MORPHOLOGICAL STUDY AND COMPATIBILITY OF PMMA BLENDS WITH PVA PREPARED IN SOLUTION

C. Parra[a]*, Y. Gualdron[b], C. Chinea[c], E. Cañizales[d], M. Gomes[a], D. Soto[d], E. Catarí[e], A. Herrera[e]

[a] Laboratory of Synthesis and Treatment of Materials, Center for Materials Engineering and Nanotechnology, Venezuelan Institute of Scientific Research, Altos de Pipe, Miranda State. Venezuela
[b] Postgraduate in Chemistry, Faculty of Sciences, Central University of Venezuela, Caracas, Venezuela.
[c]Polymers Laboratory, School of Chemistry, Faculty of Sciences, Central University of Venezuela, Caracas, Venezuela.
[d] Laboratory for Structural and Magnetic Characterization of Materials, Center for Materials Engineering and Nanotechnology, Venezuelan Institute of Scientific Research, Altos de Pipe, Miranda State, Venezuela
[e]Polymers Laboratory, "Dr. Gabriel Chuchani" Chemistry Center, Venezuelan Institute of Scientific Research, Altos de Pipe, Miranda State. Venezuela.

*Corresponding author, E-mail: cpantojave@gmail.com, +00-58-212-5041433.

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ABSTRACT

In this work, mixtures of polymethyl methacrylate (PMMA) with polyvinyl alcohol (PVA) were prepared by dissolution, to study their miscibility and possible future applications in the development of bone cements. Formulations were prepared in proportions of 70/30 and 50/50 (PMMA/PVA). The compatibility was studied by Fourier Transform Infrared (FTIR) and Differential Scanning Calorimetry (DSC). Thermogravimetric Analysis (TGA) was used to evaluate the thermal stability of the materials. The morphology of all materials was exposed using Scanning Electron Microscopy (SEM). Significant shifts in the absorptions of the carbonyl groups of PMMA and hydroxyl groups of PVA were detected by infrared, which would be associated with the formation of intermolecular hydrogen bonds of the type PVA–O–H–O=C–PMMA. The thermal behavior of the polyblends obtained by DSC showed a direct correlation with their composition, with two well-defined T_g values shifted to values lower than the T_g of the pure polymers. These results would indicate the formation of partially miscible mixtures between both polymers. The thermal stability of the mixtures obtained by TGA was slightly higher than that of the polymers alone. SEM revealed a morphology consisting of dense droplets and particles for PMMA, with a multimodal size distribution between 5 and 50 μm, embedded in a highly porous structure with interconnected multichannels, associated with PVA. These results were decisive in corroborating the formation of partially miscible mixtures prepared in solution from PMMA and PVA.

Keywords: polyblends, compatibility, morphology, polymethylmethacrylate, polyvinyl alcohol

ESTUDIO MORFOLÓGICO Y COMPATIBILIDAD DE MEZCLAS DE PMMA CON PVA PREPARADAS EN SOLUCIÓN

RESUMEN

En este trabajo se prepararon mezclas de polimetilmetacrilato (PMMA) con polivinilalcohol (PVA) por disolución, paraestudiar su miscibilidad y posibles aplicaciones futuras en el desarrollo de cementos óseos. Se prepararon formulaciones en proporciones de 70/30 y 50/50 (PMMA/PVA). La compatibilidad fue estudiada por Infrarrojo con Transformada de Fourier (FTIR) y Calorimetría Diferencial de Barrido (DSC). Para evaluar la estabilidad térmica de los materiales se empleó Análisis Termogravimétrico (TGA). La morfología de todos los materiales fue expuesta usando Microscopía Electrónica de Barrido (MEB). Por infrarrojo se detectaron desplazamientos significativos en las absorciones de los grupos carbonilo del PMMA e hidroxilo del PVA, lo que estaría asociado con la formación de puentes de hidrógeno intermoleculares del tipo PVA–O–H–O=C–PMMA. El comportamiento térmico evidenciado por DSC para las polimezclas mostró una correlación directa con la composición de las mismas, observándose dos valores de T_g bien definidos desplazados hacia valores menores que la T_g de los polímeros puros. Estos resultados estarían indicando la formación de mezclas parcialmente miscibles entre ambos polímeros. La estabilidad térmica de las mezclas, obtenida por TGA fue ligeramente superior a la de los polímeros solos. Por MEB se reveló para las mezclas, una morfología consistente en gotas y partículas densas para el PMMA, con una distribución multimodal de tamaños entre 5 y 50 μm, embebidas en una estructura altamente porosa con multicanales interconectados, asociada al PVA. Estos resultados fueron determinantes para corroborar la formación de mezclas parcialmente miscibles preparadas en solución, a partir de PMMA y PVA.

Palabras claves: polimezclas, compatibilidad, morfología, polimetilmetacrilato, polivinilalcohol

INTRODUCTION

Polymers are versatile materials with innumerable food applications [1], packaging [2], construction [3], electricity and electronics [4,5],in the aerospace industry [6], agriculture [7], biomedicine[8, 9, 10, 11], among many others [12, 13, 14].Because each polymer can have very specific applications, it is sometimes necessary to make polymer blends in order to achieve synergy in the properties of interest.They can combine superior physical, mechanical, thermal and morphological properties [15, 16, 17, 18], when compared with the starting polymers. On the other hand, its application in the production of articles and devices reduces manufacturing costs, compared to the use of pure polymers. The processes governing polymer-polymer miscibility are complex, but even so, polymer mixtures have been successfully prepared[19, 20, 21, 22]. In particular, the study of mixtures based on polymethylmethacrylate (PMMA) and polyvinyl alcohol (PVA) has been reported in the literature [23, 24], because these materials have interesting physical and chemical characteristics for use as biomaterials [25, 26].

When the method of preparation of these polyblends is dissolution, parameters such as the degree of crystallinity, stereoregularity and molecular weight of the polymers play a determining role, since these properties condition the intermolecular interactions that hold the macromolecules together and that the solvent must overcome for dissolution to occur. Thermodynamics requires the free energy of mixing to be zero or negative for the dissolution process to occur spontaneously. The free energy change for the dissolution process is given by the relationship shown in equation 1:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad \text{(equation 1)}$$

legend:

ΔG_{mix}: Variation of free energy of mixing

ΔH_{mix}: Mixing enthalpy variation

ΔS_{mix}: Entropy change in the mixing process

T: Absolute temperature

On the other hand, the heat of mixing proposed by Hildebrand and Scott[27], is expressed according to equation (2), since dissolution is a complex process governed by thermodynamics and therefore it must be fulfilled that between polymers and solvents the following is satisfied:

$$\Delta H_{mix} = V_{mix}(\delta_1 - \delta_2)\Phi_1\Phi_2 \quad \text{(equation 2)}$$

legend:

δ: Hildebrand solubility parameter

Φ: Volumetric fractions of the polymer and solvent

V_{mix}:Total volume of the mixture

The theory predicts that substances with similar “δ” will be miscible with each other and polymers will dissolve in solvents whose solubility parameters do not differ greatly from their own.Equation (3) expresses in a little more detail the great significance of the term "solubility parameter", because it clearly states how the structure of the polymer and the functional groups that make it up dictate the interactions tending to favour polymer-polymer compatibility and polymer-solvent miscibility.

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad \text{(equation 3)}$$

legend:

δ_d: Contribution of dispersion forces

δ_p: Contribution of the polar forces

δ_h: Contribution of hydrogen bonding forces

The solubility parameters of various polymers are reported in the literature[28], This is helpful in assessing which solvents will be most suitable for dissolving a particular macromolecule.

Another factor to consider when preparing polyblends is related to the stability of the mixture and indicates that its initial properties should be favourable and not change over time, under the expected conditions of use. A polymer blend is considered to be "compatible" if no phase segregation is observed. Electron microscopy is a powerful characterization technique that allows to evaluate how the domains of the different polymers that make up the material are distributed, as well as to observe the characteristic morphology developed by each polymer in the blend.

Due to of the unquestionable potential of polyblends, as well as the versatility of obtaining them by physical methods, in the present study the preparation in solution of mixtures of PMMA with PVA was carried out, with the aim of verifying their compatibility and using them in the future to elaborate advanced materials with applicability in the field of biomaterials, specifically as a solid phase in bone cements formulations.

EXPERIMENTAL

Materials

Commercial polyvinyl alcohol(molecular weight: 78.500 g/mol, ρ: 1.91 g/cm^3, Grade of hydrolysis: 90%)and polymethylmetacrylate MD-2002 (molecular weight: 164.000 g/mol, ρ: 1,23 g/cm^3), were used as starting polymers. The solvents used were: water, ethanol and 2-propanone.

Procedure

Using Bagley diagrams [29], the appropriate solvents were determined for each polymer: 2-propanone for PMMA and a 50-50 ethanol/water mixture for PVA. Mixtures were prepared in two different ratios PMMA/PVA, as shown in table 1.The masses of the polymers of about 0.1 grams were perfectly measured, added in 20 mL of solvent (2-propanone for PMMA dissolution and a 50:50 ethanol/water mixture for PVA), and immediately subjected to a continuous heating process for 2 hours under magnetic stirring, until total dissolution of the polymer was observed. Subsequently, the solutions obtained for polymethylmethacrylate and polyvinyl alcohol were hot mixed and subjected to a new heating process under stirring, until homogeneity and total clarity were observed in the solutions. Finally, the polyblends obtained were precipitated by solvent change effect, centrifuged, washed continuously with cold methanol and dried in an oven for 48 hours at 60°C.

Table I. Prepared compositions for PMMA/PVA mixtures

Mixture	PMMA ratio (%)	PVAratio (%)
1	70	30
2	50	50

Characterization

For the characterization of the prepared materials, infrared spectroscopy (FTIR) studies were carried out with a Spectrum 100 Perkin Elmer spectrometer, recording the data in transmittance mode, with scans between 4000 and 450 cm^{-1}; in order to verify the establishment of intermolecular binding interactions between both polymers, during the polyblend formation process. Scanning electron microscopy (SEM) analyses were also performed on the mixtures obtained, both to reveal the morphology acquired by the PVA and PMMA as the dissolution process unfolded, and to try to find evidence of compatibility in the mixture. For this purpose, the samples were immersed in liquid nitrogen for 5 minutes and the fracture was performed using a stainless steel blade. The exposed surfaces were coated with a gold layer using a Balzers BAE 300 ionic coater and observed under a variable pressure scanning electron microscope with a tungsten filament and EDS detector, operating at an accelerating voltage of 10 kV.

The thermal behavior of the materials was evaluated by DSC and TGA. For the DSC studies, a Mettler Toledo DSC 822e calorimeter was used, working in a nitrogen atmosphere, with 40 uL aluminum crucibles. To eliminate the thermal history of the different materials, a first heating was carried out between 25 and 400ºC at a rate of 5ºC/min, keeping the samples for 5 minutes under this condition. A second heating was then carried out at 10ºC/min for PVA and PMMA/PVA blends, and 20ºC/min for PMMA, in the same temperature range already described. The TGA analyses were obtained from a TA Instruments Thermogravimetric Analyzer, model SDT Q600, with a heating program from room temperature to 600ºC, at a rate of 10ºC/min.

RESULTS AND DISCUSSION

Infrared spectroscopy

Figures 1 and 2 show the FTIR spectra obtained for PMMA and PVA respectively.

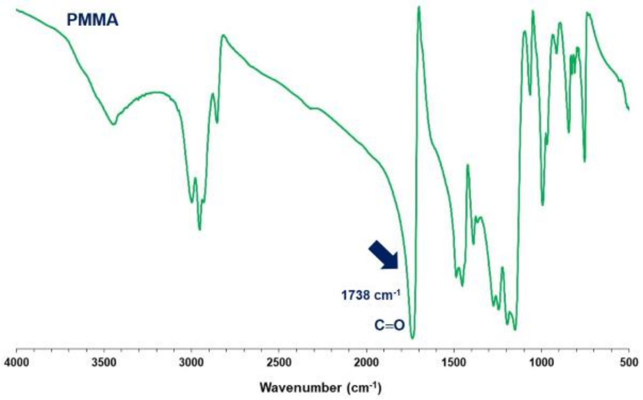

Figure. 1. FTIR spectrum of Polymethylmethacrylate

In both spectra, most of the absorption bands associated with the structures of both polymers can be seen, in agreement with what has been reported in the literature [30,31].For the spectrum of PMMA, signals are observed between 3000 and 2800 cm^{-1} corresponding to the stretching vibrations of the C–H bond of the methylene (CH_2) and methyl (CH_3) groups. The intense band at approximately 1738 cm^{-1} corresponds to the vibration of the (C=O) bond of the carbonyl group. Two bands associated with bending vibrations of the C–H of the CH_2 and CH_3 groups, symmetrical and asymmetrical respectively, can also be noted at 1300 and 1450 cm^{-1}.

Another band assigned to torsional vibrations of the methylene (CH_2) groups is observed at 1240 cm^{-1}, and followed by this at 1150 cm^{-1} the band corresponding to the extension vibrations of the (C–O) bond of the ester group appears. Other bands representing the stretching movements of the (C–C) bonds appear between 1000 and 800 cm^{-1}.

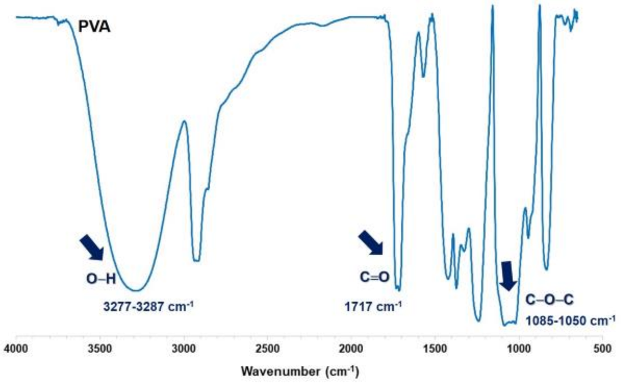

Figure. 2. FTIR spectrum of Polyvinylalcohol

In Figure 2, a broad band can be seen for PVA at wave numbers between 3287 and 3277 cm^{-1} associated with the stretching of the hydrogen-oxygen bond in the O–H groups responsible for the formation of intermolecular and intramolecular hydrogen bonds in the polymer chains[32]. Additionally, at 2924 cm^{-1} and 2854 cm^{-1} two peaks attributed to the stretching vibrations of the methylene and methyl groups are observed. Located at 1717 cm^{-1}, the band corresponding to the vibration of the carbonyl group associated with the remaining acetate groups can also be seen, since it is a partially hydrolyzed PVA. The presence of C–OH bonds of the alcohols is also confirmed, with absorption bands at 1415 cm^{-1}

(broad and intense) and at 1237 cm^{-1} (weak), as well as a bending vibration at 1330 cm^{-1} (intense) which corresponds again to the O–H bond. At wavenumbers around 1088-1050 cm^{-1}, the stretching vibration of the C–O–C bonds (of the carbonyl group) is observed.

Figures 3 and 4 show the FTIR spectra of two of the mixtures prepared by dissolution, specifically 50/50 PMMA/PVA (Figure 3) and 70/30 PMMA/PVA (Figure 4).

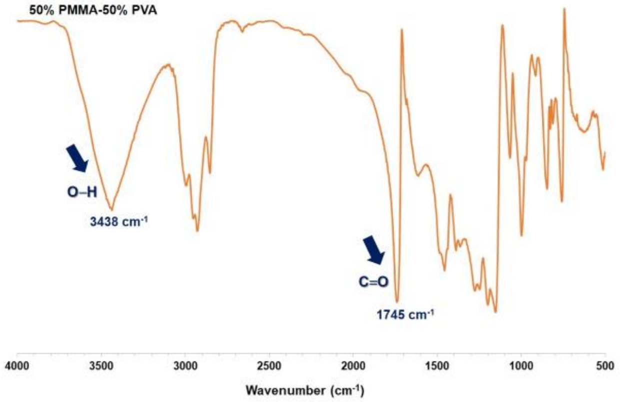

Figure. 3. FTIR spectrum of the 50/50 PMMA/PVA blend

The signals of interest for the polyblends that are the object of study of this work are those corresponding to the carbonyl functional group of PMMA (C=O), located at 1745 and 1736 cm^{-1} (figure 3 and figure 4 respectively) as well as the strong and broad absorption band that is observed at 3438 cm^{-1} (figure 3) and 3441 cm^{-1} (figure 4), assigned to the stretching of the O–H bond of the hydroxyl group. When comparing the absorptions of the carbonyl and hydroxyl groups observed in the pure polymers with those obtained in the blends, significant shifts of about 200 cm^{-1} (towards higher wavenumbers) can be seen for the O–H groups. Regarding the carbonyl group, when comparing the absorption bands in the blends with those of pure PMMA (1745, 1736 and 1738 cm^{-1} respectively), smaller shifts in the wavenumbers are observed. It is also observed in figures 3 and 4 for the blends how the broad band observed in the spectrum of pure PVA (figure 2), corresponding to the absorption of the O–H group, was transformed into a very sharp peak.

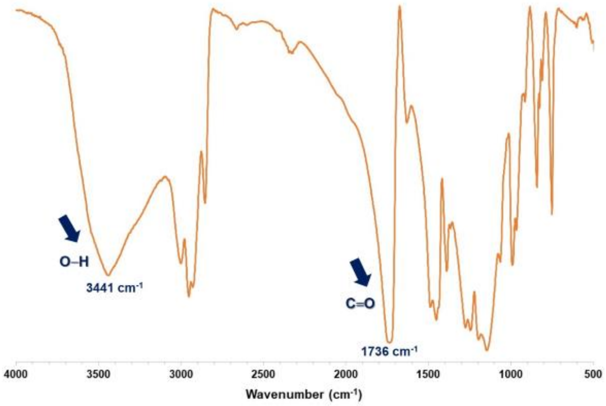

Figure. 4. FTIR spectrum of the 70/30 PMMA/PVA blend

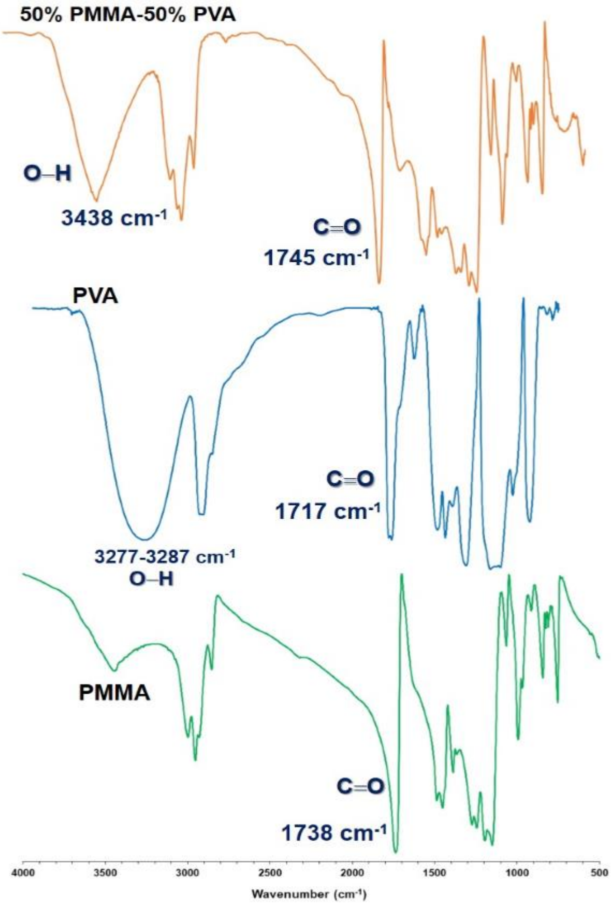

Figure. 5. Superposition of FTIR spectra of the 50/50 PMMA/PVA blend, PVA and PMMA

Figure 5, corresponding to the superposition of the spectra of the 50/50 PMMA/PVA mixture, PMMA and

PVA, graphically shows the substantial shifts of the hydroxyl and carbonyl groups that occurred in the physicochemical processes associated with the formation of the polyblends. All these facts would be showing clear indications of the formation of intermolecular hydrogen bonds between PMMA and PVA, of the type PVA–O–H–O=C–PMMA, which are schematically represented in figure 6. Similar results for mixtures of PMMA with PVA have also been reported by other authors [33, 34].

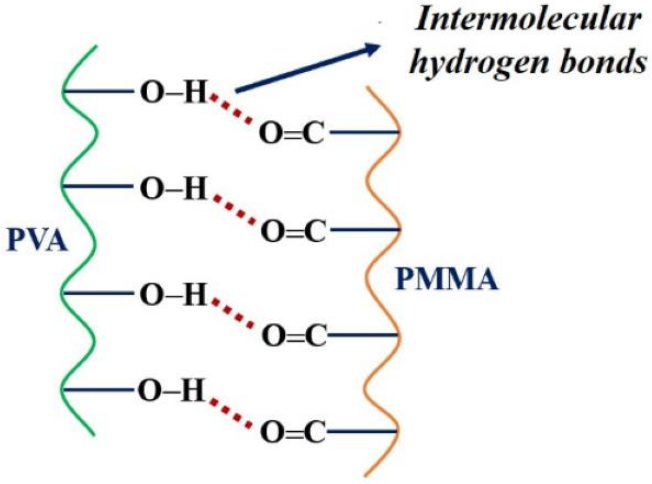

Figure. 6. Proposed hydrogen bond formation for PMMA/PVA blends

Differential Scanning Calorimetry and Thermogravimetric Analysis

A polymer blend is considered miscible when there is only a single value for the glass transition temperature (T_g), which is located between the T_g values of the two homopolymers and partially miscible when there are two T_g values that can vary with a change in the composition of the polyblend. On the other hand, if one of the components of the blend is semi-crystalline in nature, the depression of the melting temperature (T_m) can be used to estimate whether there is any degree of compatibility [35]. In this research, the DSC technique was used to determine the thermal behavior of the prepared polyblends and to constrain some important properties such as glass transition (T_g), melting (T_m) and decomposition (T_d) temperatures. Figure 7 corresponds to the thermogram obtained by DSC, for the 50/50 PMMA/PVA mixture. There, the thermal transitions corresponding to the glass transition process of PVA at 79ºC and that of PMMA at 111ºC can be observed. These values are significantly lower than those shown by PMMA (T_g: 118ºC) and PVA (T_g: 88ºC).

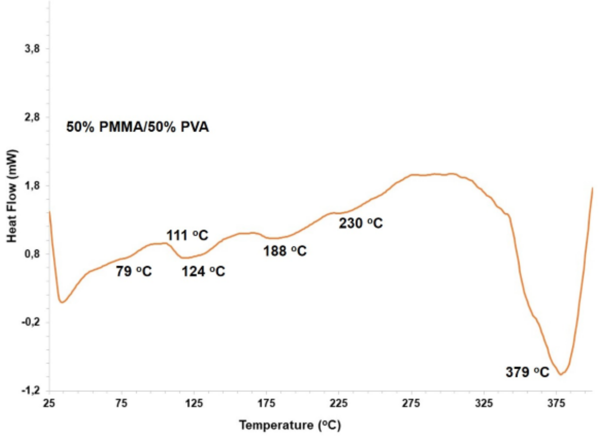

Figure. 7. DSC thermogram of the 50:50 PMMA/PVA mixture.

Also observed in Figure 7 are four other thermal transitions that are associated with the loss of water at 124ºC, the melting of PVA at 188ºC, the elimination of water as a consequence of the onset of the cleavage of the C–OH bonds at 230ºC and the complete pyrolysis of the mixture at 379ºC[36].

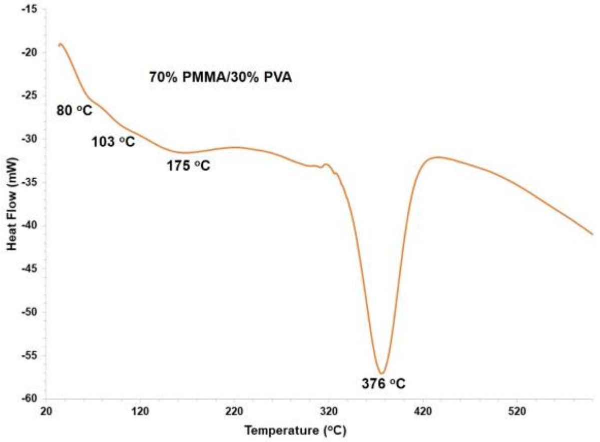

Figure. 8. DSC thermogram of the 70:30 PMMA/PVA mixture.

The 70/30 PMMA/PVA blend, whose DSC thermogram is shown in Figure 8, showed a thermal behavior slightly similar to that of the 50/50 blend, previously described. In this case, the glass transition temperature observed for PVA in the blend was 80 ºC (very similar to that obtained in the 50/50 blend), the T_g of the PMMA chain segments was 103 ºC (lower than for the 50/50 blend), at 175 ºC it could be associated with PVA melting and at 376 ºC total decomposition of the blend occurred. Similar results have also been previously reported by other authors [37]. As a summary, Table 2 shows the values corresponding to the main thermal transitions obtained by DSC for PMMA, PVA and the 50/50 and 70/30 PMMA/PVA blends.

Table II. Thermal properties of PMMA, PVA and the polyblends

Material	T_g (ºC)		T_m (ºC)	T_d (ºC)
PMMA	118		-	387
PVA	88		179	285
PMMA/PVA 50/50	PVA	PMMA	188	379
	79	111		
PMMA/PVA 70/30	PVA	PMMA	175	376
	80	103		

According to what has been reported in the literature, and in agreement with the results obtained by infrared and DSC, for the mixture compositions prepared in this research work, the formation of partially miscible mixtures between both polymers would be favored[38].

In order to evaluate the thermal stability of the polyblends studied in this research, the Thermogravimetric Analysis technique was used. The thermograms corresponding to pure PMMA and PVA, as well as to the 50:50 and 70/30 PMMA/PVA mixtures, are shown in Figures 9, 10, 11 and 12 respectively. Figure 9 shows a single decomposition plateau that starts at 359ºC (with 100% mass loss) and is completed at 410ºC, corresponding to the depolymerization and pyrolysis of polymethyl methacrylate. In this sense, it has been reported that the thermolysis of PMMA would be initiated with the formation of small free radicals whose main source would be present impurities, rupture of H-H bonds and the cleavage of the C–C bonds of the vinyl groups in position β to the vinyl group, also by random cleavage. On the other hand, approximately in the range between (350-400) ºC, the homolytic cleavage of the methoxycarbonyl side group would begin[39].

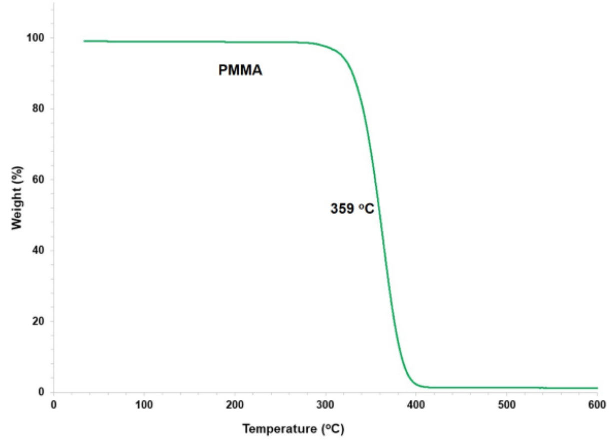

Figure. 9.TGA thermogram of pure PMMA

Regarding the thermal degradation of PVA, Figure 10 shows three distinct changes in the slope of the curve, which describe the pyrolysis of PVA.

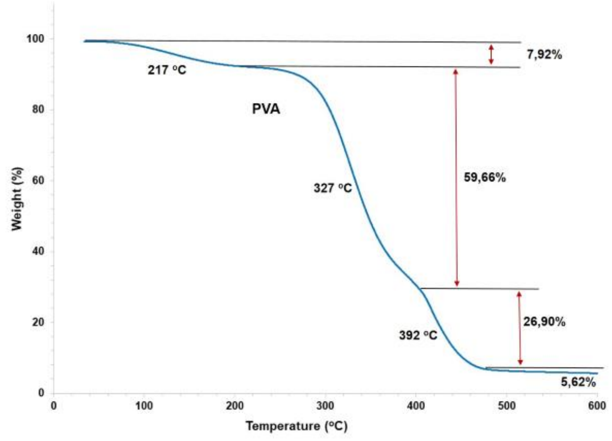

Figure. 10. TGA thermogram of pure PVA

In the initial region (130-217) ºC there is a mass loss of 7.92%, corresponding to the evaporation of the adsorbed water [40]. Next, the second and main region of mass loss can be seen (starting at 230 ºC, with a maximum degradation rate at about 327 ºC, with approximately 60% of the mass being lost at this stage. In this region, the structural degradation of PVA begins, which mainly involves the dehydration of hydroxyl groups and the formation of volatile organic compounds and conjugated and unsaturated polyenes [41].In the third mass loss region shown in Figure 10 and starting around 392 ºC, with a maximum degradation around 407 ºC, the polyene residues are transformed into alkenes and alkanes, as well as aromatics by intramolecular cyclization [42].

In relation to polyblends, Figures 11 and 12 respectively, show the degradation behavior of the 50/50 and 70/30 PMMA/PVA mixtures.

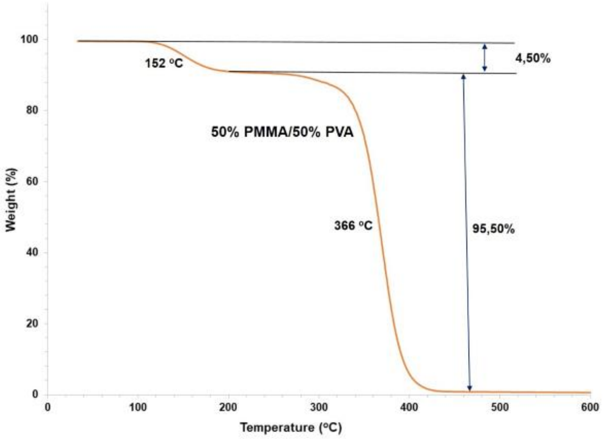

Figure. 11. TGA thermogram of 50/50 PMMA/PVA blend

Both graphs show a similar behaviour, with two well-defined plateaus associated with the mass losses of the mixtures, with 4.5% for the 50-50 mixture and 9.4% for the 70-30 mixture. For both blends, the first stage of decomposition is reached at a maximum temperature of 152 and 153 ºC. This first phase of the polyblends decomposition process would be associated with the formation and release of some small molecules and with the beginning of the cleavage of covalent bonds, to form monomers, larger chain fragments, macroradicals or a mixture of all these chemical species. In the second stage, the greatest loss of mass occurs in both mixtures, with 95.50% for the 50/50 composition and 90.60% for the 70/30 blend. The maximum temperature at which the process is completed is around 367ºC in both cases. In this second phase, pyrolysis of the polyblends occurs, thus completing the degradation process [43].

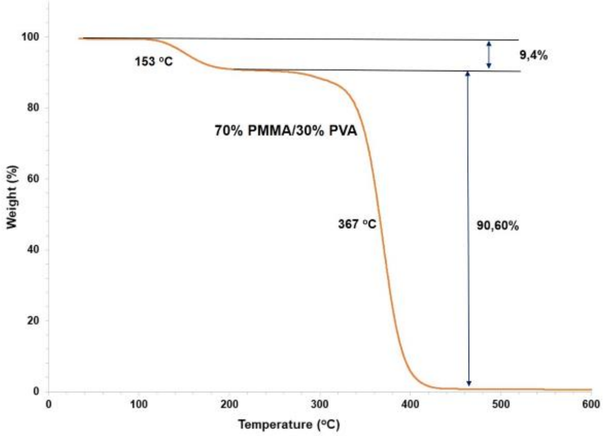

Figure. 12. TGA thermogram of 70/30 PMMA/PVA blend

In both cases it is shown that, regardless of the composition, the mixtures showed a thermal stability similar to that of the pure polymers and not superior as expected.

Scanning Electron Microscopy

In this research, Scanning Electron Microscopy studies were conclusive in order to determine on the compatibility of the PMMA/PVA mixtures. Figures 13 and 14 show the morphologies obtained before the dissolution process was carried out, both for PMMA (Figure 13) and PVA (Figure 14).In Figure 13 (a) and at a higher magnification in 13 (b), a drop-like conformation is observed [44,45] in which a continuous zone of spherical spaces can be seen, some of which have some depth, whose sizes range around 5μm, which are associated with the morphology of the spherical latex droplet type, typical of PMMA and which has been observed in other investigations [46].

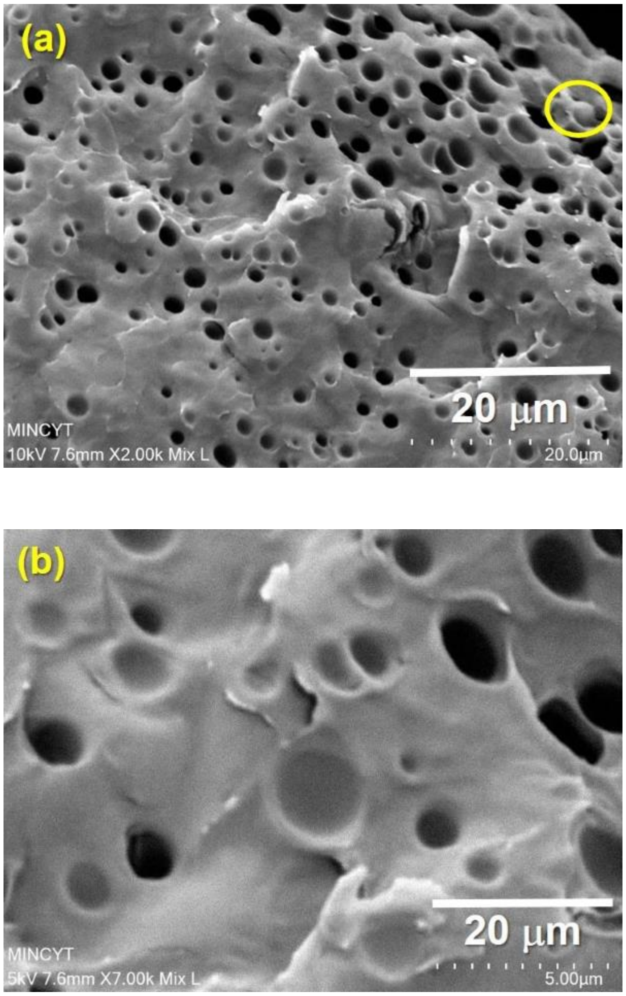

Figure. 13. SEM images of pure PMMA

Since the samples were prepared using the cryofracturing technique, the holes observed could be related to the detachment of the densest particles in the fracture phase that was carried out at liquid nitrogen temperature, during the sample preparation process. In figure (14-a) a morphology of large agglomerates with a smooth appearance in form of thin sheets can be distinguished for PVA. The magnification of the area highlighted in yellow in image 14 (a), allows to appreciate in figure 14 (b), a highly porous distribution with interconnected multichannels, which could be very appropriate for the development of scaffold structures, for the proliferation and growth of tissues, in biomedical applications [47].

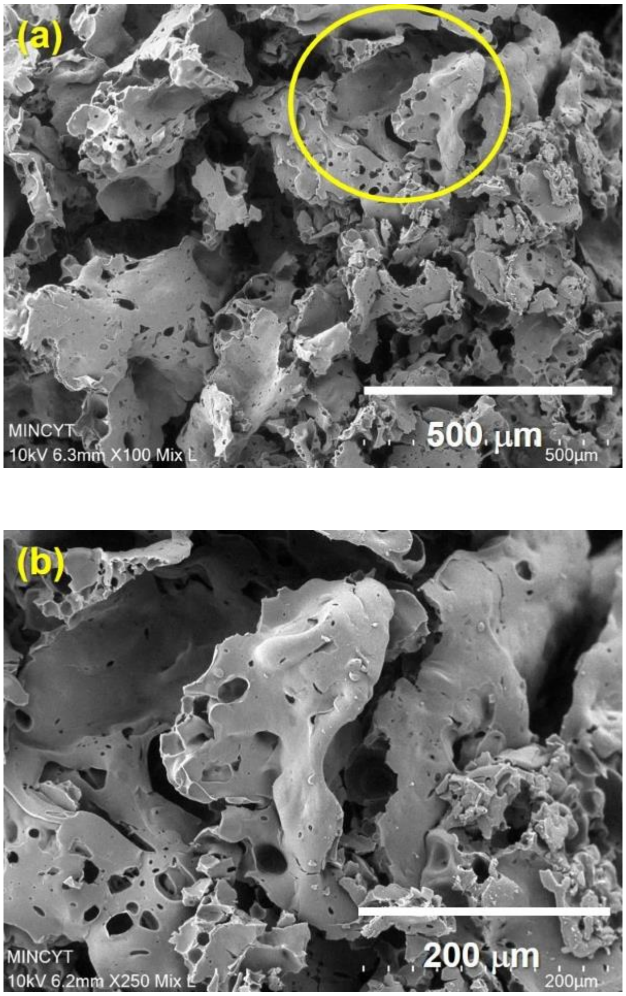

Figure. 14. SEM images of pure PVA

In relation to the mixtures of PMMA with PVA, two distinct and very well-defined areas of the material can be seen in figure 15 (a) for the 50:50 PMMA/PVA mixture, indicated by the yellow arrows. In the exposed areas, completely spherical particles are observed in a distribution that could be considered multimodal, whose sizes can range (1-40)μm, most of them forming agglomerates and embedded in the other area, whose structure is highly porous and smooth in appearance. This morphology of latex-like spheres has been observed for

PMMA synthesized under various experimental conditions, using high-frequency ultrasound as an energy source [48].

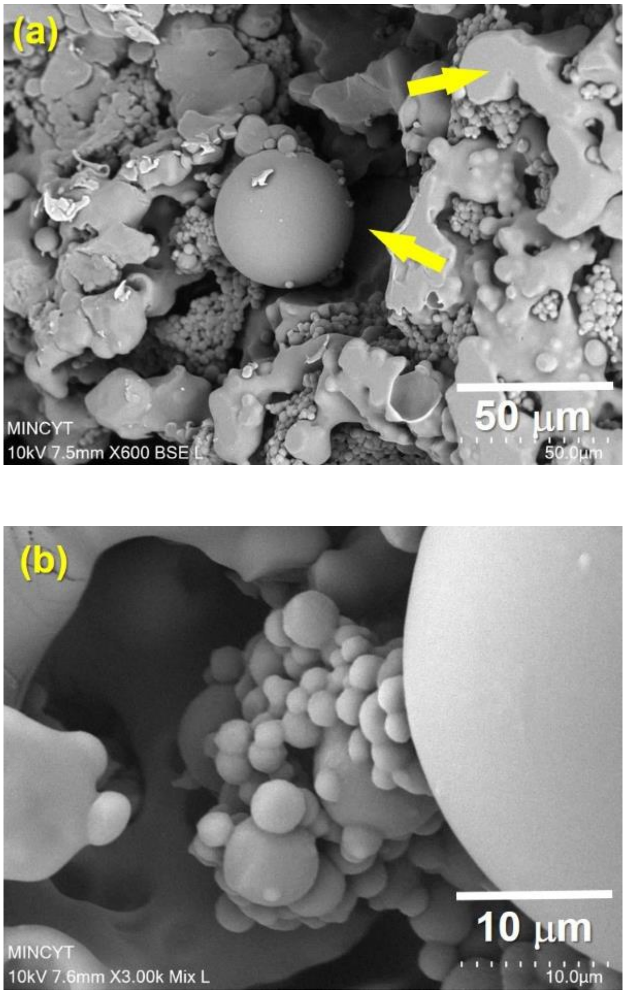

Figure. 15. SEM images of the 50/50 PMMA/PVA blend

Since the two zones shown in Figure 15 (a) are very different, this fact could be showing the coexistence of the particles associated with the spherical morphology of the PMMA latexes embedded in the porous structure exhibited by the PVA.A magnification of the central region of image 15 (a), allows to appreciate in more detail in figure 15 (b), multiple spherical particles associated with the morphology of polymethyl methacrylate of various sizes (5-50) µm, totally embedded in the porous matrix of polyvinyl alcohol. The results obtained by SEM for the 70/30 mixtures of PMMA with PVA can be seen in figures 16 (a) and 16 (b).

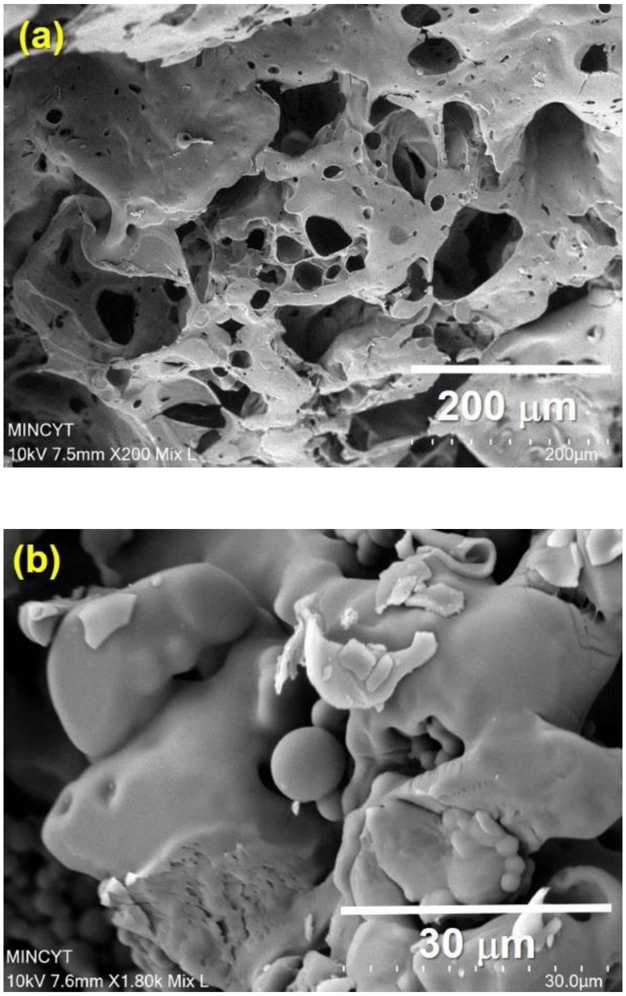

Figure. 16. SEM images of the 70/30 PMMA/PVA blend

In general, the images of the Figure 16 (a) and (b), show a morphological behavior similar to that obtained with the 50/50 PMMA/PVA mixture. In some areas of the sample analyzed, a laminar and very porous structure was observed (micrograph a), very similar to that previously seen in figure 14 for PVA. In other areas, spherical particles were again observed that can be associated with PMMA, embedded in a smooth-looking structure, much denser and more compact. In summary, by using SEM, the findings derived from the analyses carried out using FTIR and DSC techniques could be significantly corroborated, and the formation of partially miscible mixtures of PMMA with PVA would be certified, using dissolution as the preparation method.

CONCLUSIONS

The results of this research allowed us to conclude that it is feasible to obtain partially compatible mixtures of polymethyl methacrylate with polyvinyl alcohol through the dissolution process, under the conditions described, with infrared spectroscopy, differential scanning calorimetry and electron microscopy being determining analytical techniques in the characterization of these materials.

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