared wavelength at 1,602 cm^{-1} . The presence of such sequences is due to the rupture of chains and the subsequent emission of hydrogen chloride gas, and is therefore indicative of a certain amount of degradation with regards the PVC [11]. Nevertheless, this peak obtained in the spectrum, due to its low intensity cannot be used to monitor the level of degradation. Also, in the IR spectrum a peak which absorbs an infrared wavelength at 1,735 cm^{-1} corresponding to carbonyl groups, can be observed. The carbonyl group can be associated to a certain

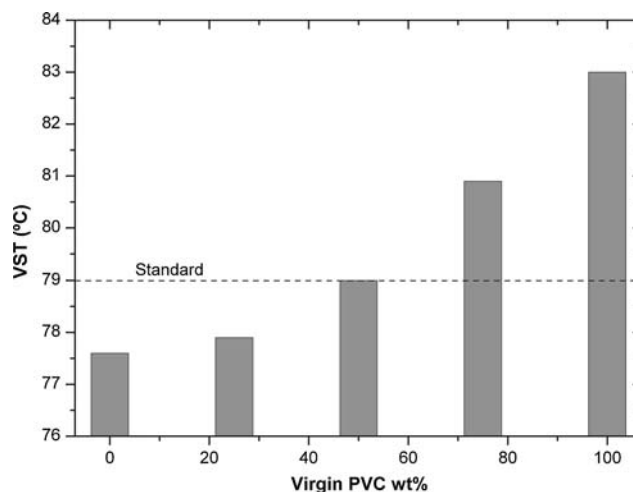


Fig. 1 Variation of VST temperature as a function of virgin PVC percentage

level of degradation. However, due to the flexible nature of PVC derived from credit cards, the presence of carbonyl groups can be a consequence of the addition of vinyl acetate, which acts as a plasticizer of PVC, thus obtaining the increase in flexibility which is a feature of the credit card. These groups were presumably the result of the application of this type of PVC, a material with a short-term life, rarely exposed to high temperatures or solar radiation during its use and usually well preserved during its storage.

With regards to the SAN and ABS copolymers, the main problem related to the recycling of ABS is the thermooxidative degradation of butadiene rubber during its service life [12]. Despite all this, no signs of degradation have been observed, due to the absence of carbonyl groups, which absorb an infrared wavelength at $1,750\text{ cm}^{-1}$ and hydroxyl groups which absorb an infrared wavelength at $3,250\text{ cm}^{-1}$, the main groups present in the thermooxidative degradation of these materials [13]. However, due to the notable decrease in mechanical properties and the increased MFI value, which indicates the rupture of chains, certain levels of degradation, although not too significant, can be deduced.

Compatibility PVC/styrenic polymers

The study of the compatibility of the PVC blends with styrene polymers was carried out by analyzing the changes in the glass transition temperature (T_g) [14]. The recycled PVC shows a T_g of $77.9\text{ }^\circ\text{C}$. This value is slightly below the usual for unplasticized PVC. This decrease in the T_g

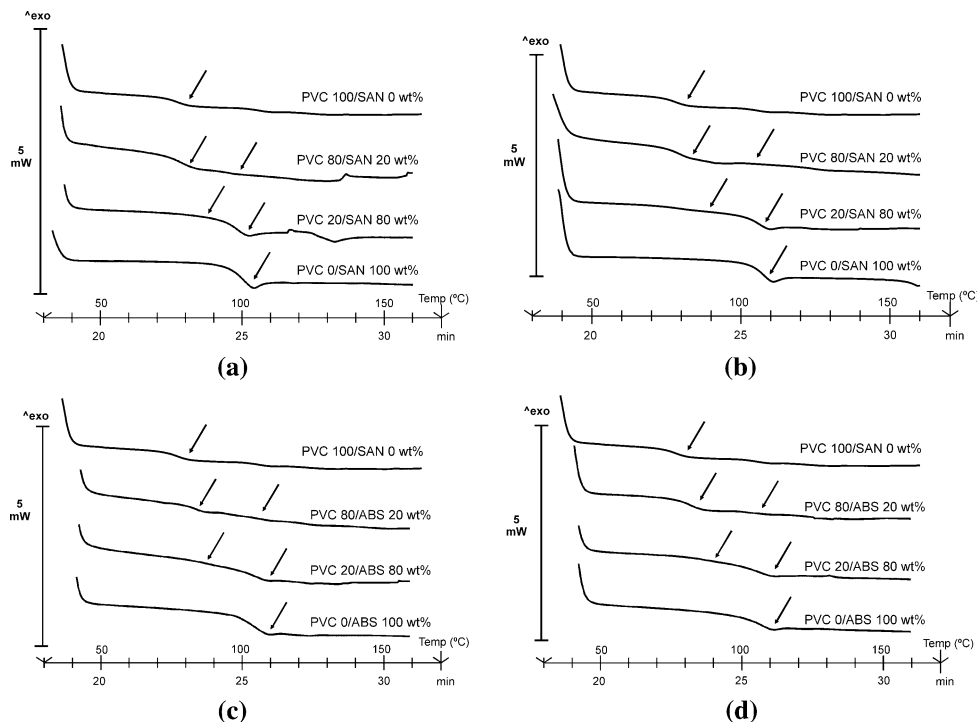
value corroborates the addition of vinyl acetate. In addition to this, virgin and recycled SAN show T_g values of $104.6\text{ }^\circ\text{C}$ and $106.9\text{ }^\circ\text{C}$, respectively, whereas the virgin and recycled ABS show T_g values of $106.2\text{ }^\circ\text{C}$ and $105.9\text{ }^\circ\text{C}$, respectively, which are the normal values for these type of polymers. In Fig. 2 the DSC curves for different concentrations of PVC/styrene polymers blends can be observed. These curves show two clearly differentiated transitions, the first one corresponds to the T_g of the PVC phase present in the blend, whereas the second one corresponds to the T_g of the styrene polymer phase. As such, with regard to the presence of two T_g , it could be concluded that this is an incompatible system. However, a significant variation in the T_g of the two phases with respect to the concentration of the blend can be observed. This fact indicates the existence of a partial compatibility between the polymers [15, 16], which can be attributed to the interaction between the polar groups of the styrene polymer phase and the polar groups of the PVC phase [17].

Partial compatibility will facilitate the obtaining of blends with higher benefits for those which can be attributed to the blends with incompatibility. And even, in some cases these blends can offer higher benefits than those presented by blends with total compatibility.

Mechanical properties

The mechanical properties are crucial when analyzing the feasibility of using a material in a specific application, a

Fig. 2 DSC scans of blends of recycled with different styrenic polymers: (a) virgin SAN; (b) recycled SAN; (c) virgin ABS; (d) recycled ABS



reduction in the mechanical properties can have a detrimental effect in its applicability, in particular in such industry sectors as the building and construction, where the service life of the material is long-term [18].

The incorporation of styrene polymers with the recycled PVC affects its toughness. In general, the incorporation of styrene polymer produces a slight decrease in the tensile strength of the recycled PVC (Fig. 3). However, since this reduction is not very important, this does not prevent its use for the fabrication of pipes and fittings. It must be pointed out that, different from the other added styrenic polymers, the incorporation of SAN causes a significant improvement in tensile strength.

With regard to the elongation at break, it is foreseeable that the incorporation of a polymer such as the SAN, characterized by a low capacity for deformation, may cause a decrease in the elongation at break. However, the incorporation of virgin SAN, as can be observed in Fig. 4, not only fails to diminish the elongation at break, but increases it up to concentrations of around 20 wt%. However, the addition of recycled SAN abruptly diminishes this property. Furthermore, the addition of virgin ABS offers an increase in this property. In contrast, the recycled ABS diminishes the elongation at break caused by the low deformation capacity of this ABS probably due to the degradation experienced by this material.

With regard to the tensile modulus, the incorporation of SAN in comparison with the ABS induces a higher increase in the tensile modulus (Fig. 5). It should be emphasized that better results are obtained with the blends with virgin styrene polymers than with recycled styrene polymers. The increase in the tensile modulus with the percentage of styrene derivative is a determining factor when applying this type of material to the building sector,

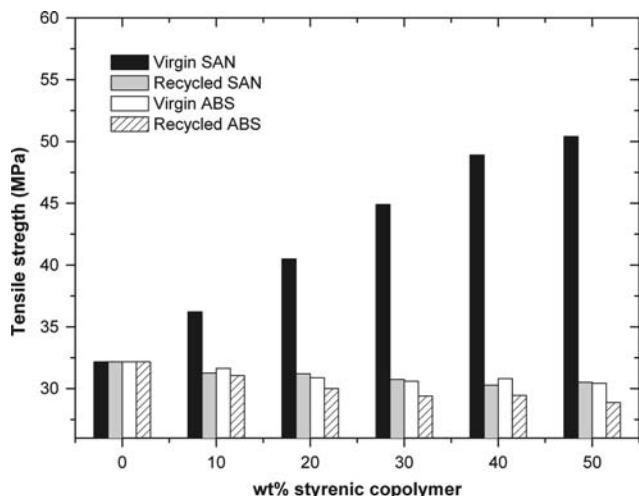


Fig. 3 Variation of tensile strength as a function of styrenic polymers content for different PVC blends

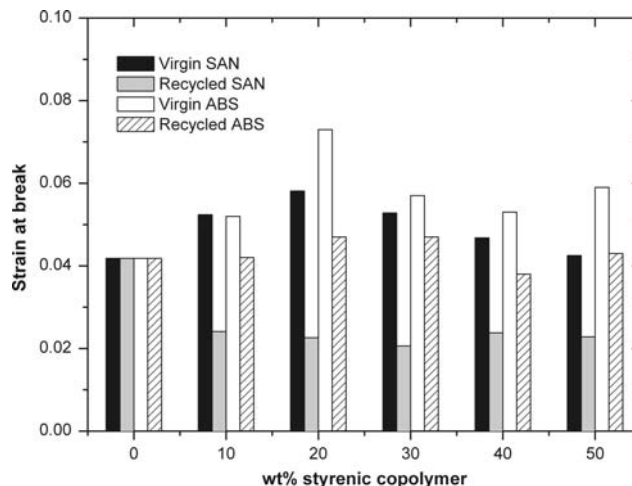


Fig. 4 Variation of elongation at break as a function of styrenic polymers content for different PVC blends

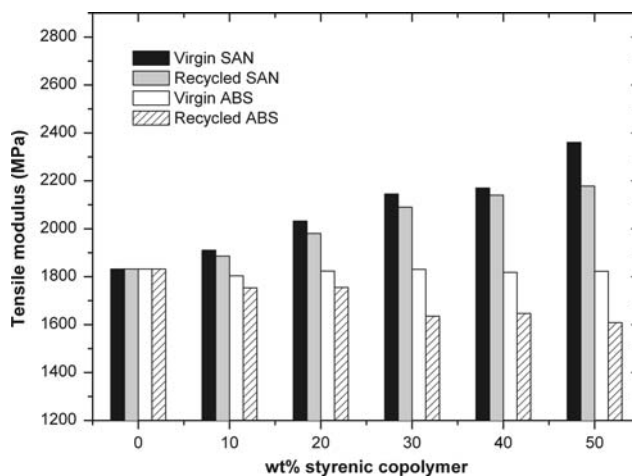


Fig. 5 Variation of elastic modulus as a function of styrenic polymers content for different PVC blends

since this property will have a significant influence on the material’s response to temperature.

The results obtained for impact strength corroborate those observed in the tensile test (Fig. 6). The incorporation of a fragile material, such as SAN causes a decrease in this property, which is more pronounced in the case of recycled SAN, reaching a notable reduction of up to 50% with only an added 10 wt%. In this case, the significant decrease of the impact strength can prevent its application in the fabrication of pipes and fittings, whenever the impact strength is a property for consideration. As expected, in contrast to that occurring with the SAN, the incorporation of the ABS increases the impact strength of the recycled PVC. However, for concentrations around 10 wt% of virgin ABS, a slight decrease is produced.

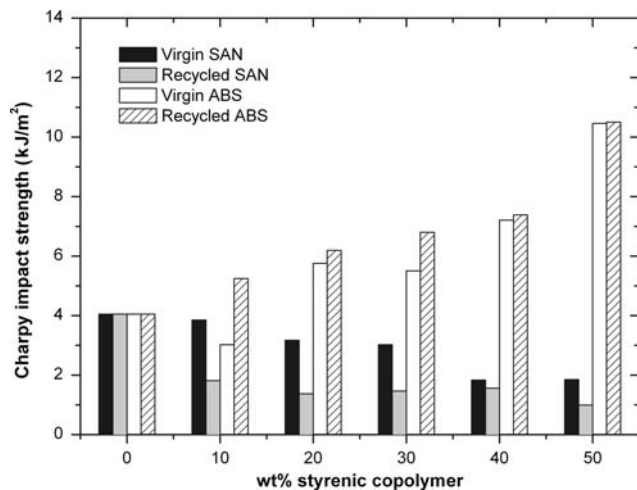


Fig. 6 Variation of Charpy impact strength as a function of styrenic polymers content for different PVC blends

Mechanical properties versus temperature

As previously stated, the main objective of this study is to improve the benefits of recycled PVC to enable it to meet the European standards, which requires a VST value not below 79 °C. In this sense, the incorporation of styrene polymers will act as a thermal stabilizer for the material, thereby increasing its VST. Figure 7 shows the variation in the VST of the recycled PVC, as a function of the blend concentration. As can be observed, the addition of the four styrene polymers considered in this article significantly increases the VST of the PVC.

It is important to note that, although the VST of the virgin styrene polymers used is lower than that of the VST of the recycled polymers, the incorporation of the virgin materials provides a higher increase in VST, since the PVC

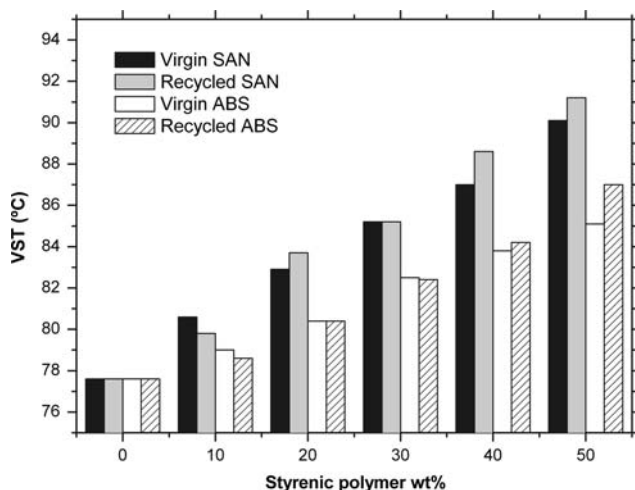


Fig. 7 Variation of the VST temperature as a function of styrenic polymers content for different PVC blends

blends with virgin styrene polymers present a higher compatibility.

Thus, the amount of styrene polymer necessary to reach a VST of 79 °C is lower for the SAN than for the ABS, and in turn, lower for the virgin materials than for the recycled materials. In all the blends, except for the PVC blends with recycled ABS, the amounts of styrene polymer which have to be added are below 10 wt%. These amounts are adequate for these types of blends, which guarantee a good result during the processing and a minimum increase in the final cost of the product.

On the other hand, the dynamic mechanical analysis (DMA) is an important tool in the study of polymeric materials, which allows the analysis of changes in material stiffness as a function of temperature. Figure 8 shows the DMA curves, expressed in terms of storage shear modulus, (G'), as a function of temperature, for recycled PVC, virgin SAN, virgin ABS, recycled SAN and recycled ABS. The behaviour of the PVC at room temperature is hard and vitreous [19], and as the temperature increases, a progressive reduction in G' is produced. This decrease is produced from 40 °C upward, in addition at 70 °C; the PVC displays a completely softer and rubber-like behaviour. With regard to the styrene polymers, it is important to note that no significant differences have been established between the styrene polymers of virgin and recycled origin. Thus, as was foreseeable from the results obtained after the mechanical characterization, the SAN has values for G' at room temperature which are notably better than those displayed by the PVC, and no reduction in G' is produced until 90 °C. Conversely, ABS shows a higher stiffness than the PVC at room temperature. However, it presents a curve with a smooth slope, which for temperatures above 60 °C, permits it to reach values for G' superior to those obtained

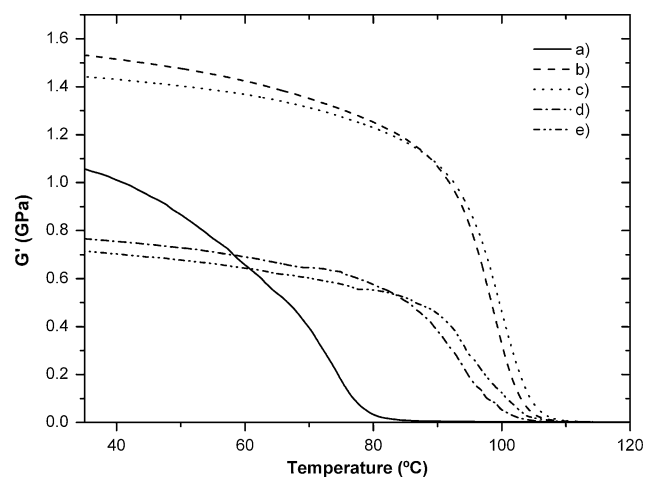


Fig. 8 Variation of loss modulus as a function of temperature for: (a) recycled PVC; (b) virgin SAN; (c) recycled SAN; (d) virgin ABS; (e) recycled SAN

by the PVC, thereby confirming the higher thermal stability of ABS compared to PVC.

With regard to the PVC blends, as the concentration of styrene polymer increases, the decrease of G' softens considerably with respect to the temperature, indicating an increase in the thermal stability of the material. This fact verifies the VST values previously obtained. In the PVC blends with virgin SAN (Fig. 9), for concentrations close to 60 wt% of SAN, there is no abrupt decrease in G' until temperatures close to 80 °C. A similar behaviour can be observed for PVC blends with recycled SAN (Fig. 10), although in these blends the increase in thermal stability is lower than that for the blends with virgin polymer for all ranges of composition. With regard to the ABS blends (Figs. 11, 12), the thermal stability produced is lower than

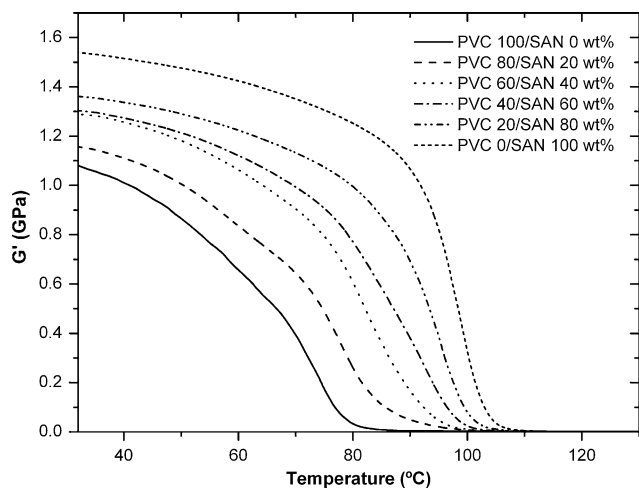


Fig. 9 Variation of loss modulus as a function of temperature for recycled PVC/virgin SAN blends with different compositions

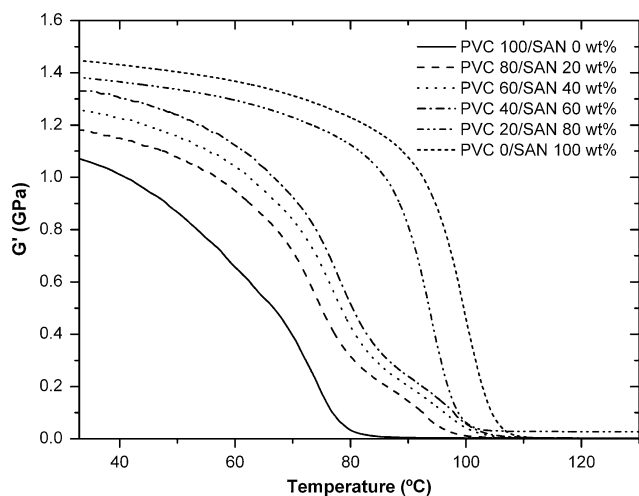


Fig. 10 Variation of loss modulus as a function of temperature for recycled PVC/recycled SAN blends with different compositions

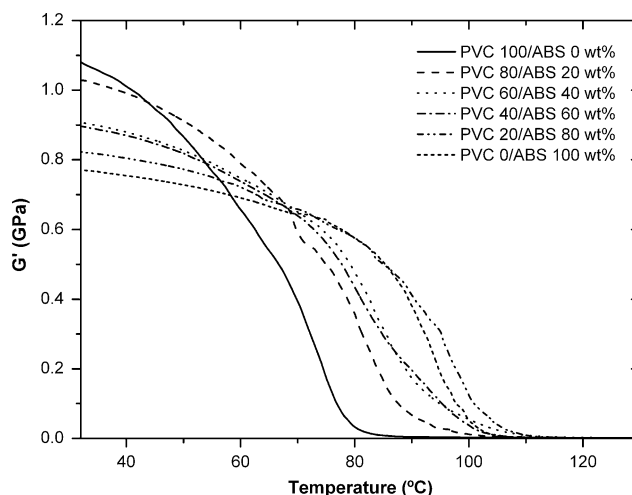


Fig. 11 Variation of loss modulus as a function of temperature for recycled PVC/virgin ABS blends with different compositions

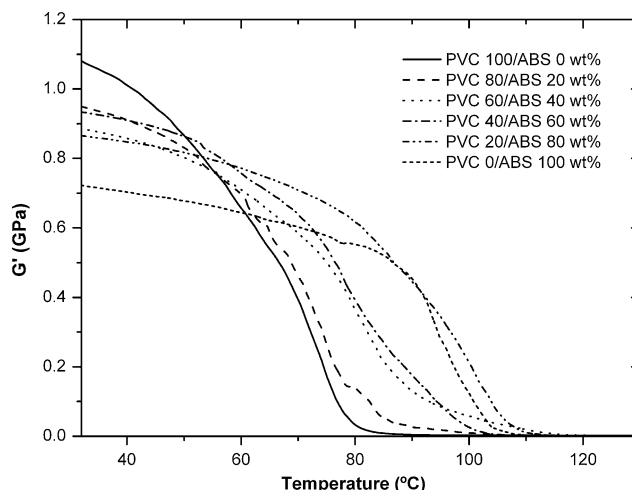


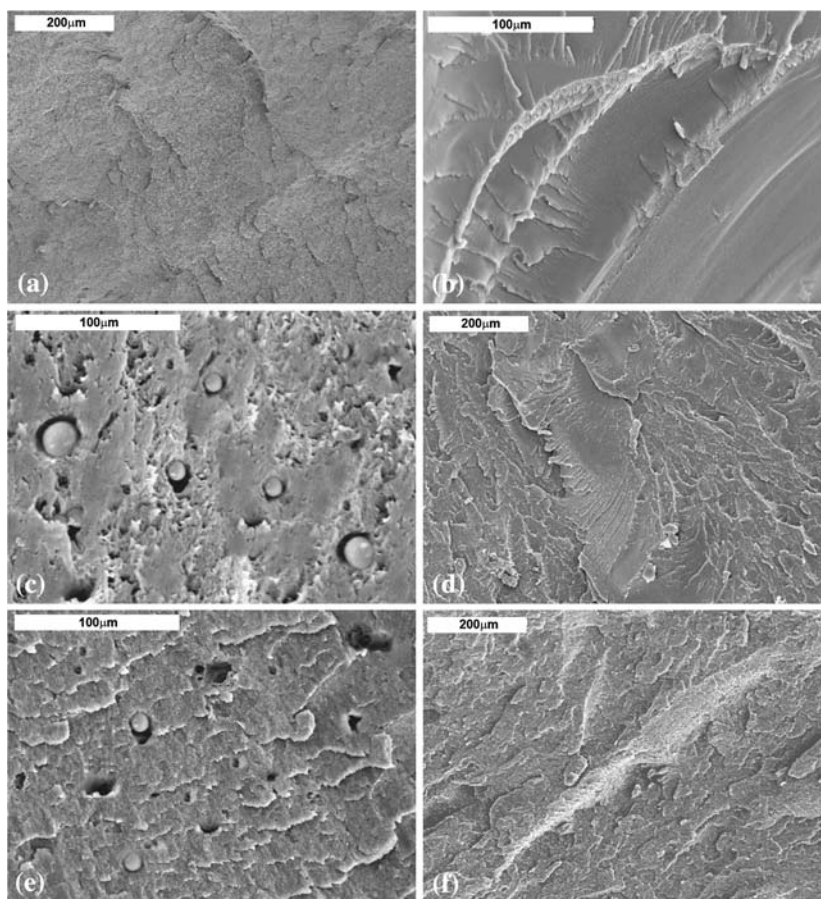
Fig. 12 Variation of loss modulus as a function of temperature for recycled PVC/recycled ABS blends with different compositions

in the SAN blends, also the blends with virgin ABS obtain better results than the blends with recycled one.

SEM investigation

The morphology of the fracture surfaces of the PVC blends with styrene polymers has been investigated using the scanning electron microscopy (SEM) of samples fractured under cryogenic conditions. Recycled PVC shows a brittle and scaly fracture surface (Fig. 13a), characteristic of a fragile behaviour [19]. Its structure is homogeneous, and no type of impurity has been observed as the cause of this fracture.

Fig. 13 SEM micrograph of fractured surfaces of: (a) Recycled PVC. $\times 150$; (b) recycled SAN. $\times 500$; (c) recycled ABS. $\times 5,000$; (d) recycled PVC 80/virgin ABS 20 wt%. $\times 150$; (e) recycled PVC 80/recycled ABS 20 wt%. $\times 500$; (f) recycled PVC 80/virgin ABS 20 wt%. $\times 150$



Similarly, recycled SAN and ABS are exempt from impurities causing a premature fracture (Fig. 13b, c). ABS presents the morphology characteristic of this type of material, where the polybutadiene phase in the form of spheres dispersed in the SAN matrix can be observed [20]. However, in the recycled ABS it is possible to observe a lack of adhesion between the polybutadiene and the SAN matrix, due to the possible degradation experienced. This lack of interaction results in the low benefits shown by this material and its subsequent blends with PVC [21].

In the PVC blends with virgin and recycled SAN, the surfaces obtained show the typical aspect of mirror region, where the fractures are preceded by craze formation and subsequent breakdown, characteristic of a fragile fracture (Fig. 13d). An apparently satisfactory interfacial adhesion between the components can be observed. As a consequence of this, its benefits are better than those offered by the ABS blends.

The PVC blends with recycled ABS (Fig. 13e) show the spheres of polybutadiene which appear to have poor adhesion with the matrix, as can be observed from the existing holes [22]. According to the aforementioned comment, this lack of adhesion plays a significant role in the reduction of the blend properties.

In contrast to the blends with recycled ABS, the PVC blends with virgin ABS (Fig. 13f) display a greater interfacial adhesion between the ABS and the PVC, mainly due to the greater adhesion observed between the polybutadiene phase and the SAN phase present in the virgin ABS. This coincides with the results obtained during the mechanical characterization, in which better properties were obtained for the PVC blends with virgin ABS than for the PVC blends with recycled one.

Conclusions

In conclusion, this work has demonstrated that the addition of styrene polymers to recycled PVC derived from credit cards facilitates an increase in its benefits, thus meeting with the requirements demanded for the fabrication of pipes and fittings in the building sector. In addition to this increase in properties, it offers a wide range of possibilities with regard to the application of these materials within the building sector.

The amounts of styrene polymer added, to comply with the existing standard cannot be considered excessive by any means and do not imply any variation in the PVC

processing system. Also, the levels of degradation observed for the recycled PVC derived from credit cards, due to the working conditions and short-term life, have not been relevant. With regard to the recycled styrene polymers derived from WEEE, nor have these shown significant levels of degradation.

The incorporation of SAN to the recycled PVC improves mechanical properties. However, a strong reduction in the ductile properties, which can be attributed to the fragile nature of the SAN itself and the lack of total miscibility amongst the components, can be observed. With regard to the ABS blends, the improvement of the ductile properties, which can be attributed to the butadiene existing in this material, must be pointed out. In general, greater benefits have been observed in the PVC blends with virgin SAN and ABS. However, from the economic perspective, the use of recycled SAN and ABS, with a lower cost than the virgin ones, will allow for a much more profitable solution.

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