The miscibility in blends containing poly(methyl methacrylate-co-methacrylic acid) [P(MMA-co-MA)] as polymer component and the dihydric phenols 4,4'-thiodiphenol (TDP) and 4,4'-methylene diphenoxy (MDP) as low molecular weight compounds (LMWC) was studied by Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectrophotometry (FTIR). Thermal properties, such as the glass transition of P(MMA-co-MA) and the melting of the LMWC, were found to be clearly affected when the compounds were blended, which was attributed to the miscibility between them. FTIR was used to investigate the specific interactions between P(MMA-co-MA) and the LMWC. The formation of intermolecular hydrogen bonds between the carbonyl groups of P(MMA-co-MA) and the hydroxyl groups of TDP and MDP were discovered. Thermogravimetric and viscometry analysis were also used as additional techniques to complement the obtained FTIR and DCS results.

**Keywords:** blends, poly(methyl methacrylate-co-methacrylic), 4,4'-thiodiphenol, 4,4'-methylene diphenoxy, hydrogen bond, low molecular weight compounds.

**INTRODUCTION**

The blending of two materials to obtain a balance of properties has been worked successfully in the metallurgical field. The appropriate combination of two or more different polymer structures to get a new polymeric material with the properties of their components is not a new idea. In this sense, the necessity to find polymer materials with new and specific applications has driven polymer blending to become one of the most important research subjects, both academically and industrially.

Even if a considerable number of problems remains unsolved in the interpolymer miscibility area, some fundamental bases have been established, such as the importance of the specific interactions (hydrogen bonding, dipolar, charge transference interactions and other) between the components. For macromolecules, the blending Gibbs free energy ($\Delta G^{\text{mix}}$) is controlled by its enthalpic contribution ($\Delta H^{\text{mix}}$) due to the entropic factor ($\Delta S^{\text{mix}}$) is normally unfavorable because of the high molecular weight of the blend components. Thus, polymer pairs with complementary chemical functions lead to miscible systems. There is much information in the literature indicating that compatible polymer blends were obtained through functionalized macromolecular systems. This information includes a wide variety of components such as addition and condensation homo and copolymers (2-20). The common factor in this kind of studies is the presence of different chemical functions in the macromolecule in order to counteract the unfavorable entropic factor mentioned above. Therefore, from this general behavior, it would be interesting to study the properties of polymeric materials blended with low molecular weight compounds (LMWC), which can potentially modify and ideally improve the properties of the macromolecular component if one considers that the unfavorable entropic factor of the polymer1-polymer2 systems is practically negligible in polymer-LMWC blends. Moreover, the analysis of this kind of blends would be interesting not only from the fundamental perspective, but these systems can also be an alternative way to recycle preexistent polymeric materials, finding new applications after modifying and improving macroscopic properties such as mechanical, thermal and thermogravimetric properties mentioned above. Furthermore, the bifunctionality of molecules like MDP and TDP could also promote a physical crosslinking effect between potentially interacting macromolecular chains. Functionalized polymers should be used to achieve this, according to a series of studies, whose reports include, but are not limited to polymers containing vinyl pyridines (4,11,34) and that presents interesting structural properties as the presence of polar and proton-donor groups that can be considered as potentially interacting LMWC, whose structural formulae are presented in Figure 1.

![Figure 1. Structural Formulae of 4,4'-thiodiphenol (TDP), 4,4'-methylene diphenoxy (MDP) and poly(methyl methacrylate-co-methacrylic acid) [P(MMA-co-MA)].](image)

The eventual interaction capability of this kind of LMWC would promote a significant association with different kind of macromolecules, originating a type of physical bulky side group, which would remarkably modify properties such as mechanical, thermal and thermogravimetric properties mentioned above. Furthermore, the bifunctionality of molecules like MDP and TDP could also promote a physical crosslinking effect between potentially interacting macromolecular chains. Functionalized polymers should be used to achieve this, according to a series of studies, whose reports include, but are not limited to polymers containing vinyl pyridines (4,11,34). N-vinyl pyrrolidone (4,13,34), vinyl phenol (2,9,13,30-33) and methacrylate (5,11,34) units. Poly(methyl methacrylate-co-methacrylic acid) [P(MMA-co-MA)] (Figure 1) is a well known functionalized vinyl copolymer previously used in polymer blends (35,36) and that presents interesting structural properties as the presence of polar and proton-donor groups that can be considered as potentially interacting units.

The aim of this work is to study the compatibility of polymer - LMWC blends to identify the effect of specific interactions on the miscibility. To do this, blends of P(MMA-co-MA) with TDP (blend A) and MDP (blend B) were studied by Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectrophotometry (FTIR), Thermogravimetric Analysis (TGA) and viscometry.
EXPERIMENTAL

Blend components
Aldrich’s P(MMA-co-MA), TDP and MDP were used. The weight-average molecular weight (Mw), the glass transition temperature (Tg) and the methyl methacrylate to methacrylic acid molar ratio of P(MMA-co-MA) are 15,000 g/mol, 107.9 °C and 1.016 respectively. Melting points of TDP and MDP are 152.8 °C and 163.8 °C respectively. Mw and copolymer composition correspond to the supplying’s values and Tg and Tm were determined by DSC.

Preparation of blends
Blends of different compositions were prepared by solution casting, using tetrahydrofuran as solvent. Then, they were evaporated at room temperature and vacuum dried at 308 K for 1-2 weeks until constant weight. The blend concentration was about 2 w/w %.

Viscometry measurements
Intrinsic viscosity ([η]) of P(MMA-co-MA) and the different blends was determined using an Ostwald-type capillary dilution viscometer in tetrahydrofuran at 298 K without kinetic energy corrections. Intrinsic viscosities were obtained using the Solomon Gotessman equation (37).

FTIR spectra
Infrared spectra of P(MMA-co-MA), LMWC and their blends were recorded on a Nicolet Magna IR 550 Fourier transform infrared spectrophotometer. Spectra were recorded with a resolution of 1 cm⁻¹. Samples were prepared directly in KBr pellets.

DSC measurements
The glass transition temperature (Tg) of P(MMA-co-MA) and blends and the melting temperatures (Tm) of TDP, MDP and blends were measured by Differential Scanning Calorimetry (DSC) from the thermograms obtained with a Differential Scanning Calorimeter Rheometric Scientific DSC Plus, with the Orchestrator program as graphical software. Samples (3-4 mg) were placed inside aluminium pans and heated under flowing nitrogen (25 mL/min), ranging from 25 to 200 °C, at 10 °C/min.

To minimize differences in the samples’ thermal history, Tg and Tm determination was performed as follows: heating until the final temperature (dynamic stage), isothermal at the final temperature (static), cooling until the initial temperature (dynamic, quenching step), isothermal step at the initial temperature (static) and, finally, heating until the final temperature (dynamic). In all cases, the Tg was evaluated from the last stage.

Samples were dried under reduced pressure in a vacuum oven prior to measurement.

TGA measurements
Thermogravimetric measurements were performed using a thermal analyzer TGA Polymer Laboratories STA 625. Samples (2-3 mg) were placed inside aluminium pans and heated under flowing nitrogen (41 mL/min) ranging from 25 to 550 °C, at 10 °C/min, obtaining the corresponding thermal decomposition profiles.

Samples were dried under reduced pressure in a vacuum oven prior to measurements.

RESULTS AND DISCUSSION
Table 1 lists the blending composition of the two series studied (blends A and B) and other properties determined as the intrinsic viscosity and the Tm values obtained from thermogravimetric analysis. Figure 2 shows the DSC thermograms corresponding to the A1-A7 and B1-B7 series, recorded during the second heating scan. P(MMA-co-MA) (A1) shows a very clear Tg value at 107.9 °C (supplier reference value 105 °C), which disappears when the content of TDP increases, from A2 to A6. This is a interesting result because even if it is difficult to attribute this behavior to miscibility between the components, if phase separation takes place, the Tg value corresponding to the pure copolymer should be clearly detected as observed for the A1 sample.

![Image](image-url)

Figure 2. Thermograms of the A1-A7 (a) and B1-B7 (b) series (25-200 °C, 10 °C/min).

(*) Tetrahydrofuran, 25 °C.

The glass transition represents an abrupt change in the mobility of the chain segments of a macromolecule in the amorphous phase. The temperature at which this transition occurs (Tg) is very affected by little local modifications (38). In this case, the molecules of TDP might act as a physical bulk side group of the P(MMA-co-MA) chain in the blend, as a consequence of some kind of intermolecular interaction. Furthermore, TDP should also act as a physical crosslinking agent in the blend. Consequently, the disappearing of the glass transition temperature can be interpreted in terms of a loss of the molecular mobility of the copolymers chains when they interact with the TDP ones.
From the thermograms shown in Figure 2, it is possible to observe another complementary fact. TDP (A7) shows a melting temperature (Tm) of 152.8 °C, which shifts to lower values as the P(MMA-co-MA) content increases (147.9 °C and 135.3 °C for A6 and A5 respectively) until it disappears when the blending composition is 50 weight % in P(MMA-co-MA) (A4). Additionally, the melting molar heats (ΔHm) were calculated from the corresponding melting peaks of the thermograms, obtaining 31.9, 13.7 and 3.4 kJ per mol of TDP for A7 (pure TDP), A6 (20 % P(MMA-co-MA)) and A5 (40 % P(MMA-co-MA)) respectively. Lower energy is required to produce the fusion of TDP as the blend becomes richer in the copolymer. These results might suggest that the crystallinity and the molecular ordering of the TDP component decreases as the P(MMA-co-MA) content increases, due to an intermolecular interaction between both components, until that TDP exists in an amorphous state and its crystallization is completely suppressed in the blends (from A4 to A2). A similar behavior has been described by Inoe et al. for TDP blended with poly(-caprolactone) (28). Therefore, in the P(MMA-co-MA)/TDP system, it is possible that some kind of interaction, such as hydrogen bonding, should be present between both components. An analogous behavior was observed for the P(MMA-co-MA) / MDP blend. The results presented in this Table show that the crystallization of TDP is completely suppressed when the content of the P(MMA-co-MA) is 50 %. When the low molecular weight compound is MDP, the same situation is obtained with a copolymer content of 60 %. This fact could be indicative of a larger interaction degree between P(MMA-co-MA) and TDP.

Table 2. Melting temperature (Tm) and melting molar heats (ΔHm) for TDP (A7), MDP (B7) and blends with P(MMA-co-MA).

<table>
<thead>
<tr>
<th>Blend</th>
<th>TDP + P(MMA-co-MA)</th>
<th>MDP + P(MMA-co-MA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>A7</td>
<td>A6</td>
</tr>
<tr>
<td>% P(MMA-co-MA)</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>Tm (°C)</td>
<td>152.8</td>
<td>147.9</td>
</tr>
<tr>
<td>ΔHm (kJ/mol)</td>
<td>31.9</td>
<td>13.7</td>
</tr>
</tbody>
</table>

(a): Tm disappears from 50 % in copolymer (A4 composition).
(b): Tm disappears from 60 % in copolymer (B3 composition).

FTIR measurements are a powerful tool to analyze the miscibility in polymer-containing blends. The position changes of the IR absorption peaks resulting from some characteristic functional groups can be attributed to the existence of intermolecular interactions (4,29,34,39). A part of the electronic density of the interacting group is displaced toward the other chemical group, and consequently lower energy is required to produce the corresponding vibration of the chemical bond involved in the interaction. The monomer units of P(MMA-co-MA) contain carbonyl groups (with a significant trend to the hydrogen bonding formation), which absorb at 1733 cm⁻¹ (stretching band). TDP and MDP have no groups that produce absorption in this region. Moreover, they also have chemical groups that can participate in the hydrogen bonding formation (phenol units). Therefore, a shifting of the corresponding stretching band can be related with hydrogen bonding between the blend components. Figure 3 presents the FTIR spectra for the A1-A7 series, and Figure 4 depicts the wave number corresponding to the stretching of C=O groups in P(MMA-co-MA) (A1), TDP (A7), and their blends with TDP and MDP in relation to the blend composition.

A significant variation in the wave number with the composition, corresponding to the stretching of O-H groups, was also detected. However, even if these chemical groups are directly involved in the hydrogen bonding proposed, the shifts are not useful for identifying the intermolecular interaction because both P(MMA-co-MA) and LMWC have these chemical groups.

Figure 5 shows the thermogravimetric profiles of the blends and the corresponding pure components of the A1-A7 and B1-B7 series. Series 6 depicts the intrinsic viscosity ([η]) variation with the blend composition for both series. Thermogravimetric (TGA) and viscometry analyses were used as additional techniques to complement the results obtained by FTIR and DSC. Intermediate thermogravimetric profiles of the blends between those corresponding to pure components (as observed in Figure 5) have been reported as evidence for polymer-polymer miscibility (34,40).

The intrinsic viscosity ([η]) of blends of P(MMA-co-MA) with TDP and MDP were measured in THF at 298 K. A monotonous diminishing of [η] with the composition is observed in Figure 6. This is an expected result because as the content of the small molecules increases, the polymer content diminishes. Nevertheless, the decreasing of intrinsic viscosity could be also attributed to a compaction of the polymer chains due to the competition of the LMWC molecules with the solvent ones for the macromolecules as reported for other polymer-LMWC blends (37). Then, the thermogravimetric profiles and the decrease of [η] obtained can be considered to be other evidences indicating miscibility.
From the decomposition curves of Figure 5, the temperature at which the weight reduction reaches 50 % ($T_{50}$) were determined for the blends and the pure components of the studied series. $T_{50}$ is a measure of the decomposition extension for each composited material. In Figure 7, a decrease of $T_{50}$ with the LMWC content can be observed. The interaction of both TDP and MDP with P(MMA-co-MA) originates a diminishment in the copolymer’s thermal stability as the blend becomes richer in the LMWC.

**4. CONCLUSIONS**

P(MMA-co-MA) shows a very clear $T_g$, which disappears when the copolymer is blended. The addition of the LMWC could be affecting the molecular mobility of the copolymer chains. A shift of $T_m$ for the LMWC is obtained as the P(MMA-co-MA) content increases, until it disappears when the blending composition is 50 and 60 weight % in copolymer, for the A and B blends respectively, which suggests that the crystallinity of the LMWC decreases as the blend is richer in the copolymer. This result is confirmed by the decrease of the melting molar heat of the LMWC in the same sense. In the carbonyl vibration region of the FTIR spectra, a decreasing of the corresponding wave number is obtained when P(MMA-co-MA) was blended with TDP and MDP for the entire range of blend compositions. The variation in the position of the carbonyl group band can be related with a change of the chemical environment of this group originated by hydrogen bonding. Then, the DSC and FTIR results can be considered as evidence indicating a general miscibility in the studied blends. In agreement with these results, intermediate thermogravimetric profiles of the blends and a monotonous diminishing of $[\eta]$ with the composition were obtained by TGA and viscometry. A decrease in the thermal stability of P(MMA-co-MA) with the LMWC content was also found.

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