Blends with various proportions of poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA) were prepared using melt mixing and studied by oscillatory mechanical measurements and low-field NMR spectroscopy to evaluate the influence of the processing method. The polymers and its blends were processed using a conventional low shear mixing chamber (LSM) and a high shear mixer (HSM). The behavior of all blends lies among those of the pure components, considering the two methods of characterization, and the data suggest phase separation between the two components. The hydrogen spin-lattice relaxation time of the PVDF/PMMA blends were measured and correlated with the components phases. The results are a contribution to data reported previously in the literature using different analytical methods. POLYM. ENG. SCI., 48:1901–1909, 2008. © 2008 Society of Plastics Engineers
to the actual morphology of the blend [4]. In this work, the rheological behavior of PVDF/PMMA blends was studied by oscillatory measurements to evaluate the influence of two processing methods.

Low field nuclear magnetic resonance is a technique that can be used to measure the hydrogen spin-lattice relaxation time ($T_1H$) of materials [13–16]. The process by which the spin system attains equilibrium from a nonequilibrium state is called relaxation. The mechanism whereby the spin system in the higher energy state can lose energy to its environment to recover the thermal equilibrium is called spin-lattice relaxation, characterized by a time $T_1$. The efficiency of the process may be correlated with factors such as temperature, solution viscosity, molecular size, and structure. For polymers in solution, it is generally short, but for solids it may be very long [13–15]. Then, the value is intrinsically related to the morphology of the system. Compact structures delay the relaxation process, whereas the introduction of amorphous domains makes the system more mobile, which reduces to some extent the spin-lattice relaxation time. Besides the relaxation times, the mobility changes, registered for the examined samples, can be correlated to the effects observed on mixing procedure [15, 16]. It is a valuable tool in obtaining information on the distribution of blends domains and interactions between both blend components. Data of $T_1H$ measured for the PVDF/PMMA blends studied in this work are presented and discussed.

**EXPERIMENTAL**

**Materials**

The polymers used were commercial grades of PVDF (Arkema; Kynar 740/$M_W = 156,000$ g/mol) and PMMA (Arkema; V052/$M_W = 55,700$ g/mol) in pellet form, kindly supplied by Autotrai Borrachas e Plásticos Ltda.

**Blends Preparation**

PVDF and PMMA (20, 40, 60, or 80 wt%) were mixed in a Haake Rheocord 9000, using a Rheomix 600 mixing chamber of $69\,\text{cm}^3$ with roller blades. The polymers and their blends were processed at a rotor speed of 100 rpm for a total mixing time of 20 min and a temperature of $190\,^{\circ}\text{C}$ (LSM). The same mixtures were also mixed in a high shear mixer (HSM) without temperature control. The polymers melted in less than a minute by the high shear imposed to the samples. After processing, the samples were removed from the mixer and cooled to room temperature.

**Dynamic Viscoelastic Experiments**

Dynamic experiments were carried out using MCR 101 Rheometer, Anton Parr Inc. The experiments were performed in parallel-plate geometry with a diameter of 25 mm and 1 mm of thickness under nitrogen atmosphere at a temperature of $190\,^{\circ}\text{C}$. An oscillatory frequency mode of 100 to 0.1 Hz was used to test the stability of the raw materials. A frequency sweep was also carried out to define the region of linear viscoelasticity. The dynamic mode was used to measure the complex viscosity and the storage and loss moduli ($G', G''$) as a function of frequency.

**Dynamic Mechanical Analysis**

Rectangular cross-section bars were prepared for each composition by compression molding by applying a pressure of $9\,\text{MPa}$ for 1 min at $190\,^{\circ}\text{C}$. After the molding step, the samples were cooled to room temperature under the pressure of $3\,\text{MPa}$. Dynamic mechanical analysis (DMA) measurements were performed on a TA 2980 analyzer from TA Instruments. Samples were cut in the dimensions of $17\,\text{mm} \times 10\,\text{mm} \times 1.5\,\text{mm}$ and were used as a single cantilever point at the rate of $5\,^{\circ}\text{C}/\text{min}$ and 1 Hz.

**Low-Field Nuclear Magnetic Measurements**

Low NMR field MARAN ultra 23, operating at $23\,\text{MHz}$ (for hydrogen) and equipped with an 18 mm variable temperature probe, was used for the relaxation measurements. Hydrogen spin-lattice relaxation times were determined directly by the traditional inversion recovery pulse sequence ($180^\circ - \tau - 90^\circ$); the instrument software calibrated the $90^\circ$ pulse of $4.6\,\mu\text{s}$ automatically. The amplitude of the FID was sampled for $20\,\tau$ data points, ranging from 0.1 to 5000 ms, with four scans for each point and 5 s of recycle delay. The relaxation values and relative intensities were obtained by fitting the exponential data with the aid of the program WINFIT. The distributed exponential fittings were performed using the software WINDXP, as a plot of relaxation amplitude versus relaxation time. The NMR measurements were carried out with samples prepared by compression molding using the DMA sampling procedure.

**RESULTS AND DISCUSSION**

The results obtained from dynamic viscoelastic measurements furnished information on shear flow properties, which allowed evaluate the PVDF/PMMA system following the approach presented by Yang et al. [6]. These authors showed that this system, under certain conditions, present a linear relationship for the logarithmic plot of the dynamic storage modulus ($G'$) versus the dynamic loss modulus ($G''$). Figure 1a and b shows the log $G'$ versus log $G''$ plots for the blends studied. The results showed that the behavior of all blends lies among those of the pure components, PMMA and PVDF, considering the two modes of processing. At low frequencies, all compositions showed a homogeneous fluid behavior. However, at
higher frequencies, the plot presents a negative deviation from linearity for blend compositions where the PMMA content is higher than 40 wt%. Similar profile was observed for PVDF/PMMA blends processed in LSM and HSM mixers.

The log \( G' \) (storage modulus) versus log \( G'' \) (loss modulus) plot helps to verify phase separation phenomena. Different relaxation mechanisms are related with frequency region as reported by Chopra et al. [11]. The relaxation phenomenon is essentially due to the phase’s relaxation at high frequencies whereas at low frequencies the relaxation mainly stems from the deformation process of the suspended droplets [11]. Yang et al. [6] found similar results in PVDF/PMMA blends processed in a twin-screw compounding machine. They showed also that log \( G' \) versus log \( G'' \) plots for binary blends, consisting of components having dissimilar chemical structures, lie between those of the constituent components. The extent of the curves spread obtained by this plot for a given polymer pair depends on, among other factors, the extent of miscibility [6]. The data presented here indicate, that at high frequencies, a possible phase separation between the two components was observed. Besides, the presence of a nonhomogeneous fluid suggests the occurrence of a degradation process of PMMA.

The loss moduli of the pure polymers and their blends processed in LSM (100 rpm) and HSM were plotted as a function of temperature showed in Fig. 2. The curves recorded for the blends processed by both mixing methods show the same profile.

The register obtained for PVDF presents a peak at \(-26^\circ C\) and a relaxation at \(72^\circ C\). The transition in the loss modulus curve at \(72^\circ C\) can be attributed to the \( \alpha \) transition and it is near the value reported in the literature [10]. The attribution to this transition as the glass transition temperature \( (T_g) \) was a point of controversy in the literature, but recently Salimi and Yousefi [17] reported the value of 65°C for PVDF based on the work of Sajkiewicz et al. [18]. It is interesting to note that the samples used in the mentioned works [10, 17, 18] were prepared by compression molding, whereas the ones used by other authors were films cast from solutions of \( N,N \)-dimethylformamide [19, 20] or \( N,N \)-dimethylacetamide [21]. So, samples obtained by melt blending would be more adequate for comparison purposes to avoid specimens that...

FIG. 1. Log \( G' \) versus log \( G'' \) plots of PVDF/PMMA blends processed in (a) low (LSM) and (b) high (HSM) shear mixers.

FIG. 2. Loss modulus as function of temperature of PVDF/PMMA blends processed in (a) low and (b) high shear mixers.
may be plasticized by traces of casting solvent. The peak in the loss modulus curve at −26°C is close to the value attributed to the β transition by Hourston and Hughes [10] as well by Saito and Stühn [21]. It can be noted that the peak related to β transition diminished and disappeared with the increase of PMMA content. It is worth to mention that samples having more than 60 wt% of PMMA did not show any crystallinity, thus in these blends PMMA hinder the PVDF crystallization. These results state the hypothesis of Hourston and Hughes [10], which adopted the interpretation given by Paul and Altmirano [22], where the α transition was attributed to the glass transition and the β relaxation was associated to the crystalline phase. According to many workers [7, 8, 10, 22], blends with semicrystalline polymers are heterophasic and present morphology with at least two phases. Therefore, in the PVDF/PMMA blends, the crystalline phase is pure PVDF and the amorphous phase is a compatible mixture of both polymers. High PMMA content in the blend prevents the PVDF crystallization and consequently only the α transition is observed in the loss modulus curve. This suggests that compatible blends of PVDF/PMMA are obtained if more than 60 wt% of PMMA is used in the mixture.

The α peak in the neat PMMA and PVDF/PMMA blends is attributed to the glass transition and the broad secondary relaxation, which could be ascribed to the PMMA β relaxation. LSM-PMMA presents the glass transition peak at 122°C and the secondary relaxation centered on 15°C attributed to the motions of the side group ester attached to the backbone chain as showed in Fig. 2a. The α transition peak diminished, broadened, and shifted progressively to lower temperatures as higher the PVDF content in the blend. The β transition followed a similar tendency. As pointed out by Hourston and Hughes [10], the shift toward lower temperatures indicate that there is a certain mixing of the polymers, but the width of the loss moduli curves shows that this pair of polymers is not miscible. On the other hand, the literature [7, 21, 22] demonstrated that the interpretation of the phenomena that occur in those systems is more complex. PVDF is a semicrystalline polymer that presents at least three main types of crystal forms α, β, and γ, which may be interconverted. Moreover, the content of a specific phase is closely related to the method of sample preparation. It depends on factors such as the method of sample preparation (melt blending or solution casting), components concentration, heat treatment, and others [23, 24].

When LSM processed blends data were compared with HSM results, it can be noted that HSM processing promoted the PMMA β transition temperature shift to lower temperatures, depicted in Fig. 2b. The curves recorded for the blends PVDF/PMMA processed by both methods also show the secondary transition observed for pure PMMA centered around 10°C. Hirata and Kotaka [7] and Hourston and Hughes [10] did not observe this relaxation in blends prepared by melt blending. Then, it can be suggested that the appearance of this relaxation could be ascribed to the shear imposed by the mixing process.

Figure 3 shows the effect of PVDF content on temperatures of the pronounced transitions. It can be noted that the decrease of the PVDF low-temperature transition (β) with the PMMA addition is quite linear and associated to the blend crystallinity as already stated. The transition obtained from the loss modulus ascribed to be the PMMA glass transition temperature shows a linear decrease for composition having until 40 wt% of PVDF. For the blends with higher PVDF content another linear relationship can be observed as a consequence of the PVDF glass transition. Wherefore, if the systems are heterogeneous and interpreted as a whole, it suggested that both glass transition temperatures were overlapped.

The line discontinuity suggests a sigmoid pattern as pointed out by Paul and Altmirano [22], and the sigmoid shape of the curve in Fig. 3 might be explained based on the occurrence of crystallinity, which pulls down PVDF from the amorphous phase changing its composition. Miscible blends would produce those effects. However, these systems present interactions that have influence on the blends properties as reported in the literature [5]. When the PVDF content is high in the blend, the crystallization process disturbs the miscibility of the polymers and the interaction between the PMMA carbonyl groups and PVDF hydrogen atoms is reduced. Specific interactions are very sensitive to the distance between the interacting groups and to their relative orientation. The strength of hydrogen bonding is influenced by the atomic distance and by the bond linearity. This is closely related with the efficiency of the contact between two unlike chains, which needs to adopt an appropriate conformation for interacting. So, the actual nature of the specific interactions is under discussion [5, 23, 24].

Hirata and Kotaka [7] reported that above the PVDF melting point (170°C) the components of the PVDF/
PMMA blend are miscible. On cooling, PVDF crystallizes from the melt, and the mixture becomes composed of a crystalline phase and an amorphous phase, which in its turn is a mix of both polymer amorphous fractions. The crystalline phase was evaluated by differential scanning calorimetry and blends having high PVDF content (>60 wt%) exhibit melting peaks [7, 10]. On the other hand, neither melting nor crystallization peaks were observed in blends having PVDF contents less than 60 wt%. In these compositions, both components are in the amorphous state, presumably mixed with high level of polymers chains interpenetration [10].

Further low-field NMR studies were carried out to evaluate the relaxation time to characterize the phase separation process in the PVDF/PMMA blends. The low field NMR measurements, that is, the measured hydrogen spin-lattice relaxation times, showed that PMMA and PVDF form partially miscible blends. Table 1 shows the T1H values obtained for PVDF/PMMA blends and the parents PMMA and PVDF all processed in low and HSMs.

Theoretical models have been developed to explain the relaxation processes observed in glassy polymers such as PMMA [25–28]. These theories postulate that PMMA mechanical relaxations may be attributed to molecular motions, where the strength of mechanical relaxation is influenced by external actions such as temperature, quenching and annealing, pressure, and mechanical deformation. When the sample is in the glass state, each motion contributes from small to significant amounts. As the polymer chain backbone is frozen into rigid conformations any long-range motion ceases below the glass transition temperature although some dynamics still persists on a more local mode. Arrighi et al. [27] reported that the origin of the mechanical relaxation times distribution has been discussed in the literature in terms of packing in the amorphous phase as well as conformational disorder. Those approaches suggest a possible explanation for the two domains obtained for PMMA when the samples were measured below the glass transition temperature. Then, it is reasonable suppose that the mobile domain may be attributed to the side ester group motions and the rigid one to the main chain.

The stress promoted by the different shear rate affects the sample deformation and then, the evolution on the potential energies barriers distributions under load is somewhat different. The data obtained for PMMA showed that the sample processed in LSM is more rigid than the one submitted to higher shear rate process as in HSM. The domain distribution presented in Fig. 4 demonstrates that domain differences were introduced in the processing of blends. Figure 4a shows that for PMMA processed with low shear rate in LSM, the rigid domain peak is sharper than the one observed for the sample processed in HSM depicted in Fig. 4b, whereas the flexible region is more rigid. This gives some support to the idea that high shear processing mode introduces an increase on structural heterogeneities which leads to a broader distribution of PMMA side groups rotational frequency.

The T1H values for neat polymers show that PVDF is slightly less rigid than PMMA. The two regions of different molecular mobility show that there are at least two types of molecular organization in this semicrystalline polymer. This may be ascribed to the polymorphism of PVDF that probably exists and to the presence of amorphous phase. The literature reports that when samples were submitted to different stresses on processing there is influence on the crystallization process and different crys-

![FIG. 4. Low-field NMR spin-lattice distribution profile of pure PMMA processed in (a) low and (b) high shear mixers.](https://example.com/figure4.png)

**TABLE 1.** Hydrogen spin-lattice relaxation time (T1H) for PVDF/PMMA blends processed in low (LSM) and high (HSM) shear mixers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T1H (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LSM</td>
</tr>
<tr>
<td>Neat PMMA</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>99</td>
</tr>
<tr>
<td>Neat PVDF</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>87</td>
</tr>
<tr>
<td>PVDF/PMMA 80/20</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>89</td>
</tr>
<tr>
<td>PVDF/PMMA 60/40</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>65</td>
</tr>
<tr>
<td>PVDF/PMMA 40/60</td>
<td>35</td>
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<tr>
<td></td>
<td>99</td>
</tr>
<tr>
<td>PVDF/PMMA 20/80</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>97</td>
</tr>
</tbody>
</table>
talline species as well as amorphous domains will be favored [17, 23, 24, 26, 29, 30]. Thus, the results can be interpreted as arising from the actual morphology presented by the samples. These results are in good agreement with data obtained from DMA measurements because at the temperature used for T1H experiment (\(\sim25^\circ\text{C}\)) all loss modulus curves (see Fig. 2) show a secondary relaxation.

PVDF domains distribution presented a different feature. Figure 5a shows two-component distribution for the rigid domain of PVDF processed in LSM and a broad profile for the one produced with higher shear rate in HSM as can be seen in Fig. 5b. These differences suggest that the two processing modes introduce unlike PVDF crystallization process. The processing in LSM could generate semicrystalline species separated from a mixed amorphous phase and in HSM a more homogeneous crystallite distribution embedded in the amorphous domain. The fraction of crystallization of each phase is generally determined by X-ray diffraction, differential scanning calorimetry, and infrared spectroscopy [29]. However, the content of the phases are under study and will be published later.

The blends with high PVDF content (80 wt%) presented different features introduced by the blend mixing. The PVDF/PMMA 80/20 sample having 80 wt% of PVDF processed at low shear rate (LSM) exhibits a tendency toward increasing stiffness as showed by the increase of T1H of the flexible region, whereas the T1H-value of the rigid region was almost the same as that found for neat PVDF. This is consistent with the description of Paul and Altamirano [22] where PVDF/PMMA blends with a certain degree of crystallinity present a two-phase type structure composed by pure PVDF and an amorphous region rich in PMMA. However, the PVDF/PMMA 80/20 sample processed at high shear rate (HSM) indicates the presence of two domains with shorter relaxation times in comparison with the one prepared at lower shear rate, which suggest that the composition of existing domains (rich in a particular component) could be different if the sample is submitted to different processes.

Figure 6 depicts the effect of introduction of PMMA on the PVDF domains. The blend PVDF/PMMA 80/20 prepared in the LSM shows the peak of the rigid domain with a shoulder on the more flexible side as can be seen in Fig. 6a. The peak is sharper than the corresponding one in neat PVDF, that is, the domain is more uniform. This profile suggests the occurrence of changes on the crystal type content. According to Kim et al. [23], the addition of PMMA precludes the nucleation of the \(\alpha\)-phase and favors the nucleation of the \(\beta\)-phase, besides be known that \(\alpha\)-phase is obtained directly from the melt [17, 23]. The \(\alpha\)-phase has trans-gauche–trans-gauche prime (tttg') conformation and \(\beta\)-phase presents a planar zigzag all trans (ttt) conformation [17]. The amount of trans–trans (ttt) conformations increased due to specific interactions with PMMA, which has an energetically sta-
ble all-trans conformation compared to the trans-gauche (tg) conformation [23]. Then, it is possible that the decrease of the \(\alpha\)-phase promoted an increase on the sample stiffness, once \(\beta\)-phase conformation provides more packing and higher melting temperature crystals [17]. The blend PVDF/PMMA 80/20 prepared in the HSM shows a smooth rigid domain distribution in Fig. 6b. These distribution fittings corroborate the interpretation of spin-lattice relaxation times. Besides the stress imposed by the mixing process, which promoted changes on the PMMA conformation, the crystallinity of PVDF decreased as indicated by Fig. 2. The rigid domain profile is more sharp than the presented by neat PVDF. This indicates that the amorphous PVDF component tends to mix with the PMMA component.

The blend PVDF/PMMA 60/40 prepared in the LSM showed a significant decrease of the two relaxation times in comparison with that having 80 wt% of PVDF. In blends with low PVDF content, a better interaction between the components could be occurring. But, similar behavior was not observed for the sample processed in HSM, which showed \(T_1H\) values near those for neat PVDF, which supports the phase separation explanation. The differences in the samples behavior could be attributed to the changes in the structural organization of the blend caused by the processing mode. This is consistent with data reported by authors already mentioned [5, 7, 9, 23] and supports the interpretation of the data presented here.

The processing mode of blends with 60 wt% of PVDF promoted different domain distribution fittings that are presented in Fig. 7a and b. The spin-lattice values indicate that PVDF/PMMA 60/40 blends prepared in LSM showed a better resolution in the distribution of domain curves with respect to blends with 80 wt% of PVDF, which is an indication of increased miscibility. On the other hand, sample prepared in HSM presents clear evidence of a different mobility distribution that suggests the formation of more rigid domains promoted by a higher shear, which results in higher \(T_1H\) values in comparison to samples prepared at low shear rate. According to the literature [5, 7], this result indicates that the blend prepared in HSM is a mixture of a semicrystalline and an amorphous polymer.

At intermediate composition the PVDF/PMMA 40/60 blend prepared in LSM, the relaxation parameter of the flexible region presented a significant increase in comparison to the neat PMMA value (>100%), whereas the more rigid phase remained unchanged. In this case, the PMMA content is high enough to prevent PVDF crystallization. However, the efficiency of the contact between the two unlike chains increased and the adequate conformation for interacting was achieved [24]. The specific interactions taking place over many units may stabilize the conformation trans–trans although other structural factors may influence their extension. On the other hand, the PVDF/PMMA 40/60 blends prepared at high shear presented just a small decrease of \(T_1H\) of the rigid domain compared to the value from neat PVDF, due to the fact that this domain did not take part in the interaction and/or phase separation was occurring. This is in accordance with data reported in the literature [5] where the authors described the existence of at least two phases where the blends contained small amounts of partly crystallized PVDF and the amorphous PVDF and PMMA mixtures.

The mobility decrease described in the interpretation of \(T_1H\) values obtained for PVDF/PMMA 40/60 prepared in LSM is well observed in the distribution profile depicted in Fig. 8a. The profile is broader than that registered for the PVDF/PMMA 60/40 and suggests that the two domains are overlapped. Otherwise, Fig. 8b shows that PVDF/PMMA 40/60 prepared in HSM presents a distribution profile sharper than the profile of the same blend prepared in LSM. Moreover, the \(T_1H\) values from the mobile domains are near that of the values obtained for pure PMMA, indicating similar molecular organization. Figure 8b shows also the flexible domain, which is a clear evidence of phase separation.

The \(T_1H\) values of PVDF/PMMA 20/80 blend with high-PMMA content (80 wt%) prepared in LSM were similar to that of the pure polymer. However, the relaxation time of the high-mobility region (amorphous phase) was slightly shorter due the interaction that might be occurring in this system. The blends prepared in HSM showed comparably smaller \(T_1H\) values for the two domains, which could be an indication that domains rich in one of the components were formed.
The distribution profiles obtained for the PVDF/PMMA 20/80 blends are presented in Fig. 9a and b. An interesting effect can be noted: the blend prepared with low shear rate (LSM) shows a distribution profile pattern similar to that obtained for pure PMMA, which corroborates the \( T_1H \) values interpretation. However, the data obtained for blends prepared in the HSM are similar to the relaxation time values and distribution profile of the blend PVDF/PMMA 80/20 prepared in the HSM, showed in Fig. 6b. This suggests that the high shear imposed to these blends promoted a similar molecular organization.

The relaxation data also showed that the blend composition has influence on the \( T_1H \) values, and in the rigid domain it was less pronounced than on the ones from the mobile region, where significant changes were observed. This could be explained by taking into account that different types of the amorphous phase were reported in the literature [7, 8]. The blend may be a multiphase system composed of a semicrystalline polymer (PVDF) and an amorphous phase, in which phase separation occurs at different levels producing various morphologies as suggested by the literature [5, 7, 8, 10, 23, 24].

The low-field NMR measurements through the hydrogen spin-lattice relaxation time showed that the addition of different contents of PMMA into PVDF produces blends with partial miscibility. These results are in good agreement with data obtained from DMA measurements.

**CONCLUSION**

The methods described showed that PVDF/PMMA blends undergo phase separation at different conditions of processing modes and blend composition. Results obtained from dynamic viscoelastic experiments are inconclusive, whereas DMA showed \( \alpha \) and \( \beta \) relaxations indicating some mixing of the polymers. However, both processing conditions used for mixing the blend components gave loss modulus \textit{versus} temperature plots that are similar. Nevertheless, different molecular organization was evidenced using low-field NMR technique. Complementary study is needed to evaluate the extension of the domains detected by the spin-lattice relaxation time.

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