Processability and Characterization of Poly(vinyl chloride)-*b*-Poly(*n*-butyl acrylate)-*b*-Poly(vinyl chloride) Prepared by Living Radical Polymerization of Vinyl Chloride. Comparison With a Flexible Commercial Resin Formulation Prepared With PVC and Dioctyl Phthalate

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This work reports the synthesis and processing of a new flexible material based on PVC produced by living radical polymerization. The synthesis was carried out in a two-step process. In the first step the macroinitiator α,ω-di(iodo)poly(butyl acrylate) [α,ω-di(iodo)PBA] was synthesized in water by single electron transfer/degenerative chain transfer mediated living radical polymerization (SET-DTLRP) catalyzed by $Na_2S_2O_4$. In the second step this macroinitiator was reinitiated by SET-DTLRP of vinyl chloride (VC), thereby leading to the formation of the block copolymer poly(vinyl chloride)-*b*-poly(butyl acrylate)-*b*-poly(vinyl chloride) [PVC-*b*-PBA-*b*-PVC]. This new material was processed on a laboratory scale. The DMTA traces showed only a single glass transition temperature, thus indicating that no phase segregation was present. The copolymers were studied with regard to their processing, miscibility, and mechanical properties. The first comparison with commercial formulations made with PVC and dioctyl phthalate (DOP) is presented. J. VINYL ADDIT. TECHNOL., 12:156–165, 2006. © 2006 Society of Plastics Engineers

INTRODUCTION

The flexible PVC market represents one of the most important applications of PVC, with increasing utilization in the plastic and rubber industries [1]. PVC is a rigid thermoplastic with glass transition temperature around 80°C which needs to be mixed with plasticizers in order to become flexible. Over the last decades, the utilization of plasticizers has been discussed owing to unavoidable migration of these compounds [2], which constitutes one of the most serious problems of this industry. Nowadays the European Union [3] has introduced restrictions on the use of some plasticizers in critical applications such as children's toys and medical devices. Among other serious problems, the loss of plasticizers results in a grave contamination of the surrounding medium, as well as the deterioration of mechanical properties [4]. Several developments have been carried out to overcome these problems, on the basis of the development of low-migration polymeric plasticizers [5] and blending with other polymers [1]. Alternatively, the other possible approach relies on polymerization via alternate mechanisms which allow the further functionalization of the molecules. The anionic polymerization was intensely studied because of its potential, although difficulties in the industrial application of this technique due to stringent conditions precluded widespread applications. During the 90's, the so-called living radical polymerization (LRP) received attention, thus providing the possibility to prepare tailor-made polymers via a radical mechanism. Several main methodologies are presented in the literature: metal-catalyzed LRP [6, 7], nitroxide-mediated polymerization (NMP) [8], and stable free

radical polymerization (SFRP) [9]. These strategies were traditionally carried out under conditions that are difficult to implement on a large industrial scale, owing to a number of factors: the need for organic solvents, long reaction times, and extremely expensive compounds that normally are not available on an industrial scale. More recently, Percec et al. [10–12] discovered a strategy to polymerize activated [13, 14] and nonactivated monomers [11, 12, 15, 16], by a controlled/living radical mechanism in aqueous systems using only widely available industrial compounds. This new methodology called single electron transfer-degenerative chain transfer mediated living radical polymerization (SET-DTLRP) provides the reversible activation–deactivation step required to accomplish LRP by the combination of competitive single-electron transfer (SET) and degenerative chain transfer. The implementation of this methodology on the industrial scale is being carried out [17], concerning the study, development, and optimization of new materials. In this work the first scale-up of flexible material based on PVC without any kind of plasticizer is presented. The thermal, mechanical, and viscosimetric properties of the block copolymer PVC-*b*-PBA-PVC were evaluated. Moreover, the results obtained during the processing of this material for different formulations and the dynamic mechanical thermal analysis obtained for each formulation used are presented. The final product was also compared with commercial formulations comprising PVC with 30, 70, 100, and 120 phr DOP.

EXPERIMENTAL

Materials

The tetrahydrofuran HPLC-grade uninhibited, sand, aluminum oxide, iodoform (99%), sodium dithionate (85%), sodium bicarbonate (99%), and *n*-BA were purchased from Sigma–Aldrich. The *n*-BA was purified through an alumina oxide column. The polystyrene standards were purchased from Polymer Laboratories. The Methocel F50 was purchased from Dow Chemical Company. The PVA was purchased from Syntomer. The PVC (suspension grade, $K_v = 66$, $M_n = 60,750$, $M_w/M_n = 1.9$, $\eta = 1.145$, $R_g = 15.2$ nm) and the materials used in the compounding were obtained from Previnil.

Polymerization of n-BA via SET/DTLRP

The polymerization of α,ω-di(iodo)polyBA macroinitiator, regardless of the scale of reaction (50 mL, 2 L, and 5 L), was carried out according to the procedure described by this group in a previous publication [18].

Typical Procedure to Synthesize the Block Copolymer PVC-b-*PBA*-b-*PVC* by the SET-DTLRP of VC Initiated From α,ω-Di(iodo)polyBA Macroinitiator (Glass Scale)

In a 50-mL Ace Glass 8645#15 pressure tube equipped with bushing and plunger valve, 16 mL of deionized water, 678.92 mg of a 3% aqueous solution of PVA (2940 ppm w/w relative to VC), and a 469.30 mg of 1.86% aqueous solution MF50 (1260 ppm w/w relative to VC) were charged. The contents were stirred and bubbled with nitrogen for 10 min. The other compounds were then weighed (catalyst ($Na_2S_2O_4$, 144.98 mg, 0.148 mmol), macroinitiator (α,ω-di(iodo)PBA, 2.00 g, 0.018 mmol), buffer ($NaHCO_3$, 31.04 mg, 0.037 mmol), sodium *p*-toluenesulfonate (*p*TsNa, 144.98 mg, 0.074 mmol)) and added to the tube. The tube was frozen in MeOH/Dry Ice and precondensed VC (7.87 mL, 0.111 mol) was added. The tube was closed and degassed through the plunger valve by applying 20 cycles of reduced pressure, followed by filling the tube with inert gas at −40°C. The valve was closed and the reaction mixture was kept in a controlled temperature water bath for selected reaction times. At the end of the reaction, the excess of unchanged VC was distilled and the block copolymer was filtered and rinsed three times with deionized water. After drying in a vacuum oven to constant weight, the block copolymers were characterized. The procedure used to prepare the copolymer in the 2-L and 5-L reactor was based on the description above [17].

Sample Preparation for Size Exclusion Chromatography

Around 40 mg of block copolymer was allowed to dissolve completely in a 10-mL dilution flask over 24 h. The solution was passed through an alumina and sand column, precipitated in water, and filtered under vacuum. The polymer was then dried in the oven at 40°C under vacuum to constant weight. Approximately 20 mg of polymer was dissolved in 10 mL of THF under stirring for 24 h. The exact concentration was determined by considering the weight measured and the 10 mL of solvent used (all the samples were prepared with concentrations of around 2 mg/mL).

Characterization Techniques

The chromatography parameters of the samples were determined by using a HPSEC instrument: Viscotek (Dual detector 270, Viscotek, Houston, USA) with differential viscometry (DV), right angle laser light-scattering (RALLS, Viscotek), and RI (Knauer K-2301). The column set consisted of a PL 10 μm guard column (50 × 7.5 mm²) followed by two MIXED-B PL columns (300 × 7.5 mm², 10 μm). The HPLC pump (Knauer K-1001) had a flow rate of 1 mL/min. The eluent was previously filtered through a 0.2-μm filter. The system was also equipped with a Knauer on-line degasser. The tests were done at 30°C, using an Elder CH-150 heater. Before the injection (100 μL), the samples were filtered through a PTFE membrane of 0.2 μm. The system was calibrated with narrow polystyrene standards. The differential refractive index (dn/dc) for 670 nm was determined by using the Viscotek Software 3.0. The analysis of light scattering data by Viscotek software

TABLE 1. Formulations used for processing the block copolymer PVC-PBA-PVC.

Sample (formulation)	Processing aid (phr)	Internal lubricant (phr)	External lubricant (phr)	External lubricant (phr)	Time for processing (min)	Processing temperature (°C)
S1	10	2	2	10	7	150
S2	10	2	2	2.5	5	150
S3	10	2	2	1	5	150
S4	8	2	2	1	5	150
S5	5	2	2	1	5	150
S6	2	2	2	1	5	150
S7	1	2	2	1	5	150
S8	0	2	2	1	2	150

was done by assuming the second virial coefficient to be zero, considering the low solution concentrations used in this work. The ^{1}H NMR spectra (500 MHz) were recorded on a Bruker DRX 500 spectrometer at 32°C in CDCl$_3$ and THF-d$_8$ with tetramethylsilane (TMS) as internal standard. Dynamical mechanical thermal analysis (DMTA) of thick specimens (6.5 × 6 × 2.0 mm^3) was performed by using a Triton Tritec 2000 instrument in single cantilever bending used in multifrequency mode, with a standard heating rate of 2°C min^{-1}. The block copolymer was also characterized in powder form in the constrain layer damping mode, with a standard heating rate of 2°C min^{-1}, at a frequency of 1 Hz. The T_g was determined as the peak in tan δ (Tan $\delta = E''/E'$), where E'' and E' are the loss and storage modulus, respectively. The TGA curves were determined using a Netzsch STA 449C Jupiter instrument, and the tests were carried out at 2°C/min. The dependence of yield stress on strain rate was evaluated in the unaxial mode, using a Hounsfield H10KT instrument at a strain rate of 100 mm/s following the standard ISO 527 (Parts 1 and 2).

Processing and Sample Preparation

The materials studied in this work (block copolymer and PVC) were premixed with a determined mass of each compound (formulations in Table 1) in a glass beaker and were milled on a laboratory two-roll mill at 150°C for 9 min. Two millimeter-thick plates were preheated at 120°C for 2 min and were then compressed for 3 more min at the same temperature. For tensile tests dumbbell-shaped samples were cut from the plates, following the dimensions indicated in the Standard ISO 527.

RESULTS AND DISCUSSION

Synthesis and Characterization of Poly(vinyl chloride)-b-poly(butyl acrylate)-b-poly(vinyl chloride)

The α,ω-di(iodo)PBA macroinitiator used was first synthesized by SET-DTLRP in water at 25°C for 5 h, according to the procedure described. The block copolymer was then synthesized by SET-DTLRP of VC initiated from the α,ω-di(iodo)PBA and was catalyzed with Na$_2$S$_2$O$_4$ in

water at 42°C. The suspension agents used were methocel F50 (MF 50) and poly(vinyl alcohol) (PVA88), which was 87–89% hydrolyzed and had a weight-average molecular weight (M_w) of 124,000–186,000. The results were reproduced on a small scale in the 2-L and 5-L pilot reactor. The stirrer pattern comprised two flat baffles at 200 rpm [19]. The relative amounts of each compound were readjusted according to their roles [12, 17, 20] in the reaction and the scale considered [17].

The synthesis of the block copolymer PVC-b-PBA-b-PVC was proposed in a previous publication, where the kinetics and preliminary characterization were carried out on a small scale [20]. In that work, the macroinitiator was purified in order to remove any unconverted monomer, which may have been responsible for a delay in the beginning of the polymerization. This conclusion is based on controlled experience that showed the impossibility of polymerizing VCM by SET-DTLRP in the presence of BA monomer [21]. In this work, the copolymer was prepared simply by adding VC to the macroinitiator without any purification. This procedure, in spite of being less ideal from the kinetics point of view, is preferable for industrial application.

In Table 2, the characterization of a target block copolymer prepared on three different scales is presented.

The results shown in Table 2 suggest that the modification introduced [17] in the copolymerization procedure did not induce any change in the final product, with regard to the conversion and molecular weight, after the same 24 h. Moreover, there are significant decreases in the M_w/M_n resulting from the increase of reactor size. Apparently this behavior can be ascribed to the more stringent control over

TABLE 2. Characterization of the same block copolymer prepared in different reaction scales.

Reactor	M_n	M_w/M_n	IV(dl/g)	dn/dc	PBA[a] (%)	R_g (nm)	Conversion (%)[b]
50-mL	193768	2.2	1.9	0.0743	0.64	28.5	80
2-L	200431	2.0	2.0	0.0742	0.63	27.6	84
5-L	209356	1.8	2.1	0.0771	0.61	30.0	87

[a] Determined by NMR.
[b] Total conversion, based on 100% conversion in the first step (preparation of the α,ω-di(iodo)PBA).
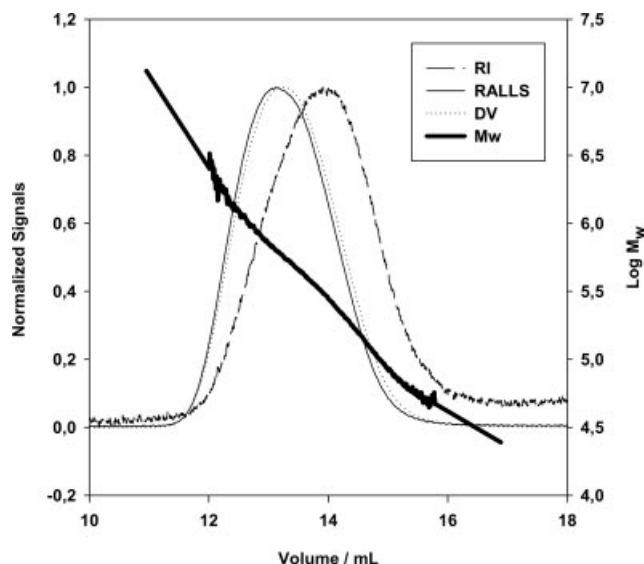
FIG. 1. Chromatograms obtained for block copolymer PVC-*b*-PBA-*b*-PVC prepared in the 5-L reactor.

the heat and mass transfer on the two pilot scales, when compared with the 50-mL glass reactors. Previous studies related to the implementation of this technique for the VCM polymerization have shown that on a scale of 150-L, the M_w/M_n may be lower (1.7) [19]. However, an even lower M_w/M_n is unlikely because of the heterogeneous nature of this polymerization system.

The TriSEC chromatogram of the block copolymer prepared in the 5-L reactor is presented in Fig. 1.

The chromatograph traces shown in Fig. 1 are smooth, demonstrating the quality of the polymer samples and the instrument performance.

Structural Analysis

The NMR spectra of the PBA obtained by SET-DTLRP of BA at 25°C and the block copolymer PVC-*b*-PBA-*b*-PVC are presented in Fig. 2. Both spectra show the normal signals obtained for the SET-DTLRP of BA and the further copolymerization with VC. The signal assignments are fully described elsewhere [18, 20] and are not repeated here. The resonance peaks obtained show that the preparation of the block copolymer PVC-*b*-PBA-*b*-PVC was successfully achieved in the 5-L pilot reactor.

Processability

The preliminary processing of the block copolymer PVC-*b*-PBA-*b*-PVC (M_n = 209 kDa, PVC = 39%) was studied in a two roll-mill laboratory equipment. Since, to the best of our knowledge, this material had never been prepared previously, no information was available about its behavior during the processing. For this reason, typical formulations used for flexible PVC materials were tested as a starting point.

The preliminary processing tests were aimed at establishing a formulation capable of processing this material for further analysis. In Table 1 the times necessary to pro-

cess a film of copolymer are presented, which were determined visually according to the appearance of the films during the processing. However, all the formulations were allowed to process for 9 min for two reasons: to guarantee the same thermal history in order to verify the possible influence of the used compounds on the mechanical and thermal properties of the block copolymer, and to allow the upcoming comparison with the commercial product made with DOP that normally is processed for 9 min. The evolution of each formulation was carried out considering the ease of processing and the final appearance of the processed product. In a further study, the influence of each formulation in the mechanical and thermal performance of the material was evaluated by DMTA, as shown later.

The first formulation (S1) showed that adhesion to the rolls was relatively hard to achieve, most probably because of an excess of lubricant (stearic acid). Such compounds are intended to migrate towards the interface polymer/rolls and are responsible for enhancement of the heat transfer between the roll and the films that are being formed. The decrease of this compound (S2) increased the adhesion, and apparently the processing was completed after 5 min, although some residues of stearic acid were present on the roll after the processing time. Concerning the appearance, the film appeared more glassy. A further decrease of stearic acid (S3), led to the formation of a film very similar to the previous one but without residual amounts of external lubricant. Further tests showed the possibility of eliminating the use of processing aid K175, which is a relatively expensive additive, compared to the other compounds, and decreasing the time needed to process the materials. This observation is remarkable,
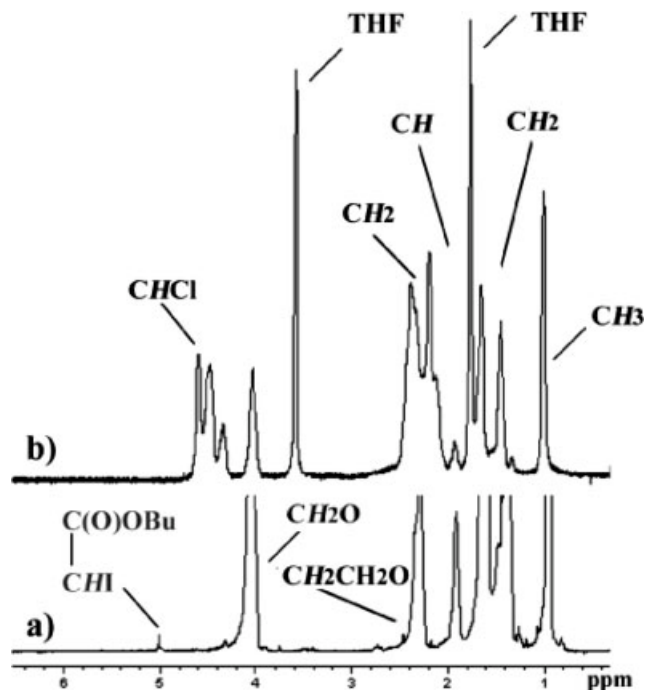

FIG. 2. ¹H NMR spectra of (a) the macroinitiator α,ω-di(iodo)polyBA; (b) the block copolymer PVC-*b*-PBA-*b*-PVC prepared by SET/DTLRP.
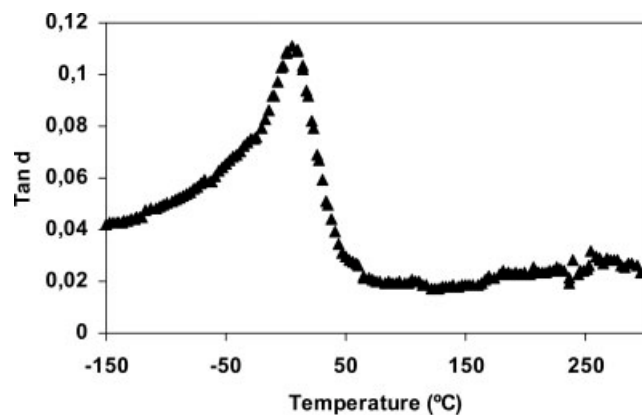
FIG. 3. Tan δ of the copolymer PVC-PBA-PVC in powder form by constrain layer damping.

since the result was obtained with the reduction of the compounds used in the initial formulation. In this way, a preliminary formulation was achieved which allowed the processing of the block copolymer PVC-*b*-PBA-*b*-PVC.

Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis is an extremely versatile and sensitive method that enables the complete scan of relaxation mechanisms in viscoelastic materials. Typically, it is used to determine the glass transition temperature, which is defined as the temperature where the molecular chains of a polymer receive the energy necessary to overcome the energy barriers for segmental motion. This region is also characterized by the maximum loss of applied energy, usually as a peak in the trace of tan δ. Tan δ represents the ratio between the storage and loss moduli and is not affected by the geometry used. For specific applications, the material needs to sustain stress at subambient temperatures. The advantage of the DMTA technique is the possibility of analyzing the material's response to cyclic excitation over wide temperatures and frequency ranges [22].

The loss modulus of the block copolymer (powder form) obtained in the constrain layer damping mode (Fig. 3), indicating the presence of a single broad peak of tan δ, suggests the absence of any microphase separation, although the structure seems to be relatively heterogeneous concerning the amount of PVC incorporated in each PBA chain. Another reason might be the motion of PBA segments belonging to the main chains of the block copolymer. If this is the reason, decrease of broadness of the damping curve with the decreasing of the PBA segment length would be expected for a copolymer with the same final molecular weight. This test was performed using the copolymer in the form of a powder in order to determine the possible influence of the other compounds that were used in the formulations to be processed. The absence of peaks in the region of -43 and $90°C$ [20] corresponding to the T_g of the PBA and PVC is extremely

important, since it shows that the copolymer behaves as a single material.

Figure 4 presents the comparison between the DMTA trace of a block copolymer and the commercial PVC product with 70 phr of DOP.

In the glass region, where modulus curve E' is roughly constant, the atoms that constitute the polymer chain are restricted to vibrational motions, with the result that the bulk polymer behaves as a stiff and glassy material. The copolymer (Fig. 4a) exhibits E' which is higher for the lower temperatures, but the presence of a significant plateau within this region is very tenuous. This performance could be linked to the heterogeneity of the copolymer composition regarding the distribution of PVC through the PBA macroinitiator chains and to the presence of the segment of PBA with $M_{n,\text{TriSEC}} = 115,000$ in the copolymer. At very low temperatures, the segments of PBA have the energy necessary to initiate the rotational movements, which leads to decrease of the elasticity modulus of the copolymer. For plastic materials, the glass–rubber transition normally takes place within a narrow range of temperature that decreases with the homogeneity of the sample under test. Nevertheless, it is known that the presence of materials which contribute to the material softening generally leading to broad regions of transition. This conclusion can be reached also by analyzing the samples with DOP. The latter sample has a broad region of glass–rubber transition. After this transition region, the trace suffers a more pronounced decrease, which is generally ascribed to the onset of long-range movements that results in a softer and rubber-like polymer. After the glass transition region, it appears that the rubbery plateau region is characterized by physical entanglement of the materials which constitute the copolymer and which hinder the flow within the rubbery region. These transitions are also observed in the damping loss (tan δ) curve; as the temperature increases, the damping goes through a maximum in the transition region and a decrease in the rubbery region [23]. The absence of pronounced peaks in the region characteristic of the PBA indicates clearly that all the chain ends were reinitiated, a result which is also confirmed by the absence of the resonance peaks in the NMR spectrum that correspond to the r and m stereoisomers of —CHIC (O)OBu active chain ends (Fig. 2b).

By analyzing the other samples prepared with different formulations it is possible to observe a similar behavior either for log E' and tan δ. The magnitude and nature of the changes in the dynamic modulus of elasticity are determined by both the intramolecular and the intermolecular interactions. However, the latter interactions have greater influence on the different physical states of the polymer [23].

The dynamic mechanical tan δ peak is expected to shift to higher temperatures with increasing frequency for any thermally activated relaxation process as shown in Fig. 3. Among other advantages, the utilization of multifrequency analysis in DMTA runs allows the user to dis-
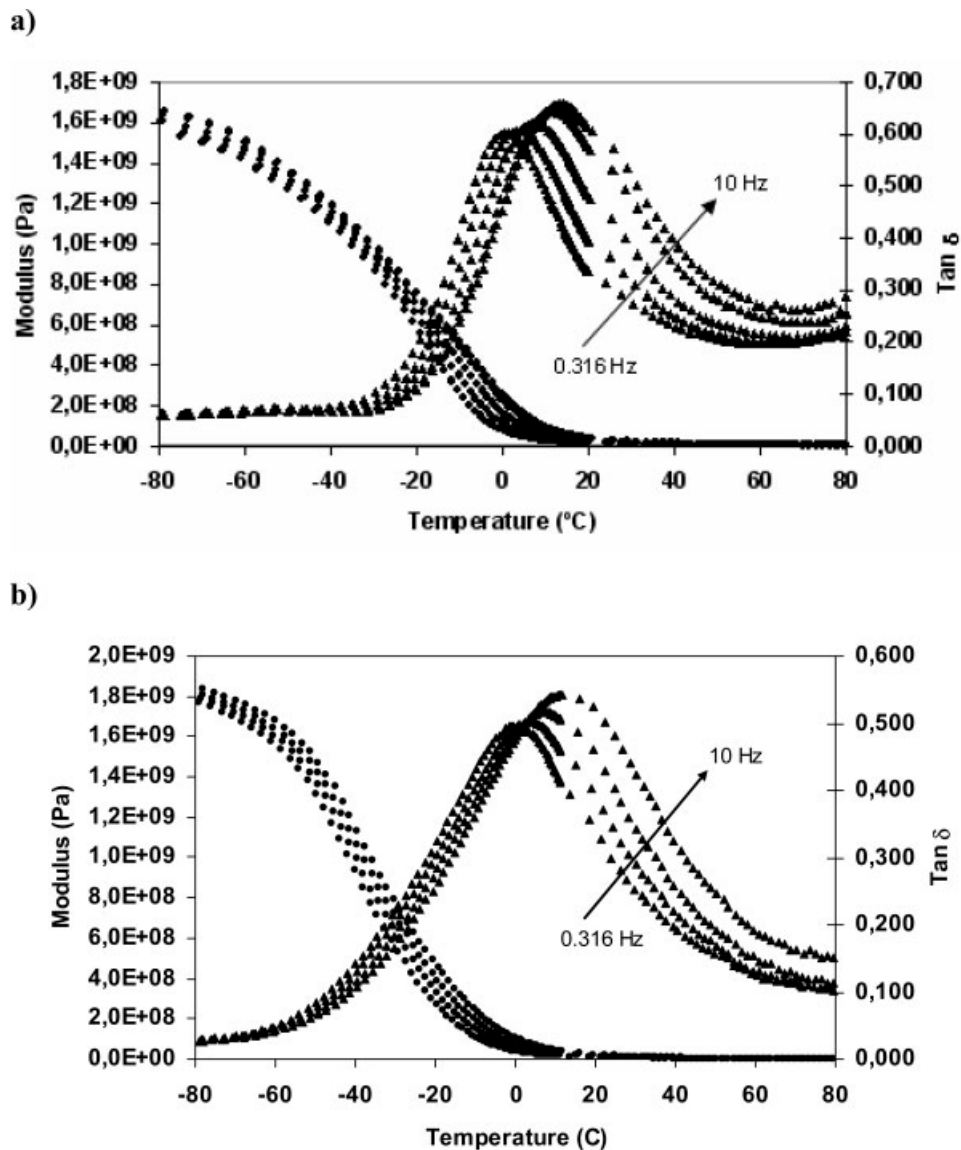
a)

b)

FIG. 4. Comparison between dynamical mechanical thermal performance in multifrequency (0.316, 1, 3.16, 5, and 10 Hz) of two samples with the same glass transition temperature; (a) block copolymer PVC-PBA-PVC prepared by SET/DTLRP (S6); (b) conventional PVC resin prepared by free-radical polymerization with 70 phr of DOP.

tinguish between the frequency-dependent processes such as the molecular relaxations (α and β transitions) and those that are not frequency-dependent such as melting, curing, crystallization and thermal degradation.

The apparent activation energy (ΔH) for α-relaxation can be determined from the Arrhenius rate relationship

$$\ln f = -(\Delta H/RT) \qquad (1)$$

where f is the frequency of analysis, R is the universal gas constant, (ΔH) is the activation energy and T is the temperature in degrees Kelvin.

The results obtained for different parameters taken from the DMTA traces are presented in Table 3.

As expected, the temperature that corresponds to the maximum damping changed around 10°C for all samples

in the range of frequency between 1 and 15 Hz, showing the frequency dependence of the α transition. The results presented suggest that the processing formulation can influence the mechanical and thermal properties of this copolymer. Hence, different values were obtained for ΔH, E' and tan δ. It should be noted that the block copolymer used for each formulation was prepared in the same batch. Among the block copolymer results, the formulation S1 is the one that leads to a less stiff material. This result can be linked to the excess of stearic acid (as referred to in the processing part) that contributed to inefficient contact between the material and the rollers, with the result that the polymer was insufficiently processed. The difference between the formulations S1 and S2 is not fully understood at the moment, although it might be related to any

TABLE 3. Influence of the different formulations on the mechanical and thermal properties of the block copolymer PVC-PBA-PVC. Comparison with PVC and PVC with DOP.

Sample (formulation)	T_g (°C) 1 Hz	T_g (°C) 15 Hz	(ΔH) kJ/mol	r^2	E' (-80°C) $\times 10^9$	Tan d (1 Hz)
S1	3.0	14.6	72.2	0.951	0.6	0.435
S3	8.7	20.8	69.1	0.994	1.2	0.611
S4	4.3	13.8	86.6	0.991	1.3	0.569
S6	4.2	13.1	89.6	0.997	1.6	0.607
S7	5.6	15.5	85.0	0.993	1.0	0.688
S8	5.5	16.0	83.6	0.988	0.9	0.692
PVC	84.6	91.5	199.6	0.962	2.80	0.81
PVC 30 phr DOP	48.34	55.5	142.1	0.987	2.42	0.56
PVC 70 phr DOP	9.6	18.9	96.0	0.997	1.9	0.50
PVC 100 phr DOP	-12.8	0.1	75.3	0.999	1.6	0.642
PVC 120 phr DOP	-21.1	2.3	68.2	0.995	1.3	0.761

synergistic effect between the formulation additives which was maximized for the latter formulation. Moreover, the decrease of stearic acid certainly promoted the heat transfer between the film and rollers, thus leading to efficient heat transfer at the material/rollers interface. The apparent activation energies obtained for the block copolymers are in the same range of values for all samples and also are quite similar to those of the commercial products. Additionally, the high values of r^2 obtained for the different formulations studied should be stressed.

Concerning the commercial products, the increase of DOP resulted in a decrease of the mechanical properties due to the increase of the free volume between the PVC chains. In the same trend, as the content of DOP increased the T_g decreased.

In the overall analysis, the results show the important role of the processing formulation in the polymer performance, since the same starting block copolymer (prepared in the same batch) can lead to a material with a different storage modulus. The PVC with 70 phr of DOP is the commercial product that better resembles the block copolymer prepared when the comparison criterion is the glass transition temperature. The block copolymer PVC-PBA-PVC appears to be free of any phase separation, which results in its behaving as a single material, even considering the high molecular weight of the PVC and PBA segments.

The comparison between the storage modulus of the copolymer (different samples) and the commercial flexible PVC is presented in Fig. 5.

Figure 5 shows clearly that during the α-relaxation transition the block copolymer prepared by SET-DTLRP has a behavior similar to that of PVC with 70 phr of DOP. Nevertheless, this material is not as stiff as the PVC with 70 phr of DOP. When compared to the PVC with 100 phr of DOP, the block copolymer shows better mechanical properties in the range of temperatures from -80 to 0°C.

Tensile Tests

The tensile curves provide an important insight into the material strength. In this test the material is continu-ally subjected to an increasing uniaxial force and its elongation is monitored. The mechanical evaluation is based on three parameters: tensile strength, yield strength or yield point and elongation at break. Numerous references are available concerning tensile studies for either PVC or plasticizer formulations. This test is extremely sensitive to the conditions used, especially to the temperature and rate of strain. As the temperature of the test increases, the material becomes more flexible. Thus for a given stress, the material deformation is greater; the rate of strain is also an important issue to be considered, since for higher values the materials appear to be stiffer. For these reasons, the tensile test results presented in Fig. 6 were obtained under the same conditions of heat treatment, thermal history, temperature, and stress applied during the test (as described in the Experimental section). The tensile tests were carried out at room temperature and under a strain rate of 100 mm/s, which are typical conditions for flexible materials.
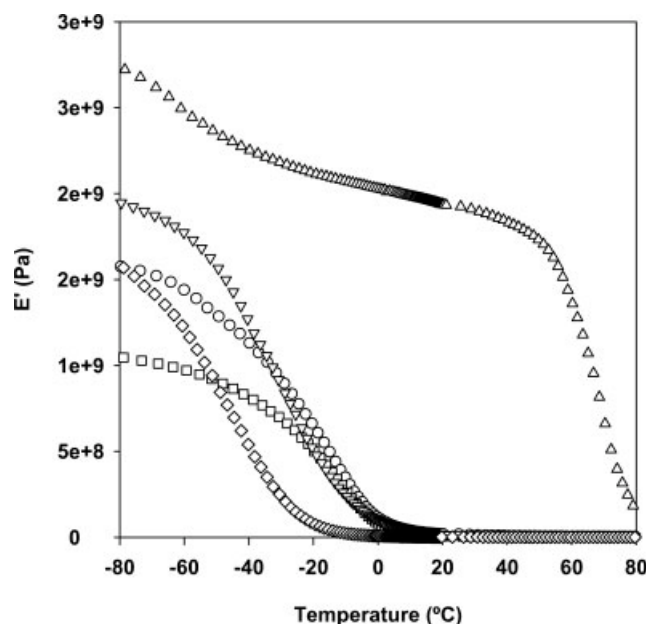

FIG. 5. Storage modulus (E') of ($\triangle$) PVC; ($\bigcirc$) block copolymer PVC-PBA-PVC (S6); ($\square$) block copolymer PVC-PBA-PVC (S8); ($\triangledown$) PVC with 70 phr of DOP; ($\diamondsuit$) PVC with 100 phr of DOP.
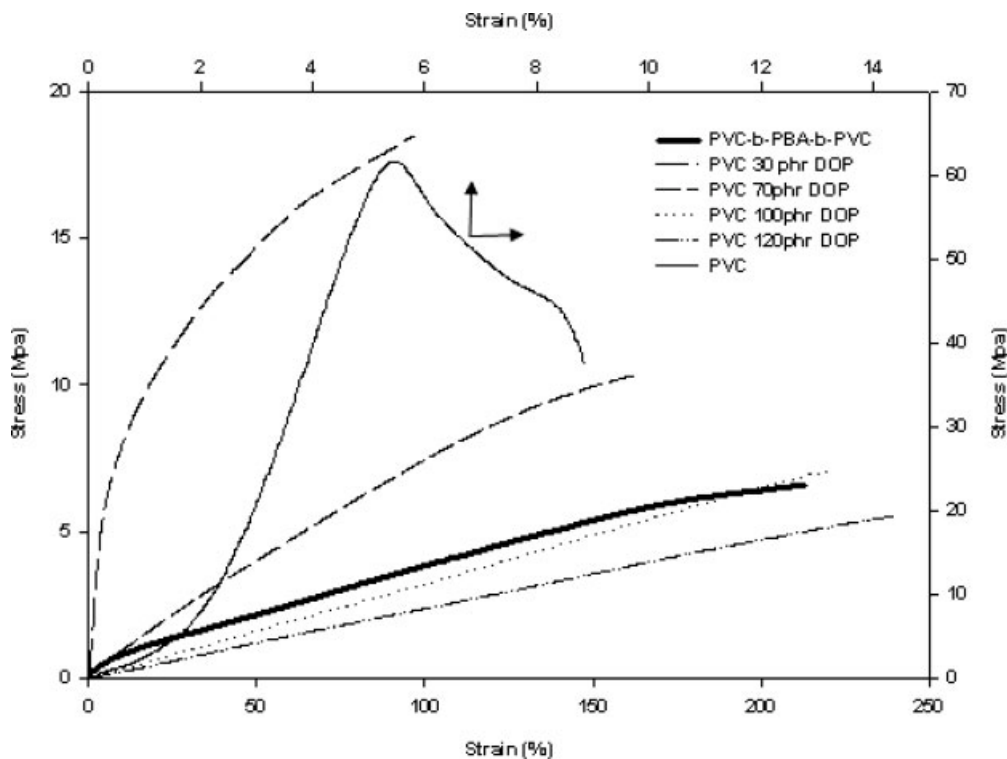
FIG. 6. Stress–strain curves for a block copolymer PVC-*b*-PBA-*b*-PVC (S8) and some flexible PVC made with DOP.

Two different scales were considered in order to compare the materials in the same plot. The ordinate and abscissa axis for PVC are represented on the top and right axis, respectively. The other products are represented traditionally. The PVC curve shows an elastic region until a stress value of 59 Mpa is reached. In this region the dependence of stress–strain is linear ending in the yield point (strain = 8.5%). The initial slope provides the value for the elasticity modulus (Young's modulus) which is a direct measure of the material stiffness. When the load exceeds the value of yield point, the deformation becomes irreversible even after removal of the applied load. This point defines the border between the reversible and irreversible deformations. In the practical sense, the yield point stress is a direct measure of the strength of the material and its resistance to permanent deformation. The tensile strength or ultimate strength is a measure of the stress required to break the material completely. The elongation at break defines the maximum elongation achieved by the specimen at the breaking point.

The preparation of this copolymer achieves a transition between a polymer that is typically hard and strong to a soft and tough material that resembles an elastomer. In terms of mechanical properties, this change represents the transition between products with high modulus, high yield stress, ultimate strength, and low capacity to elongate to a material with low modulus, low yield stress, and high elongation.

The low rigidity of the PBA induced a decrease in the yield stress. From this standpoint, the PVC confers rigidity

to the block copolymer, and the PBA confers ductility that is responsible for the observed high elongation at break. The stress–strain curve of the copolymer shows typical characteristics of elastomers, such as the low elastic moduli, high strain, and reversiblity along with the test until break. At the molecular level, under stress the bulk material behaves as a single material, as shown in DMTA tests, adopting an extended conformation which can revert to formed dimensions when the stress is removed. The copolymer shows the absence of the yield point, meaning that until 214% of elongation is reached no irreversible deformations occur. This is a typical result for an elastomeric material. Since both polymers are present in the same chain, when the force or load is applied and reaches the PBA segment, its intensity is softened. The comparison between the mechanical properties of this copolymer and the commercial products prepared with

TABLE 4. Mechanical properties of block copolymer PVC-*b*-PBA-*b*-PVC and some flexible PVC made with DOP.

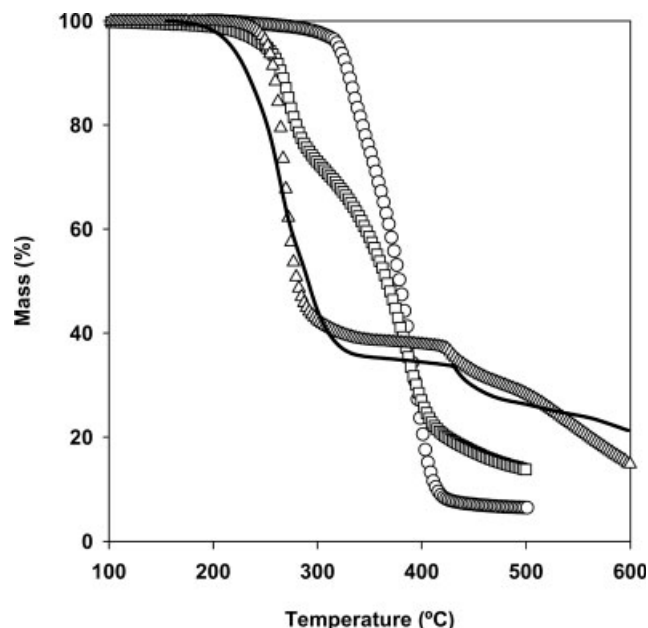| Sample	Yield point (MPa)	Rupture tension (MPa)	Elongation at break (%)	T_g (°C)
PVC-*b*-PBA-*b*-PVC (S8)	–	6.8	214	6.0
PVC	59	39.0	9	85
PVC −30 phr DOP	–	18.4	97	9.6
PVC −70 phr DOP	–	10.3	163	6.0
PVC −100 phr DOP	–	6.9	217	−12.8
PVC −120 phr DOP	–	4.6	230	−21.3

FIG. 7. TGA traces of ([circo] PBA, (□) PVC-PBA-PVC (S8), and (△) PVC prepared by SET-DTLRP at 42°C; (line) PVC with 100 phr of DOP.

DOP suggests that from the mechanical standpoint this new material resembles PVC with 100 phr of DOP.

The results obtained in tensile tests are summarized in Table 4.

Considering the results presented in Table 4, which represent an average of five measurements, it can be concluded that for the specific applications that traditionally employ PVC with 100 phr of DOP, this copolymer represents a real alternative. Although, when the main requirement is the thermal behavior of the material, the glass transition temperature of the copolymer is similar to that of PVC with 70 phr of DOP. This result suggests a different mechanism of plasticization that results from the use of DOP or the PBA block copolymer. An optimization process is being carried out which will be published soon [17].

Following the conclusion reached in a previous publication [20], the copolymer presents a higher thermostability (Fig. 7) when compared with the commercial product. This conclusion was also reached during the processability tests, since the proposed material could be processed without any stabilizers and with no signs of thermal degradation.

CONCLUSIONS

Some mechanical differences have been registered between the new copolymer and PVC/DOP. The results presented here are extremely encouraging, and provide the possibility of preparing new and different materials made of PVC. This technology also represents an important industrial advance leading to the preparation of flexible compounds free of conventional plasticizers. Furthermore, the processing formulation will need to be refined in order to maximize the mechanical properties.

The preparation of flexible PVC formulations without the need for additives which can be released from the PVC matrix is an important factor for the flexible PVC markets that are being lost every day. The processing tests show that the block copolymer is easier to process, uses simpler formulations and requires shorter processing times. The copolymer showed higher resistance to the processing temperature due to its intrinsic higher thermostability. This behavior is intimately linked to the fact in the case of the copolymer, the PVC is polymerized by a living radical mechanism and for that reason is free of structural defects [12].

The possibility of tailoring PVC with the introduction of nonextractable compounds makes the stringent control over parameters such as the porosity unnecessary. The only concern will be to obtain the necessary porosity to allow the VCM venting.

Finally, this technology, because of high levels of control over the composition, allows us to prepare homopolymers and copolymers with controlled structures that will be added to the PVC chains, leading to the formation of new and specific products.

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