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Influence of alternative polymeric plasticizer to DOP in thermal and dynamic-mechanical properties of PVC

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ABSTRACT

Polyvinyl chloride (PVC) is a very versatile polymer with many applications. Due to the easy incorporation of additives and plasticizers in this resin. The most used plasticizer for PVC is dioctyl phthalate (DOP), however its use has been restricted by several organizations because it presents potential toxicity. In this way, the objective of this work is to evaluate thermal, physical and dynamic-mechanical characteristics for a polymeric plasticizer alternative to DOP, polyisobutene base. As a method of comparison, the contents of the materials were kept constant, and only the plasticizer content of the samples was altered. Results indicated that the PVC compounds obtained satisfactory plasticizing results and that don't have chemical transformations. In addition, the plasticizer evaluated has a higher thermal stability when compared to the compound with DOP, proving to be a promising result.

Keywords: Polyvynil chloride, polymeric plasticizer, dioctyl phtalate.

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1. INTRODUCTION

Polyvinyl chloride (PVC) is a polymer that stands out increasingly in the world market. Currently, PVC is the second most consumed thermoplastic in the world, with a consumption of over 33 million tons per year [1]. In flexible PVC compounds the main additive used is plasticizer as the PVC resin is naturally rigid due to its high glass transition temperature. The use of plasticizers in PVC is essential in order to be able to change certain properties of the resin, and thereby to obtain a material that can be applied in several flexible products.

The most common industrial plasticizers, called phthalates are used in various consumer product applications. Dioctyl phthalate (DOP) is a plasticizer used specifically for PVC, having a great cost-benefit ratio and excellent properties for general applications [2]. The Institute for Technological Research states that the phthalactic plasticizer class is being regulated due to the fact that some plasticizers (DOP, for example) have potentially harmful health [3, 4]. Phthalates are considered hazardous waste and are classified as pollutants when industries release them into the environment. The European Union has banned the use of some phthalates in cosmetics and other consumer products in response to concerns about exposure and toxicity [2, 5]. In Brazil, there is only one restriction on its use as a plasticizer in reusable materials that are not in contact with fatty foods and as a process agent in a concentration of up to 0.1% in the final product [6].

All plasticizers can be separated into two groups: monomeric and polymeric [7]. According to their molecular weight plasticizers are classified as monomeric those having less than 500g.mol^{-1}. The polymers have a broader molecular weight range, ranging from 500 to 2000g.mol^{-1}. According to Gottesman, polymeric plasticizers are not as efficient compared to monomeric ones, however, polymerics significantly reduce migration, extraction and volatility [8]. They can be easily incorporated into products that offer high plasticity, low temperature resistance and glossy surface [9].

Thus, in view of the potential toxicity of DOP, this work aimed to investigate the influence of a polymeric plasticizer (polyisobutene base) alternative to the use of phthalates in the thermal and dynamic mechanical properties. In this way, it becomes possible to study a plasticizer in order to replace DOP.

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2. EXPERIMENTAL

3.1 Materials

The materials used to prepare the compounds were: PVC resin obtained by the process polymerization in suspension and plasticizing oils. PVC was purchased from BRASKEM (Norvic® SP1000) containing a K value of 65 ± 1 and a volume density of 0.52 ± 0.03 $g.cm^{-3}$. Dioctyl phthalate (DOP) was purchased from Elekeiroz (EKFLEX® 8815), with a density of 0.983 $g.cm^{-3}$, with a molar mass of 390 $g.mol^{-1}$. A polymeric plasticizer polyisobutene (PIB) with a molar mass of 1300 $g.mol^{-1}$ was used, and this was dissolved in a solvent carboxylic acid Bis (2-ethylhexyl) cyclohexane1,2-dicarboxylate (DOCH), which acted as a secondary plasticizer. This solvent is a carboxylic acid based with a molar mass of 397 $g.mol^{-1}$ and density (20°C) of 0.95 $g.cm^{-3}$. Thermal stabilizer CaZn and stearin were also used. The contents of the remaining elements in the formulations were kept constant, as reported in Table 1.

Table 1: Formulation of the compounds in per hundred PVC resin

Material	Compound 1 (phr)	Compound 2 (phr)
PVC Resin SP1000	100	100
Polymeric Plasticizer (PIB/DOCH)	50	0
DOP	0	50
CaZn Thermal Stabilizer	3	3
External Lubricant	0.1	0.1

The resin and additives were blended in the formulations described in Table 1 in an intensive mixer for PVC compounds, under the conditions of 1500 RPM and ambient temperature, with addition temperature of 100°C. At the end of this step, the homogenized material, designated as reported Nunes *et. al.* of PVC compound (dry-blend), was cooled to 60°C under stirring in the cooler of the mixing equipment [10].

After this process, the samples were extruded in a twin-screw extruder with a length-by-diameter ratio (L/D) of 32, and the thread rotation was maintained at 260 RPM. The temperatures of the heating zones (feed direction to the nozzle) were stored at 145, 145, 150, 150, 155, 155, 150 °C.

3.1 Characterization

For the analysis of the chemical structure of the material, Fourier Transform Infrared Spectroscopy (FTIR) analysis was used. The tests were examined by spectroscopy Perkin Elmer FTIR Frontier in the range of 4000 to 600 cm^{-1}. In this test the standard was adopted ASTM D2124-99 [11]. Six scans were performed. Due to the characteristics of the samples, the analysis was carried out using in ATR (Attenuated Total Reflection) mode, which provides a superficial analysis of the material by means of infrared ray reflection [12].

For TGA analysis, the standard ASTM E1131-08 [13] was used, and the samples were examined by Perkin Elmer TGA 4000 equipment. The analysis parameters used were a heating ramp from 30 °C to 900 °C, with a heating rate of 20 $°C.min^{-1}$, conducted in an inert atmosphere (nitrogen). The initial mass of the samples was 5.500 mg ± 1 mg.

For DSC analysis, the standard ASTM D3418-15 was used, and was realized in a Perkin Elmer DSC 6000 equipment. The amount of material used in this analysis was 9.0 mg ± 1 mg. These samples were sealed in airtight pots with the assistance of an encapsulating press. For the resin and PVC compounds, a first run was conducted in order to erase the thermal history of the material, so that the samples were heated from 30°C to 170°C at a rate of $30°C.min^{-1}$, and an isotherm was maintained at this temperature for one minute. It was then cooled at a rate of $30°C.min^{-1}$ until -70°C, maintaining this temperature for ten minutes. Finally, a second heating was carried out at a rate of $30°C.min^{-1}$ until 180°C. For the pure plasticizers the same process was performed, but the first heating was not carried out since the materials are already in the liquid state.

In order to obtain information regarding the viscoelastic properties of the material, the dynamic mechanical analysis (DMA) technique was used. This assay was performed using Perkin Elmer DMA 8000 equipment. The test was conducted at a heating rate of 2 $°C.min^{-1}$ using 0.010 mm amplitude and a frequency of 1.0 Hz. For determination of the behavior viscoelastic was obeyed the standard ASTM D4065.The glass transition of the material can be analyzed by this method. Second Menard and Menard [14], through the DMA test, the T_g of the material can be obtained in a number of ways. The method chosen for the determination of the glass transition of the material was through the peak of the tan δ curve, and the values obtained will be compared with those obtained in the DSC test. For the determination of T_g the standard

ASTM E1640 was followed.

3. RESULTS AND DISCUSSION

The FTIR spectra of PVC resin, plasticizers (polymeric and DOP) and plasticized PVC compounds are shown in Figure 1.

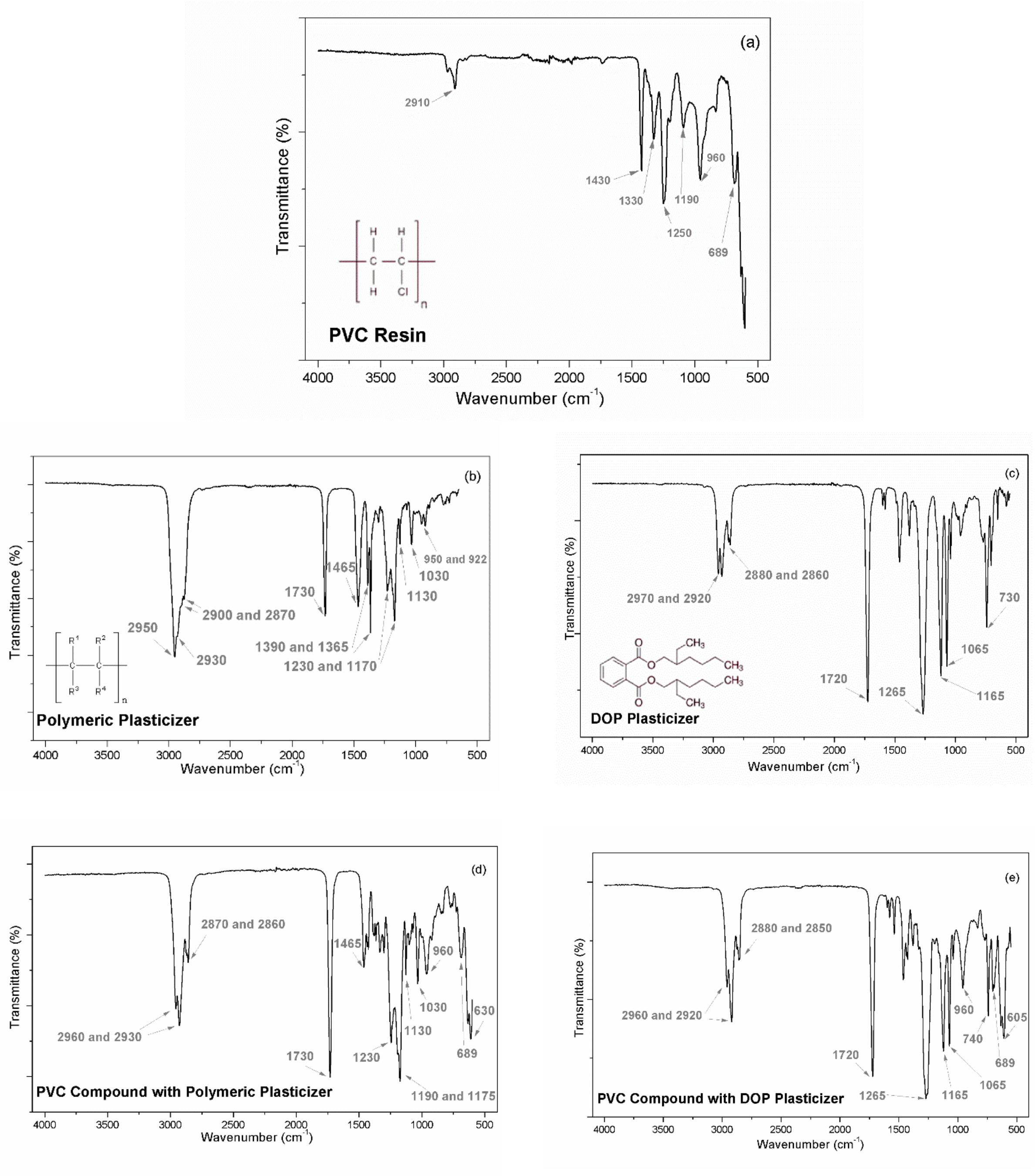

Figure 1: Spectrum obtained by FTIR-ATR assay of sample of: (a) PVC Resin; (b) Polymeric Plasticizer (c) DOP Plasticizer; (d) PVC Compound with Polymeric Plasticizer; (e) PVC Compound with DOP.

Figure 1 (a) represents the spectrum of the PVC resin and it is possible to observe the 2910 cm^{-1} band, which corresponds to the axial deformation of the C-H group of -CH_2 [15]. The 1430 cm^{-1} band corresponds to the angular deformation of the C-H group. At 1330 cm^{-1} is related to the deformation of the C-H group from -CH_2-Cl. The 1250 cm^{-1} band corresponds to the axial vibration of the C-H group. At 960 cm^{-1} it refers to the axial vibration of the C-C group. The presence of chlorine can be observed through the 689 and 60cm^{-1} bands, which refer to the C-Cl group [16-19].

According to Figure 1 (b), which represents the spectrum of the polymeric plasticizer, the band pairs are observed at 2950 and 2930 cm^{-1} and at 2900 and 2870 cm^{-1}, which represent the axial vibrations of -CH_3 [16]. At 1730 cm^{-1} is related to the axial deformation of the carbonyl group C=O from ester present in the structure [20]. For the use of this polymer as plasticizer, it was necessary to use a solvent that acted as a secondary plasticizer, which has ester in its structure. Therefore the ester bands are due to this solvent. The 1465 cm^{-1} band refers to the angular deformation of -CH_3 and -CH_2 [17]. The pair of bands at 1390 and 1365cm^{-1} is equivalent to the angular deformation CH_3 of C- $(CH_3)_n$ [21]. The axial vibration of the C-C group of C- $(CH_3)_n$ is observed in the 1230 and 1170 cm^{-1} bands [21]. At 1130 cm^{-1}, the C-O axial deformation of the ester group occurs. Reis *et. al.* reports that the 1030 cm^{-1} band refers to the C-O asymmetric deformation of the ester group, which, according to the authors, ester bands are stronger in this region [22]. These characteristic bands are also corroborated by the evaluation of PVC compounds with application in the footwear industry, showing no significant band differences [23].

Figure 1 (c) shows the DOP plasticizer spectrum, where the bands 2970, 2920 cm^{-1} and 2880, 2860cm^{-1} correspond to the axial vibration of the -CH_3 group [16]. The 1720 cm^{-1} band refers to the axial deformation of the carbonyl group C=O from ester [24, 25]. In addition, the 1720, 1265 cm^{-1} and 1125, 1065cm^{-1} bands correspond to the C-O axial deformation of the ester group [20]. In the 730 cm^{-1} band the aromatic ring present in the DOP structure is observed [16].

The spectrum of the compound with polymeric plasticizer can be seen in Figure 1 (d). A result was obtained in which the spectra of PVC resin and plasticizer overlapped. Thus, it is possible to observe that there was no chemical change of the resin with the plasticizer. The band corresponding to chlorine in the 605cm^{-1} resin was changed to 630 cm^{-1} in the PVC compound. This is because the polymeric plasticizer has in its composition much more hydrogen than the DOP. This feature causes a deformation to occur in the molecules of the material, since chlorine and hydrogen have high attraction forces, and this can result in the chlorine band change.

Figure 1 (e) corresponds to the spectrum of the plasticized PVC with DOP, in which the peaks of both the resin and the plasticizer are observed. This reinforces the claim made by Larsson *et. al.* that phthalates such as DOP are not chemically bound to PVC, so that the spectrum of the plasticized material is an overlap of the spectra of the resin and the plasticizer [4].

The TGA analyzes of the pure components and the plasticized PVC compounds correspond to the thermograms shown in Figure 2, which it is possible to observe that the PVC resin is more thermally stable than plasticized compound in the first thermal stage of decomposition. Data obtained from the decomposition intervals are presented in Table 2.

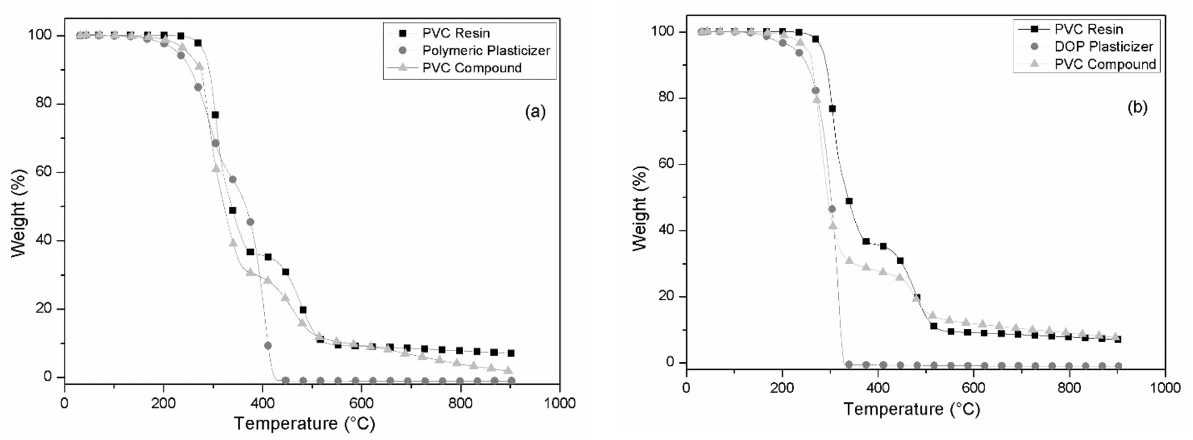

Figure 2: TGA overlapping curves of PVC, plasticizer and PVC compounds with: (a) Polymeric Plasticizer PIB; (b) DOP;

The thermogram of the PVC resin presented two different weight loss processes. The first one was 63.9% in the range of 225 to 388 °C. In this process, according to del Carpio *et. al.* [26] and Shah *et. al.* [27], the dehydrochlorination of PVC occurs. This percentage corresponds to the loss of stoichiometric mass of 58.4%, however, it is estimated that this difference is attributed to the fact that a drying process was not performed on the PVC, so that the resin contained retained moisture. The second weight loss process of 26.4% in the range of 388°C to 549 °C, occurs due to the formation of aromatic and allylic compounds, and the degradation of hydrocarbons [28]. After loss of hydrogen chloride and breakage of the double bonds, cross-linking formations can occur in the polymer chain, called cross-linking [29]. This explains the residue of approximately 10% of the initial mass of the PVC resin, since the formation of self crosslinking occurred due to the formation of double bonds (-C=C-), with the degradation of C-Cl.

Table 2: Results obtained by TGA analyzes of the samples evaluated.

Decomposition stage	Temperature / Weight loss	PVC Resin	Polymeric Plasticizer	DOP Plasticizer	PVC with Polymeric Plasticizer	PVC with DOP Plasticizer
	$T_{3\%}$(ºC)	275	209	193	235	224
1st	T_{onset} (ºC)	225	126	130	180	180
	% weight	63.9	40	3	69	71
2nd	T_{onset} (ºC)	388	340	202	382	385
	% weight	26.4	60	97	20	15
3rd	T_{onset} (ºC)	-	-	-	560	565
	% weight	-	-	-	8	4.7
Ash	% weight	9.7	-	-	3	9.3

It is possible to note a weight loss of 40% in the range of 126 to 340°C, as observed in the thermogram of the polymeric plasticizer in Figure 2 (a). This loss corresponds to the degradation of the solvent (secondary plasticizer) present in the plasticizer, the second loss process of 60% in the range of 340 to 442 °C, corresponds to the decomposition of the constituent polymer of the plasticizer. In Figure 2 (b) it is possible to observe the DOP thermogram, which also presented two mass loss stages. The first loss of 3% between 130 and 202 °C, corresponds to the degradation of the solvent alcohol present in the plasticizer. The remaining 97% is degraded in the range of 202 to 337 °C with a mean point of 318 °C, is attributed to the decomposition of dioctyl phthalate.

The thermograms of the plasticized compounds presented an overlapping behavior of the curves of PVC resin and plasticizers. However they presented three stages of mass loss as verified by Pita and Monteiro [30], the first referring to PVC dehydrochlorination, the second associated with dehydrohalogenation, and the third stage the decomposition of the main chain structure. According to the Institute for Occupational Safety and Health (IFA), the temperature of decomposition of plasticized PVC is around 180 °C, at which temperature both plasticized materials began the decomposition process [31]. In the case of Figure 2 (b), it is observed that the degradation of the plasticized material with DOP of 71%, in the range of 180 and 385 °C. That corresponds to the beginning of degradation of the plasticizer with the dehydrochlorination of PVC. In the second stage of mass loss of 15% between 385 and 565 °C, there is no longer the presence of DOP in the material, since it has already been totally degraded in this temperature range. Thus, as the initial process temperature is close to the final dehydrochlorination temperature of the PVC, the formation of crosslinks occurs during the ends of the hydrocarbon degradation present in the material. At the end of the third mass loss process of 4.7% from 565 to 900 °C, a percentage of approximately 10% of inorganic load is observed due to the formation of crosslinks, a behavior similar to pure PVC resin. This behavior was also obtained by Mattana *et. al.* [32], which suggests that the behavior is initiates in the defects of the chain, that is, in the weak bonds. These results are corroborated by the evaluation of PVC compounds with similar content of plasticizers, which showed three stages of degradation and ash [33].

The compound with polymeric plasticizer presented a distinct behavior of the plasticized material with DOP. As observed in Figure 2 (a), the thermogram of the material was also presented as an intermediate behavior of the curves of the resin and plasticizer. During the first mass loss of 69% in the range of 180 and 382 °C, the degradation onset of the solvent of the plasticizer occurred along with the dehydrochlorination of the PVC. However, unlike PVC compound with DOP, during the second mass loss (20%) between 382 and 560 °C and inflection point at 458 °C, there is still a presence of plasticizer in the material. This characteristic, during the second stage of mass loss, influences the formation of crosslinking. Polymeric plasticizers are defined as substances with high molecular weight, which decrease migration, extraction and volatility. Studies conducted by Bueno-Ferrer *et. al.* conclude that polymeric plasticizers increase the thermal stability of PVC. [34]. Based in the results, after the dehydrochlorination, the plasticizer molecules present in the material make it difficult to form double bonds (-C=C-). Thus, at the end of the third process of mass loss of the material with polymeric plasticizer, there is only one residue of 3%, since the presence of plasticizer after dehydrochlorination prevented the formation of crosslinks in the material. It is noteworthy that the decomposition kinetics of the compound PVC plasticized with polymer was slower, as observed by the larger DTG peaks.

Differential scanning calorimetry (DSC) analyzes of the pure components and the plasticized compounds are shown in Figure 3. Transitions such as T_g and T_m are related to the gain or loss of energy by the molecules, in the case of use of plasticizers, they reduce the interactions between the polymer chains and consequently reduce T_g. As the chain spacing of the polymer is increased, the properties of T_g and T_m also decrease [35]. It can be seen from Figure 3 that the PVC resin and the plasticized materials during the second heating, and for the plasticizers in the first heating.

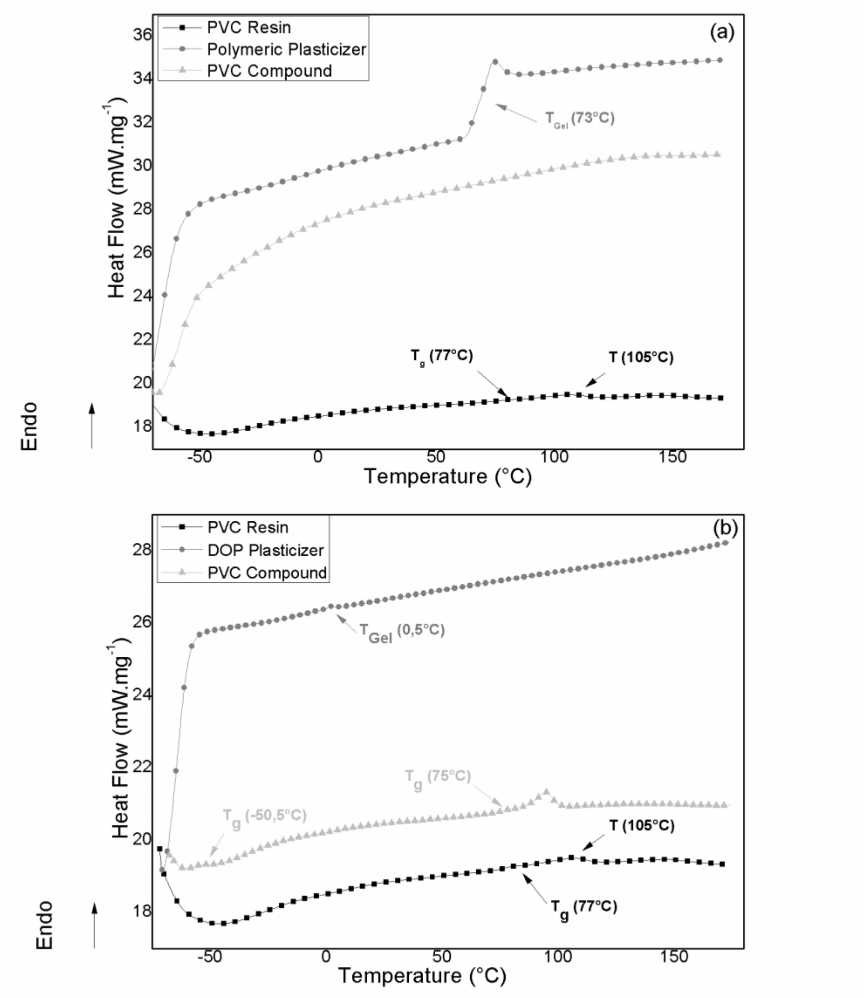

Figure 3: DSC curves of second heating of PVC plasticized with: (a) Polymeric plasticizer PIB; (b) DOP.

According to Wilkes *et. al.* PVC has T_g close to 80 °C, and as expected the PVC resin showed a T_g at 77 °C, which can be observed in Figure 3 [36]. Madaleno *et. al.* also confirms this value obtained from the same method around 83.3 °C [37]. The PVC resin also showed an endothermic event at 105 °C ($\Delta H=0.36$ J.g^{-1}), which can be attributed to a relaxation peak [38, 39].

An evaluation of the polymeric plasticizer in Figure 3 (a) shows that there was a chemical interaction in the solution of the polymer with its solvent DOCH, but no chemical reaction occurs. This interaction is responsible for the formation of a gel point, at about 73°C, of the polymer and its solvent, that is, below this temperature the plasticizer has the behavior of a gel. The DOP plasticizer also presented a gel point, however softer, at approximately 0.5 °C [40, 41].

When PVC is plasticized, a decrease in T_g is expected due to the separation of chains and an increase in the overall mobility of the material, causing a weakening of the intermolecular interactions [35, 42]. It is observed that the plasticized material with DOP showed, as observed in Figure 3 (b), a transition at -50.5 °C and another at 75.3 °C. This large reduction in T_g was also observed by Perito [43], which suggests that the chains spacing reduces the forces of secondary intermolecular attraction, reducing the energy level necessary to give mobility to the entire chain, consequently reducing the T_g of the polymer. This variation of T_g occurs because, as the plasticizer content is increased in its formulation, a reduction of the glass transition is caused [10].

It is possible to observe that the material with polymeric plasticizer shows no indication of thermal events. This behavior can be attributed to the fact that the plasticizer acted in order to separate the PVC chains, hindering the crystalline formation, even if it is relatively low in the PVC compounds, making the material amorphous. The material also did not present a glass transition, this can occur due to the method being ineffective for the determination of T_g in PVC compounds [44]. Therefore, the determination of T_g of the material should be done by DMA, since it is around 10-100 times more accurate and sensitive when evaluating the glass transition, which may be undetectable in the DSC test [14].

The DMA analyzes of the pure compounds and the plasticized materials are shown in Figure 4 and Figure 5. The storage modulus (E') and loss modulus (E") of PVC compounds are shown in Figure 4.

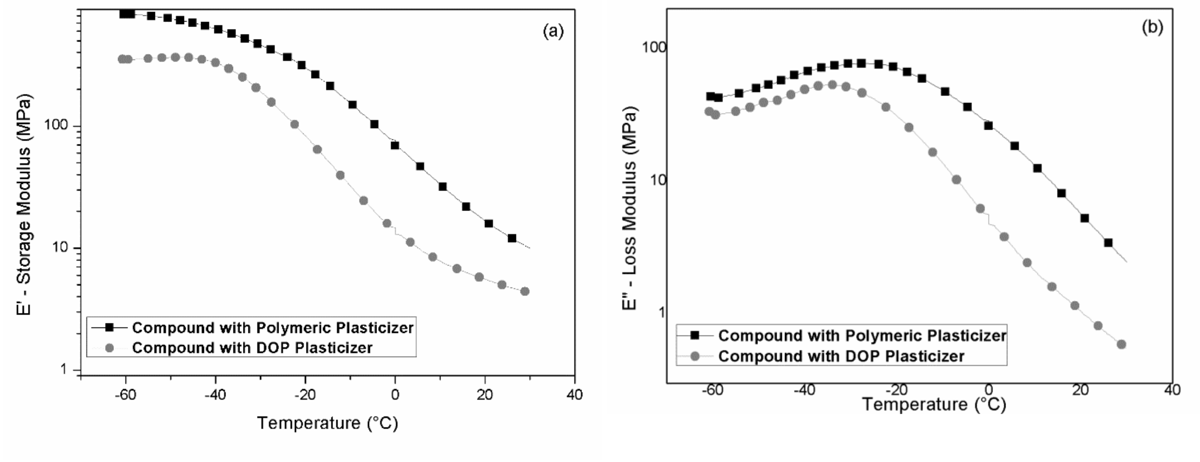

Figure 4: Results obtained by DMA (a) Storage Modulus of plasticized PVC; (b) Loss Modulus of plasticized PVC.

Observing the storage modulus in the Figure 4 (a), at very low temperatures the compound with polymeric plasticizer shows a much more elastic behavior than the DOP reference. That can be attributed to the fact that at low temperatures the elastic behavior of the polymeric plasticizer is predominant compared to the reference. This indicates that at low temperatures, PVC with DOP shows a greater distance from the chains. When compared to the material with polymeric plasticizer, the reference manages to store a smaller amount of energy, since it has a larger free volume.

Comparing the storage modulus (E') shown in Figure 4 (a), it is noted that the behavior at low temperatures corresponds to a material with a greater capacity to store energy. This character to store remains throughout the test, however as temperature is increased the difference between the modules is decreased, so that at the end of the test the storage and loss modules of both materials are closer, than at the beginning of the test. However, even with this decrease, the materials still have a higher elastic energy when compared to the loss modulus.

From the results shown in Figure 4 (a), the storage modulus of the plasticized PVC composite showed higher elastic modulus and higher temperature stability, since the decay is slower when compared to the DOP compound. In relation to the loss modulus Figure 4 (b), the viscous dissipation of the plasticized PVC compound with DOP was more pronounced, exhibiting a shift of the temperature from the peak to the left (lower T_g) when compared to the compound with the polymer plasticized compound.

The tan δ curves of the plasticized materials are shown in Figure 5. The PVC compound with DOP showed a glass transition at around -10 °C. When comparing this result with that obtained by DSC, a variation of about 40 °C is observed. This variation is attributed to the fact that the DMA assay is more sensitive for T_g evaluation [14]. In addition, the DSC method uses a much lower amount of material than that used in DMA, and if the material does not have a good homogenization, it may influence the test result. Mattana obtained a result of T_g of PVC plasticized with DOP close to the value obtained in this work, determined by the DMA method [45].

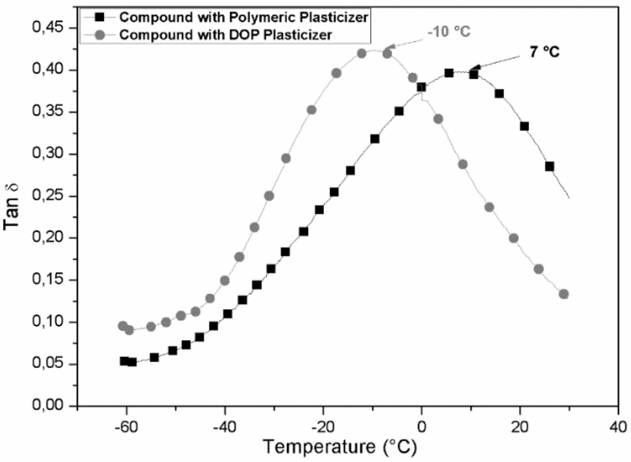

Figure 5: Tan δ curves of the PVC compounds obtained by DMA.

The PVC compound with polymeric plasticizer presented a glass transition at approximately 7°C, as observed in Figure 5. This result can not be detected by DSC, which indicates a better efficacy of the test for the determination of T_g. Further reduction of T_g was expected since the polymeric plasticizer has a molar mass much higher than DOP. A study by Ferruti *et. al.* indicates that the molar mass influences in a greater reduction of T_g, since a larger spacing occurs in the main chains of PVC [46]. In addition, the author further notes that the longer the plasticizer chains, the greater the entanglement of the PVC material. It is possible to note that the plasticized material had a higher temperature range when compared to the reference with DOP. This behavior was also verified by Madaleno *et. al.* [37], which conclude that this temperature range suggests that there is a microheterogeneity between the PVC and the plasticizing polymer.

4. CONCLUSIONS

A polymeric plasticizer polyisobutene (PIB) dissolved in a solvent carboxylic acid Bis (2-ethylhexyl) cyclohexane1,2-dicarboxylate (DOCH) was used in substitution to DOP plasticizer (50PHR) were add to PVC resin and their properties evaluated. The presence of polymeric plasticizer had a direct influence on the degradation temperature of PVC, resulting a higher thermal stability.

The results obtained in this work contributed to an aid in the selection of alternative plasticizers to dioctyl phthalate. Based on these results, there is a strong tendency for applications in flexible follow-ups, such as footwear industry.

In addition to this evaluation of alternative use of plasticizer, it is suggested that studies of chemical stability. It is concluded that the plasticizer evaluated does not directly replace the DOP, and for some applications the material already presents better performance than this one. It is evident the increased study of plasticizers alternative to DOP, with thermal stability being one of the main desired factors due to the low stability of the PVC resin.

5. ACKNOWLEDGMENTS

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