

Incorporation of SBR Rubber Waste into PVC/CARBONATE Systems

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Research Article

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Abstract

The objective of this work was to evaluate the functionalization of the PVC/CARBONATE polymer system with the addition of SBR and the Polyvinyl chloride-PVC system and CaCO₃ carbonate through the incorporation prepared in a torque rheometer. Variations in SBR concentrations in the Poly (vinyl chloride) (C₂H₃Cl) and CaCO₃ system under processing conditions to obtain a balance of the mixture in a controlled environment of temperature, time and torque. The mixtures made were characterized and analyzed in terms of their physical and mechanical properties in terms of traction, hardness and fluidity. By FTIR, it was observed that there were no changes in the bands due to the presence of SBR-R in the increase of its percentage of SBR in the PVC/CARBONATE system. The results showed that the addition of rubber residue to the PVC/CARBONATE system causes variations in the mechanical properties of traction and hardness, justifying the reduction of mechanical strength in the addition of rubber to the formulations. XRD reveals the different behavior of the curves, predominantly with low crystallinity in the presence of rubber residue. The behavior of TGA in mass loss in a temperature-controlled atmosphere changes in the flow behavior, presenting lower MFI, leaving the material more viscous and with lower flow in relation to the expected behavior in the injection process. Although the proportions caused changes in the mechanical properties, the results were significantly satisfactory, considering that the composition for the purpose of the study obtained good results. Allowing up to the proportions of 25 and 50% to be applied and alternatives for the development of products with rubber residues according to the desired properties.

Introduction

Currently, plastics and rubbers are being widely used to produce a wide range of products, building construction; materials, packaging, non-utensils, etc. degrade and last a long time in the environment. The increase in the generation of waste materials (plastics and rubbers) in the world has led to the need to create adequate methods to reuse these wastes and reduce their simple effects on the environment [1].

The important environmental concerns about the final destination (disposal) of solid waste, sustainability, ecology, biodegradability and industrial recycling have become important environmental concerns when thinking about new materials [2]. the increase of industrial production occurred in the years, a destination of the main industrial residues occurred in a tornado in all the later problems [3].

Brazil has been standing out as one of the main ones, as a comprehensive example of synthetic synthetic rubbers, nitrile rubber (NBR), styrene-butadiene copolymers (SBR), ethylene-propylene-diene terpolymer (EPDM), among others [4]. Currently, 60-70% of all used rubbers are used in the production of tires, while 5-10% in the production of tires, and the rest in civil construction, adhesives, coating, applications, cables and others [5]. The reuse of thermoset polymers and rubbers is hampered by the fact that materials have a complex and heterogeneous composition [6].

Therefore, new recycling technologies have been developed in order to make possible the reuse of these wastes in the development of new materials [7]. Technological advances in the industrial sector in recent decades have allowed even more studies on composites of traditional and special polymeric materials due to their wide use as raw material and correlated to the performance of new mechanical properties [8].

The global production of rubber materials in 2017 was around 26.7 Mtons divided into 12.31 Mtons of NR and 14.46 Mtons of synthetic rubber [9]. Styrene-butadiene copolymers (SBR) used as an additive and filler to improve the processing characteristics and final properties (such as mechanical strength) of various materials. Poly(vinyl chloride)-PVC is a thermoplastic in common use with a great versatility of applications due to the use of additives in its formulation, which makes it possible to change its thermal, mechanical and morphological properties. PVC properties can vary from an extremely flexible polymer to an extremely rigid polymer [10].

Polyvinyl chloride (PVC) is a polymer with great potential for technological applications that most applies to the preparation of composites and one of the most accepted additives in their formulations. PVC can be considered the most versatile among plastics as main characteristics of properties such as: good weather resistance, good chemical resistance, good mechanical resistance and toxicity, good toughness and flexibility, also presenting compatibility with various polymers.

SBR-R (styrene-butadiene copolymer) is an elastomer considered to be of general use. It has properties such as reasonable aging resistance, good abrasion resistance, good seawater resistance [11]. SBR has low mechanical strength, requiring the addition of reinforcing fillers in its formulation. However, SBR is less chemically reactive with slow curing kinetics, which requires more accelerator [12-13]. Rubber waste from the footwear and tire industries is a source of environmental pollution and waste of raw material with good properties and high added value [14]. Calcium carbonate is an inorganic compound with a form of CaCO_3 and a tetradic molecular structure.

The functionalization of SBR in grafting with polyvinyl chloride (PVC) aims to study the ideal proportion in the compatibility of polymeric mixtures. Since synergy is intended to meet tension for energy exerted by the polymers, which may result in improvements in applications such as: tensile strength. This work has as main objective the recovery of waste butadiene styrene copolymer (SBR) from the footwear industry in the region of Campina Grande - PB, which generates about 51 t/year of waste, of which 8.9% are discarded SBR.

Therefore, for the mixture of the compositions of the materials for this, the factors studied were: to determine the concentrations of residues of rubber SBR in the system with polyvinyl chloride PVC, obtaining mixture in the equipment Haake PolyLab QC Rheometer from Thermo Scientific of the Rheology Laboratory of the academic unit of Materials Engineering at UFCG and the performance of the Tensile, Shore A Hardness and Fluidity Index (MFI) tests.

Experimental

MATERIALS

The following were used: Poly (vinyl chloride) (PVC) NORVIC® SP 1000, produced by Brasken, in the form of powder granules in transparent natural color Value K 65+1, density $0.52 + 0.03 \text{ g/cm}^3$, granulometry $\geq 95\%$.

The rubber residue comes from the scraps of the manufacturing process of the footwear industry. It is known that the residues come from styrene-butadiene rubber (SBR) in the form of black powder constituted by the complex mixture of styrene-butadiene copolymer and additives, such as: mineral fillers, butadiene and styrene elastomer, pigments, accelerants, flow agents and vulcanizing agent (acceleration matrix: carbon-carbon and carbon-sulfur)[15].

The calcium carbonate (CaCO_3) used was precipitated calcium carbonate (Grade S600F10 NC010), manufactured by the company QUIMVALE, supplied by the company Alpargatas (Campina Grande/PB). In the form of granules in natural color, odorless, absolute density 2.65 g/cm^3 , insoluble in water, pH 9.0 to 10.20 (10% white solution), and is indicated for injection process.

METHODS

Preparation

Rubber waste comes from the shavings of expanded SBR insoles that were collected from the footwear industry Alpargatas S.A., headquartered in the city of Campina Grande/PB. The material burrs were ground in a facade mill, from Marconi, model MA580. The determination of the size of the specific mesh 40, 425 mm in ABNT sieve was carried out following the ASTM D-1921 standard, using a PRODUTEST sieve and a set of GRANUTEST sieves standardized by ABNT through EB-22.

The incorporation carried out in the torque rheometry were performed in an internal mixer Haake PolyLab QC Rheometer from Thermo Scientific, operating with roller-type rotors, rotation speed of 60 rpm under temperature of 160°C , samples with 190g for 10 minutes, in an atmosphere of air. The following were analyzed: the behavior of the temperature and torque profiles in the reactions up to 160°C ; using the pcr concentration of SBR-R. And the proportions of carbonate CaCO_3 composing the system in the concentration also followed the same pcr of CaCO_3 .

The screw profile used is configured with distributive and dispersive modules, for better homogeneity. Extruder let out was pelleted and dried under vacuum at 60°C for 24 hours. Specimens of SBR Rubber Waste into PVC/CARBONATE Systems were injection molded using an Arburg Model Allrounder 207C Golden Edition (Radevormwald, Germany), with temperature profile of 175°C in all zones, and mold at 60°C and injection pressure 1200 bar. The tensile specimens were molded according to ASTM D638 (Type I), respectively.

Table 1 - Produced blends with added PVC (wt. %) content. "SBR e CaCO_3 " means compound.

Compounds	PVC (%)	Resíduo borracha SBR-R (%)	CaCO ₃ (%)
PVC Ca100	93	-	7,0
PVC SBR-R-25 Ca-75	93	1,7	5,3
PVC SBR-R-50 Ca-50	93	3,5	3,5
PVC SBR-R-75 Ca-25	93	5,3	1,7
PVC SBR-R-100	93	7,0	-

CHARACTERIZATIONS

The torque rheometry tests were performed in a Thermo Fisher Scientific mixer, Haake Rheomix 3000 (Waltham, Massachusetts, United States) operating with roller-type rotors, rotation speed of 60 rpm under temperature of 160°C, samples with 190g during 10 minutes in an air atmosphere.

The following were analyzed: the behavior of the temperature and torque profiles in the reactions up to 160°C; using the pcr concentration of SBR-R. And the proportions of carbonate CaCO₃ composing the system in the concentration also followed the same pcr of CaCO₃.

The tensile test specimens were molded, according to ASTM D 638 Type I (2002), in an Arburg Allrounder Hydraulic Injection Molding Machine. The processing conditions for the four zones were at a temperature of 175°C, mold temperature of 60°C and injection pressure of 1200 bar. The samples were obtained according to the ASTM D 638 standard.

Fourier transform infrared (FTIR) spectroscopy analyses were performed in a Spectrum 400 da Perkin Elmer FT-IR/FT-NIR (Massachusetts, United States), attenuated total reflectance mode was applied, with scans ranging from 4000 cm⁻¹ to 500 cm⁻¹.

The X-ray diffraction analysis was performed on impact specimens, conducted using a BRUKER X-ray diffractometer, model D2 PHASER (Massachusetts, United States), with copper K α radiation, 40 kV voltage, 30 mA current, with 2 θ ranging from 2° to 30° and scanning rate of 2 °/min.

Thermogravimetry (TGA) analysis performed on a simultaneous TG/DSC device SDT Q600 from TA Instruments (Kyoto, Japan) using 5 mg samples, heated from room temperature (~ 23 °C) to 500 °C, with heating speed flow of 10°C/min and nitrogen flow of 100 ml/min.

Tensile test was performed on injected specimens according to ASTM D638-03 standard adapted, with specimens type IV (tie) with a thickness of 10 mm using an EMIC DL 2000 (São José dos Pinhais, Brazil) universal testing machine with elongation rate of 50 mm/min and load cell of 20 kN at room temperature (~ 23°C). Presented results are an average of ten specimens.

Shore A hardness performed in accordance with ASTM D2240, in Shore-Durometer Type “A” Woltest Hardness (São Paulo, Brazil), with a load from 0 to 100 controlled by calibrated springs with standardized indenters. The reported results are an average of five experiments.

The fluidity properties of the polymeric specimens were evaluated using the equipment used was the MELT Flow Modular Line from Ceast MF20 from the Laboratory for the Development of New Materials (Alpargatas – Campina Grande), in Campina Grande. Flow tests were conducted at standardized length as per ASTM D 1238. The results obtained are the average of three individual tests on each sample calculated by equation (1).

$$\text{MFI} = \frac{m}{t} \times 600 \quad (1)$$

Where:

m = mass of the molten sample obtained at the capillary outlet;

t = is the melt collection time.

The test conditions were: initial mass of 5 g, applied load of 20 kg, test temperature of 175°C and capillary diameter of 2.095 ± 0.005 mm.

Optical microscopy (OM) images were captured on the surface of the injected specimens. An optical microscope, OLYMPUS DSX1000 (Tokyo, Japan) was used. Optical microscopy with a capacity of 1,200x performed at 300 and 600x magnification to verify the surface of certain samples.

Results And Discussion

Torque Rheometry

Torque rheometry graphs of PVCCa100, PVC/SBR and PVC/SBR/Ca blends are shown in Figure 1. Torque measurements were used to evaluate the processability, dynamic stability and reactivity of the compounds studied. The granular structure begins to be partially destroyed by breaking the grains into primary particles, thus reducing torque values to a minimum. With the progressive application of shear under heat, the particles undergo a new densification process forming a homogeneous gel state.

Initially, between 0 and 1 minutes there is an increase in torque due to the fusion of the solid material that enters the chamber, which requires a lot of energy for the rotation of the rotors. After 3 minutes, the presence of torque stability as a function of time for PVCCa100, but for the PVC/SBR/Ca and PVC/SBR systems there was a decrease in torque after 3 minutes, characteristic of thermal instability. There is also an increase in torque for PVC/SBR, suggesting higher viscosity materials due to the addition of SBR, as well as interaction between the phases.

Figure 2 shows graphs of temperature and energy as a function of time for PVCCa, PVC/SBR/Ca and PVC/SBR. It can be seen in Figure 2 temperature reduction between 0-2 minutes, due to feeding and consequently energy absorption by the materials. Between 4 and 5 minutes it can be seen that the PVCCa100 has a lower final temperature (159°C), while the PVC/SBR/Ca have similar temperatures, around 160°C. From Figure 2 it is possible to observe that PVCCa100 has lower energy when compared to PVC/SBR/Ca system, probably due to the increase in viscosity.

FTIR Spectroscopy

Figure 3 illustrates FTIR spectra of PVC, e compounds SBR, PVC/SBR e PVC/SBR-Ca, before and after compounds. There are absorption bands for PVC at 1250 referring to CH₂-Cl, in his analysis identified the band at 1268 cm⁻¹ and attributed to angular deformation in CH₃, the bands at 500 cm⁻¹ are attributed to stretching of C-Cl, at 1260 cm⁻¹ are attributed to angular deformations of CH-Cl and CH₂-Cl, and the band at 970 cm⁻¹ is attributed to the out-of-plane angular deformation of the C-Cl group [16].

The band at 1720 cm⁻¹ is attributed to probably axial deformations of the plasticizer ester, absorption bands between 1724-1748 cm⁻¹, probably attributed to the presence of plastificate, to the axial strains of C=O of esters and, between 1221 and 1254 cm⁻¹, referring to axial strains of the C-O-C cluster of esters [17].

And the band referring to the axial deformation of C-H at approximately 2910 cm⁻¹ The absorption bands between 2857 and 2962 cm⁻¹ refer to group stretches CH (in -CH₃, -CH₂- and -CH=) and were observed in all components of the compositions [18].

Figure 3 includes the FT-IR spectra of some NR/SBR mixtures studied. The analytical bands chosen, 699 cm⁻¹ for SBR, are assigned, respectively, to vinylidene (w CH₂) and dC-H (aromatic substitution) groups. The baseline for the band for SBR, from 730 to 635cm⁻¹. [19] Figure 3 shows those of the PVC compound and the polymer blend of SBR/PVC overlaid; In this image it can be seen that the spectrum of mixture of residuos SBR, PVC/SBR-Ca and PVC/SBR is a resultant of the spectra of the compound of PVC, showing the same previously mentioned peaks.

X-Ray Diffraction

To assess the effect on the crystallinity of the compounds, XRD analyzes were performed; the data collected from the SBR residues and after incorporation in the formulations seen in the XRD graph of Figure 4. The SBR polymers showed amorphous behavior or with low crystallinity as a broad band, characteristic of the amorphous phases of the SBR residues.

According to Rodolfo et al (2006), PVC is considered an amorphous or low crystallinity polymer, and this characteristic varies according to the polymerization conditions [20]. And According to (CANEVAROLO JR, 2002) the increase in the amount of crystals in the polymer and consequently the increase in its density promotes an increase in the modulus of elasticity, wear resistance and durability of the polymer. This

effect is observed, but changes in the processing procedure or post-treatment of polymers can alter this direct relationship between crystallinity and mechanical strength [21].

When analyzing the compounds with SBR of the Figure 4, both for PVC/SBR with addition of CaCO₃ and for PVC/SBR, they showed a tendency of crystalline peak (more intense for compositions with CaCO₃) at 29.5° characteristic of crystallites corresponding to CaCO₃ crystals.

Lower intensity peaks are also present in PVC/SBR100 specimens, probably CaCO₃ is present in the SBR residue composition characteristic of the planes. Thus, the proportions of 25 and 50% of SBR with the addition of CaCO₃ indicate a clear increase in crystallinity, as will be corroborated later by the tensile strength data.

Thermogravimetry (TGA)

Figure 5 illustrates the TGA plots of the investigated compounds and Table 1 shows the computed parameters, that is, T_{D10%}, T_{D50%}, T_{D99.99%} SBR showed only three stages of thermal decomposition, between T_{D10%} 331, T_{D50%} 443 and T_{D90%} 780°C, with (Table 1). After the addition of SBR to the PVC, a third decomposition step, characteristic of SBR, takes place. Adding 25% SBR to PVC gives an increase of T_{D10%}=261, T_{D50%}=309, and T_{D90%}=659, but there is a decrease from adding 100% to T_{D90%}.

In relation to compounds with the addition of SBR, with a lower degree of crystallinity as observed by XRD, in general there was a subtle reduction in thermal stability.

Table 2 - Thermal stability parameters of investigated compounds.

COMPOUNDS	T _{D10%} (°C)	T _{D50%} (°C)	T _{D90%} (°C)
SBR	331,6	443,77	780,43
PVC Ca100	255.51	307.17	662.08
PVC SBR-R-25 Ca-75	261.86	309.96	659.90
PVC SBR-R-50 Ca-50	255.51	307.15	616,46
PVC SBR-R-75 Ca-25	256.89	309.67	659.09
PVC SBR-R-100	264.45	306.31	613.64

T_{D10%} = temperature of 10% of degradation; T_{D50%} = temperature of 50% of degradation. T_{D90%} = temperature for 90% of degradation.

Tensile Test

Figure 6 shows tensile loads for PVCCa100, PVC/SBR/Ca and PVC/SBR under study. The tensile loads of PVCCa100 decreased from 330.1 MPa for the composition with SBR to 281.9 MPa, being directly related

to the tendency of lower crystallinity, corroborating the XRD data. In materials, when there is less stiffness, it indicates a decrease in tensile strength. After the addition of SBR, the tensile load reduces as well as the elastic modulus and consequently the stiffness due to the characteristics of SBR in the PVC/SBR system. There is load reduction 1.4%; 5.6%; 11.2% to 14.6% of the compositions with SBR.

Figure 7 shows the tensile stress in tensile strength (MPa) data. With the addition of 25% of SBR there was no reduction in this property. For the other compositions in the increase of SBR, it went from 7.96 to 7.12 (reduction of 14.1%) in relation to PVCCa100, while the addition of 50 and 75% of SBR was 10.6% and 4.1% was sufficient to promote reductions in tensile strength and tensile strength.

Shore A Hardness

Regarding shore A hardness, the addition of SBR led to a slight increase in hardness. Increases of up to 7.8% were observed for PVC/SBR. Figure 8 They showed an increase behavior in the hardness of the PVC/SBR-Ca compositions of 6.7; 2.5 and 5.2% for the average of 5 samples of their respective compositions in figure 16. The Shore A hardness increased by less than 10% compared to the standard PVCCa100 sample.

Test fluidity

The melt flow index (MFI) is a measure of the viscosity of a polymer in its melting state and is determined by calculating the mass (in grams) that passes through the matrix in ten minutes.

Fluidity is reduced when compared to PVC Ca100 values. However, when considering that the incorporation of a recycled material, with cross-links in contents, significantly compromises the viscosity of the material where, the properties are impacted.

Knowing the flow rate is vital for anticipating conditions and controlling your processing. Generally, materials with greater fluidity depending on the application are used in injection molding. For the compositions, there is a reduction in MFR with SBR fraction up to the proportion 25/75% with an effectiveness of 93%. However, the above proportions promote lower efficiencies to the point of having only 34% for PVC SBR-R-100 compared to the desired standard of PVC Ca100 and consequently there is a considerable increase in viscosity with increasing SBR Figure 9.

Optical microscopy (MO)

Figure 10 e 11 shows MO images of the surface of the specimens under study, before being subjected to tensile tests. For magnifications up to 300x and 600x. the images show not so smooth surfaces, with small deformations showing rupture of the specimens in the tensile test, typically more fragile, with differences due to the low crystallinity of PVC and between SBR.

PVC/SBR combines rough surfaces with signs of plastic deformation displayed, while increasing SBR content reduces strength properties. For the PVC/SBR-Ca and PVC/SBR systems, voids were found on the

surfaces, characteristic of the phenomenon of pulling out with SBR particles, being a surface with roughness in relation to PVCCa100 with the others 25,50 75 and 100% of SBR, as well as different possible morphologies. Where with higher SBR content, there was a reduction in the interaction with PVC. The interaction between the components, although of low intensity, can be attributed to the polarity existing in the chemical structure of PVC by the chlorine atom [22].

From the morphological analysis of all systems, it was possible to observe that the compounds with higher content of SBR showed a tendency to points of low adhesion and between the polymeric phases. The low adhesion and probably favored the formation of pores and consequently points of fragility.

Figure 12 shows MO images of the surface of the bodies and presents 600x images. For the 600x samples we show the 3D points for the samples, points in red on the axis of each 3D sample show imperfections or voids caused by the residue in the specimens. That is, tendency to rupture in the tensile test.

Conclusions

The addition of SBR rubber residue to PVC presented lower torque results for ternary samples with SBR in relation to the concentrations of the PVC compound with CaCO₃. This result may indicate a lower efficiency of this incorporation. The FTIR samples characteristic of PVC were not modified by the presence of SBR nor with the variations of increase of its percentage and also by the presence of CaCO₃, showing that its chemical groups were not affected.

Through XRD, it can be seen that the incorporation of SBR to the PVC compound above 75% strongly reduces the crystallinity, promoting lower tensile strength, higher Shore A hardness and lower thermal stability.

The tensile strength was reduced by up to 14.6% in relation to the composition of the PVC compound with CaCO₃ or PVC-Ca100. On the other hand, the Shore A hardness resistance increased by 5.2% in relation to non-SBR-R compatible ones. The addition of SBR was sufficient to show differences in mechanical properties in increasing the fraction of SBR-R rubber residue.

The PVC/SBR-R/CaCO₃ system with rubber residues in the proportion of 25%, with an MFR of 36.4, is a good alternative for loading and recycling SBR-R compounds. For injection molding application, above fraction may reduce possibilities of using SBR with filler. The higher the percentage of incorporation there is a drop in the specific properties desired.

Optical images showed characteristic void surfaces of the SBR particles, as well as discontinuity phases, mainly with the addition in larger fractions of the SBR 25 to 100% SBR under study.

We can conclude that these results indicate an alternative for new applications with the use of waste rubber, depending on the desired properties, even before we dispose of this industrial waste, which can

promote and minimize the effect of undesirable disposal costs on the environment and generate value for a new material.

Declarations

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CONFLICT OF INTEREST

There is no conflict of interest and all authors have agreed with this submission and they are aware of the content.

DATA AVAILABILITY

Data will be made available on request

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Figures

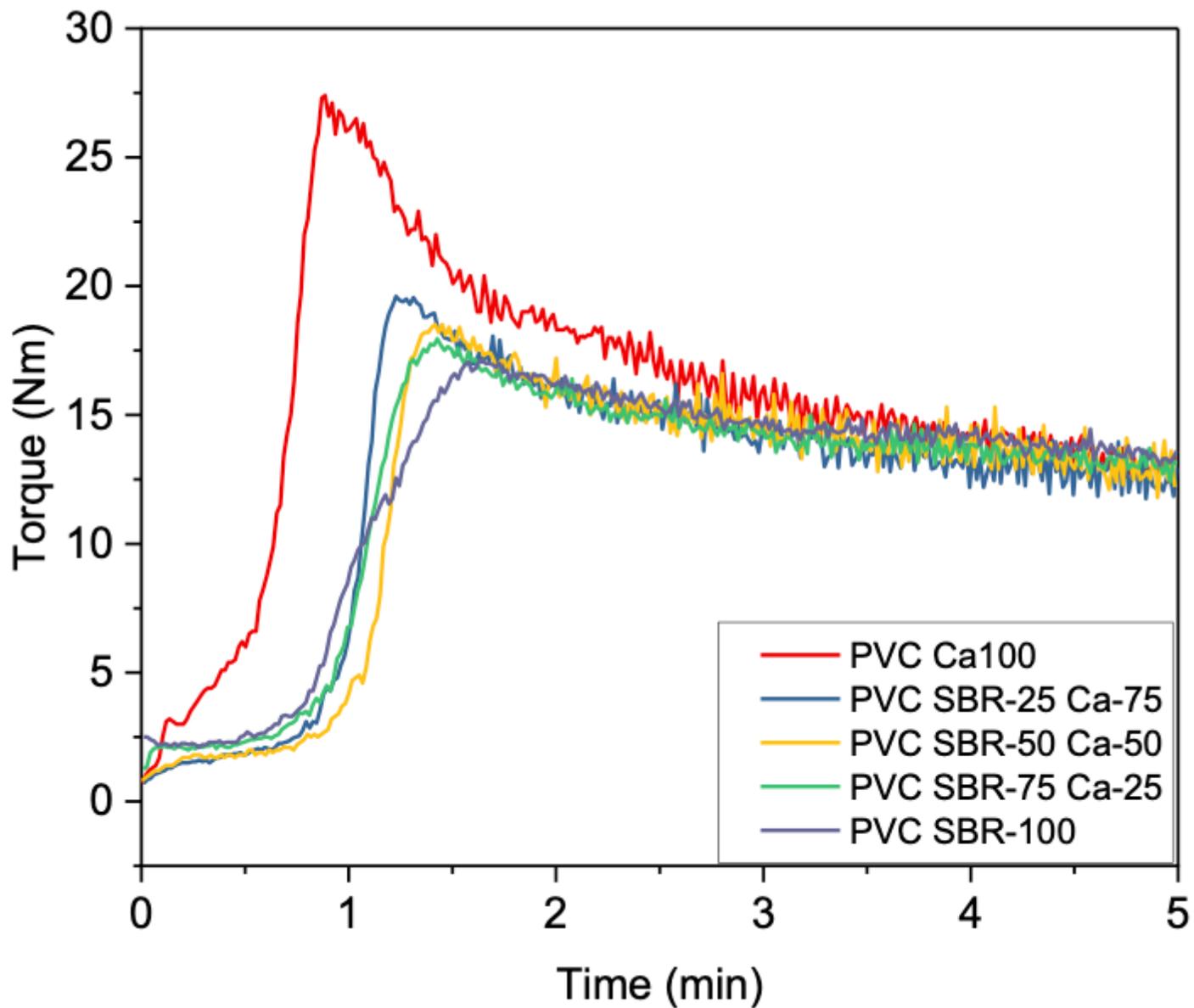


Figure 1

Torque versus time PVCCa, PVC/SBR and PVC/SBR/Ca..

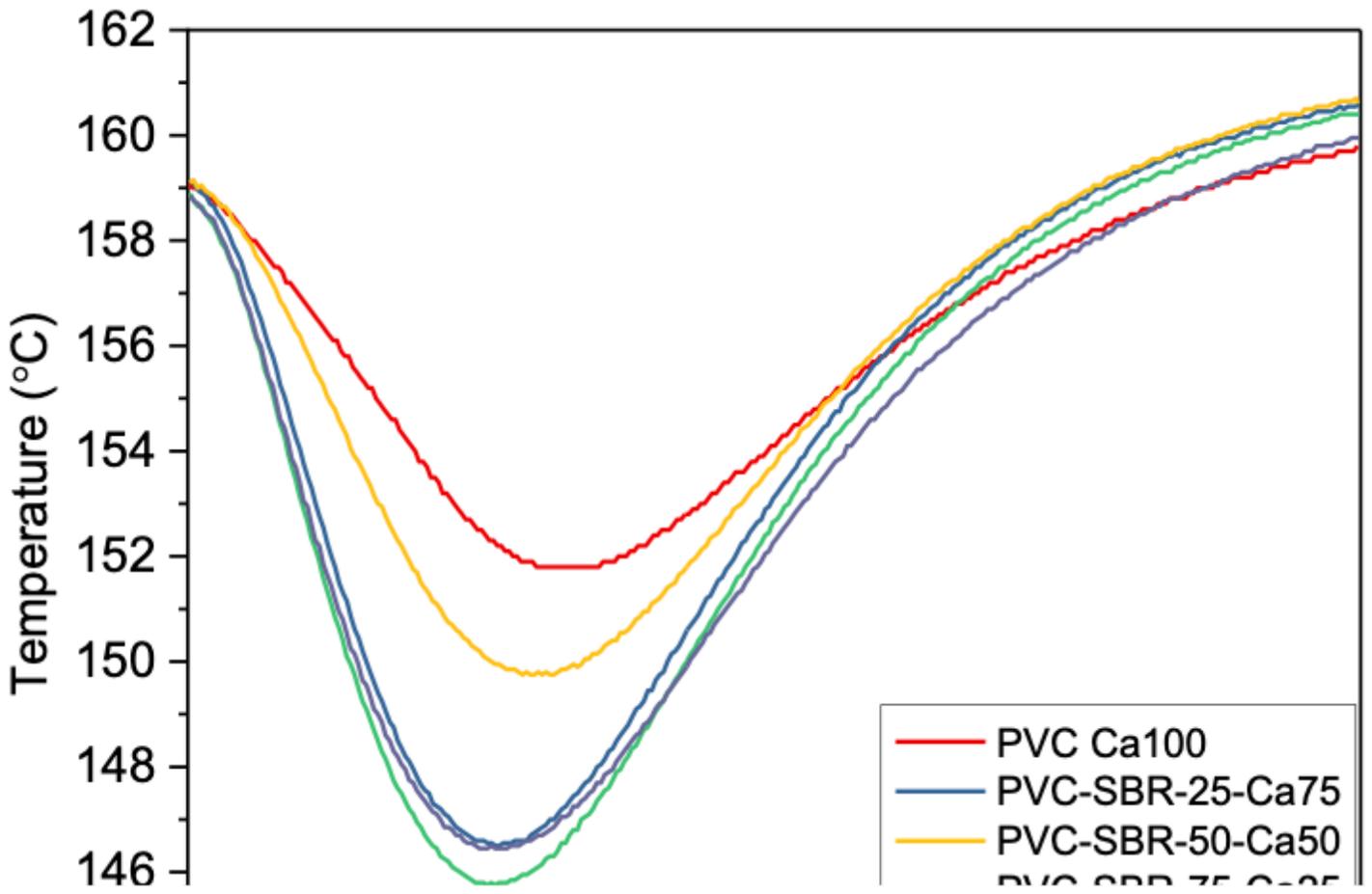


Figure 2

Temperature as time function for PVCCa, PVC/SBR and PVC/SBR/Ca.

Figure 3

FTIR spectra of SBR, PVCCa and PVC/SBR e PVC/SBR-Ca.

Figure 4

X ray diffractograms of SBR, PVCCa and PVC/SBR e PVC/SBR-Ca.

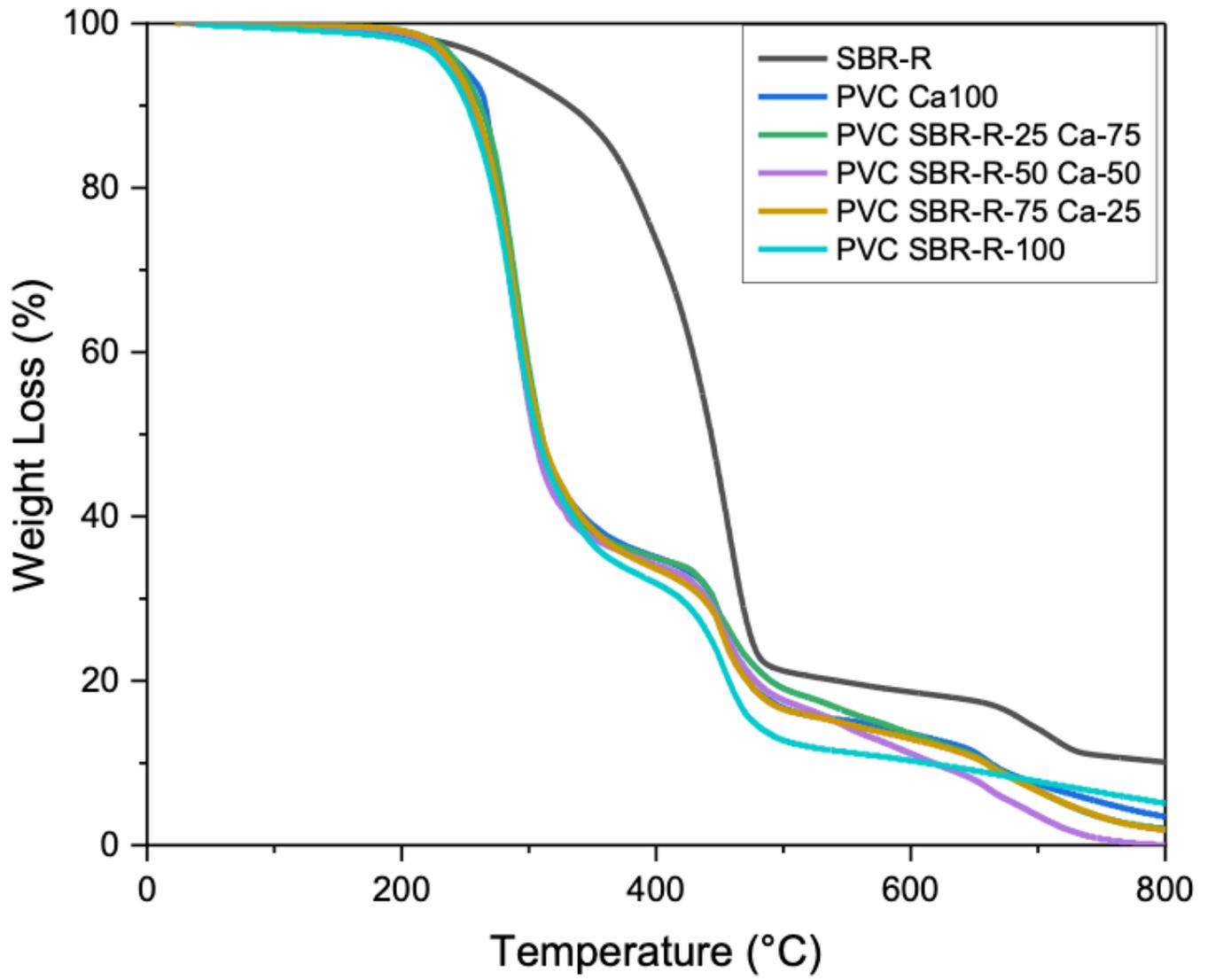


Figure 5

Weight loss of investigated compounds.

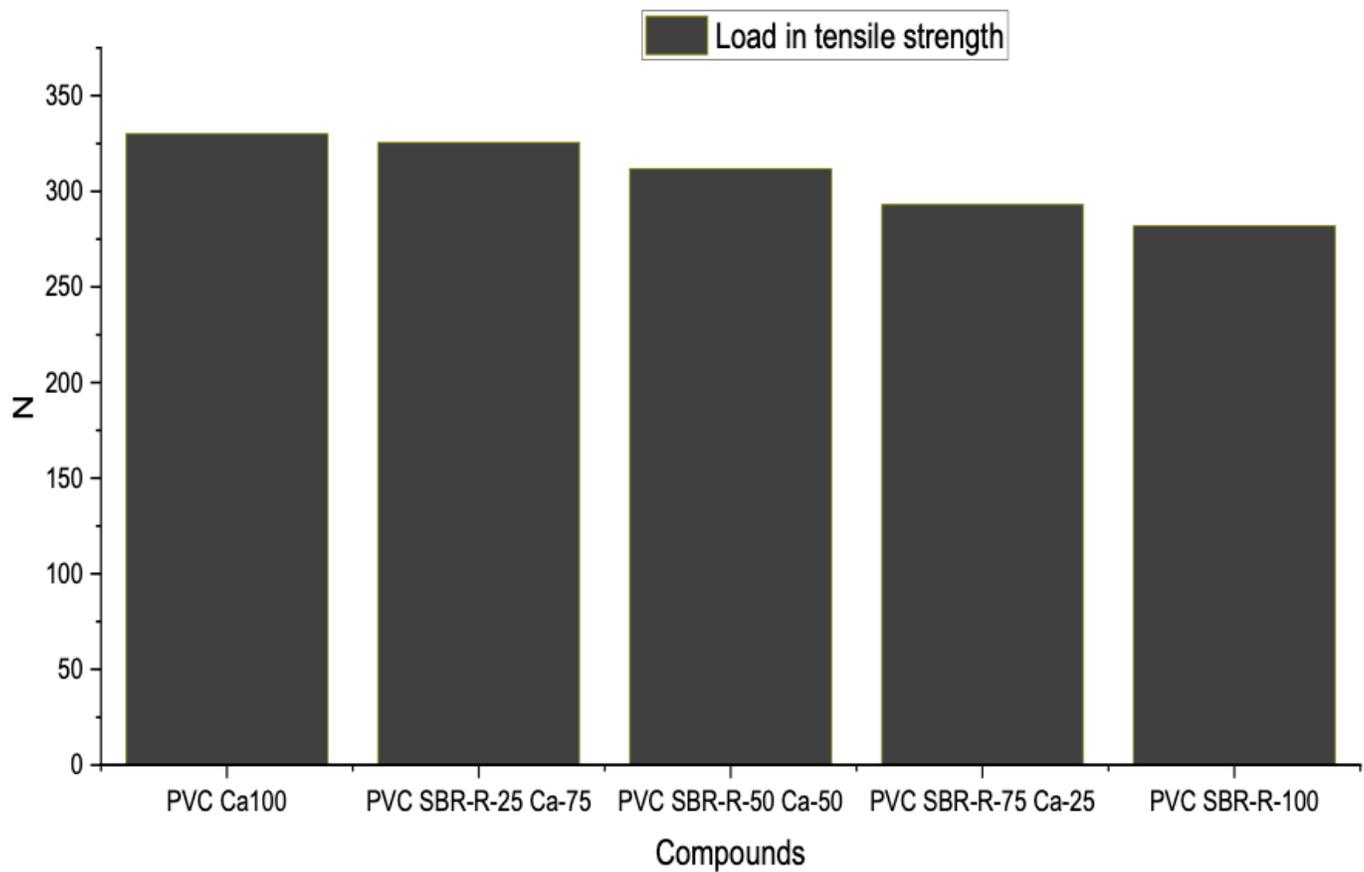


Figure 6

Elastic Modulus of elasticity for PVC, PVC/SBR-Ca e PVC/SBR compounds.

Figure 7

Tensile Effort in Tensile Resistance for PVCCa100, PVC/SBR e PVC/SBR-Ca compounds.

Figure 8

Shore A Hardnessfor PVCCa100, PVC/SBR e PVC/SBR-Ca compounds.

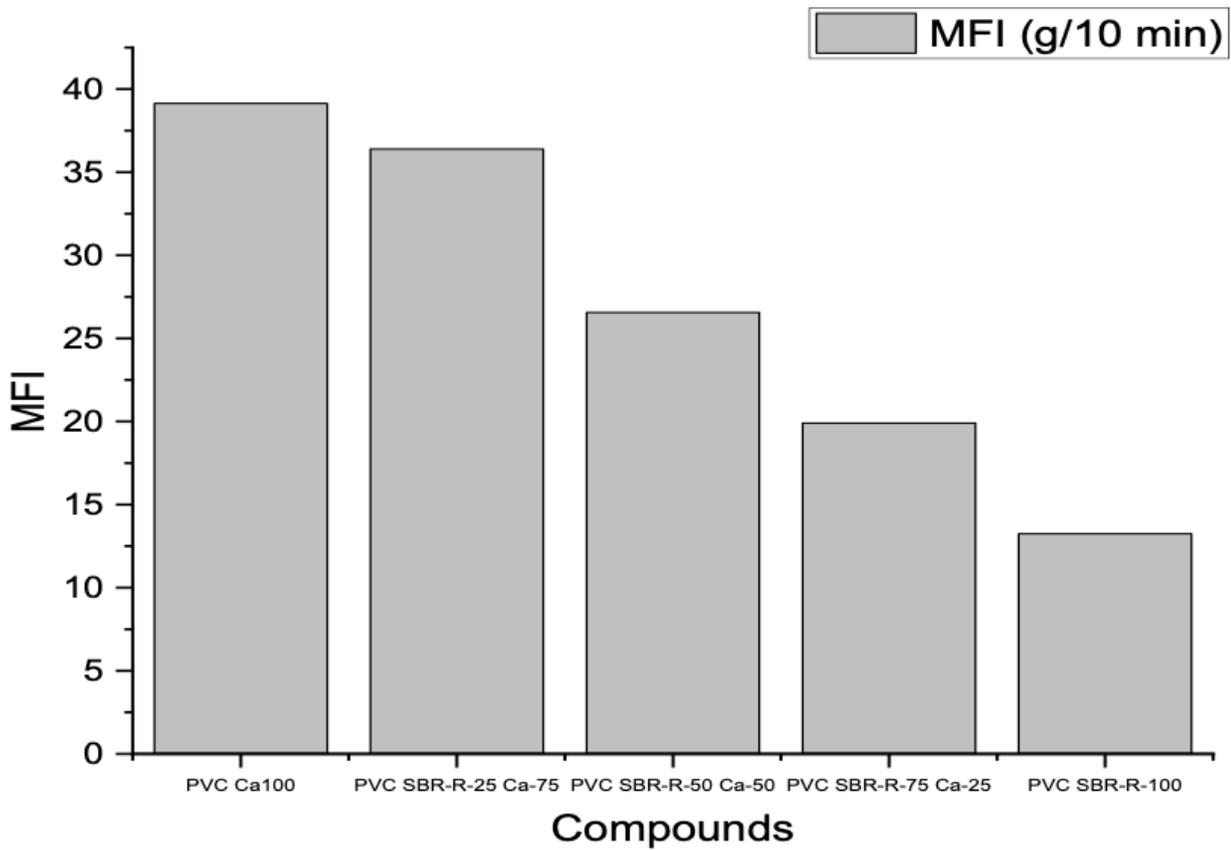


Figure 9

Fluidity Index for PVC, PVC/SBR-Ca e PVC/SBR compounds.

Figure 10

MO images of PVC, PVC/SBR-Ca e PVC/SBR compounds, with magnifications of 300x.

Figure 11

MO images of PVC, PVC/SBR-Ca e PVC/SBR compounds, with magnifications of 600x.

Figure 12

MO images 3D of PVC, PVC/SBR-Ca e PVC/SBR compounds, with magnifications of 600x.