

Polyvinyl alcohol–polyethyleneglycol blends with tungstophosphoric acid addition: Synthesis and characterization

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Received 12 July 2007; accepted 30 September 2007

Abstract

New materials, based on a Keggin-structured compound (tungstophosphoric acid) immobilized in a polymeric matrix formed by a blend of polyvinyl alcohol and polyethyleneglycol with 400, 2000, and 6000 Da molecular weight, were prepared and characterized. Hydrogels with physical type links were produced, using the freezing–thawing technique, and are an alternative to the matrices traditionally obtained by developing chemical links by the use of cross-linkers. The supported tungstophosphoric acid retained its Keggin primary structure intact. There is evidence of a heteropolyacid–polymeric matrix interaction, which could occur between the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ Keggin anions and protonated hydroxyl groups $\text{C}-\text{OH}_2^+$ of the support. An effective immobilization was achieved, because there was no anion solubilization when the materials were put in contact with toluene at reflux. By differential scanning calorimetry and thermogravimetric analysis, it was observed that the materials containing tungstophosphoric acid can be used as catalysts in reactions carried out at temperatures lower than 160–200 °C, without degradation of the solids, the temperature being dependent on the tungstophosphoric acid content and, at a lesser extent, on the polyethyleneglycol molecular weight.

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Keywords: Polyvinyl alcohol; Polyethyleneglycol; Tungstophosphoric acid; Freezing–thawing

1. Introduction

In the recent years, the field of materials science has witnessed the advent of new compounds such as hydrogels and organic–inorganic hybrids. The driving force in the development of this field is the new and different properties that these materials possess, compared to traditional or conventional compounds. Particularly, hydrogels have created great expectations due to their diverse present applications as matrices for controlled-release medicine, biocompatible devices for medical uses, biomembranes, enzyme, cell and tissue encapsulation [1,2].

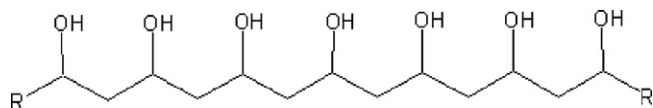
The polyvinyl alcohol (PVA) has the ability to produce hydrogels and it is widely utilized in biotechnology and in the pharmaceutical industry [3,4]. The chemical structure of PVA is shown in Scheme 1. The PVA is industrially manufactured by polymerization of vinyl acetate to polyvinyl acetate, followed by a hydrolysis to PVA with release of the acetate groups. This

conversion is not complete, and it is necessary to determine the degree of hydrolysis achieved, because the content of residual acetate groups has serious consequences for the chemical properties, the solubility, and the crystallization of the polymer.

A hydrogel can be defined as a cross-linked polymer, obtained from an aqueous solution, which presents a hydrophilic character, and at the same time can be swollen by immersion in water though remaining insoluble. The PVA can become cross-linked by diverse techniques. One of them is the use of agents that develop chemical links between the chains, such as glutaraldehyde, in the presence of sulfuric acid [5]. However, an undesirable fact of using this technique is the presence of reaction wastes, which leads to the need of subsequent extractions. An alternative method is to create covalent bonds in the polymeric network by gamma-ray irradiation [6], its main advantage over the above method being the absence of wastes in the resulting structure. A third method to prepare hydrogels is based on the generation of physical interactions between the different chains. These noncovalent interactions stabilize the hydrogel, and at the same time give sites with structural stiffness that can form crystalline zones from which the polymer matrix develops [7,8]. At molecular level, the PVA crystallites can be described as a

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Scheme 1. Polyvinyl alcohol chemical structure.

structure of double threads linked between each other by hydrogen bonding, and also by van der Waals interactions between threads. These nuclei are spread between the amorphous zones of the matrix [9].

On the other hand, environmental care is nowadays a priority, and requires new solutions for technological processes that are not eco-friendly. This is the case of homogeneous catalytic processes used for organic synthesis that employ compounds with Brønsted acidity, such as sulfuric, polyphosphoric or hydrofluoric acids, which generate a large amount of toxic and corrosive wastes, and need a high amount of energy for their subsequent reutilization or final conditioning. So, the development of new solid materials and their use in heterogeneous catalysis open a range of perspectives associated with a lower generation of wastes, thus leading to a higher compatibility with the environment.

For these reasons, no effort has been spared in the search of solid catalysts with acid characteristics, such as zeolites, Nafion-H, and Keggin heteropolyacids (HPA) [10,11]. The Keggin HPA are typically represented by the $H_{8-n}[XM_{12}O_{40}]$ formula, where X is the heteroatom, n is the X valence, and M is the polyatom. The bulk HPA presents a strong acid character [12] but have a low surface area (typically $1\text{--}10\text{ m}^2\text{ g}^{-1}$), and a low porosity (lower than $0.1\text{ cm}^3\text{ g}^{-1}$). These poor textural characteristics, together with a high solubility in polar solvents, lead to the search of supports that can adequately immobilize the HPA.

The catalytic activity of the immobilized HPA strongly depends on the support properties, the catalyst concentration, and the pretreatment conditions to which the material is subjected. Besides, for practical purposes, a necessary condition is that the support can firmly retain the catalyst while it is in the reaction medium.

The use of tungstophosphoric acid (TPA) supported on different materials as alternative catalyst in liquid-phase reactions has been reported [13]. In a previous work [11], we studied the behavior of HPA supported on different carriers in a liquid-phase esterification reaction. Particularly, promissory results were obtained with a sample prepared by equilibrium impregnation of TPA on PVA–polyethyleneglycol (PEG) beads. So, in the present work, the immobilization of TPA in similar polymeric matrices obtained by the freezing–thawing method [14] is studied. Unlike the previous study, samples were synthesized now by addition of TPA to PVA–PEG blends, before its freezing, the aim being to observe the characteristics of the materials prepared by a new route. In addition, the effect of the PEG molecular weight used to prepare the blend is studied. To the best of our knowledge, these systems were neither obtained nor characterized before. The characterizations carried out on the synthesized solids are presented. The results are discussed taking into account the need of determining the optimal preparative conditions, before using the new materials as acidic catalysts in liquid-phase reactions.

2. Experimental

2.1. Sample preparation

Small spheres of polymer (approximately 2 mm in diameter) were prepared, using the freezing–thawing method. Polyvinyl alcohol (Mallinckrodt) with a 98% hydrolysis degree, and a 35,000 Da molecular weight was used to prepare spheres with adequate mechanical stability. Polyethyleneglycol with 400, 2000 and 6000 Da molecular weight (noted as L (low), M (medium), and H (high)) was used to obtain the polymeric blends.

The solutions were prepared by dissolving 2 g of PVA and 2 g of PEG in 18 g of distilled water, at a temperature of 90°C , and under continuous stirring up to total dissolution of both compounds. Then tungstophosphoric acid (Fluka p.a) was added, keeping the stirring, until a homogeneous mixture was obtained. The PVA:PEG weight ratio was fixed at 1:1, and the TPA concentration at 0, 20, and 40% (w/w) in the final matrix.

Afterwards, the warm solution was dropped over liquid nitrogen, which was utilized as fast freezing medium. A Dewar flask guarantees that the subsequent thawing is performed at a slow rate, after nitrogen has vaporized. The samples thus obtained were dried at room temperature for 24 h, and then were thermally treated at 70°C for 24 h. The materials will be named PXWYY, where PX indicates the PEG used as PL, PM and PH, and WYY indicates the TPA concentration in the sample as W00, W20 and W40.

2.2. Physicochemical characterization

2.2.1. Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectra were obtained with IFS 66 Bruker FT-IR equipment, and pellets of the sample in KBr were used. The measurements were performed in the range between 400 and 1500 cm^{-1} .

2.2.2. X-ray diffraction (XRD)

To obtain the X-ray diffraction patterns, samples were frozen in liquid nitrogen and mechanically powdered. Philips PW-1714 equipment with built-in recorder was employed. The conditions used were Cu $K\alpha$ radiation ($\lambda = 1.5417\text{ \AA}$), Ni filter, 20 mA and 40 kV in the high tension source, scanning angle between 5° and $60^\circ 2\theta$, and scanning rate 2° min^{-1} .

2.2.3. Scanning electron microscopy (SEM)

Samples for scanning electron microscopy were frozen in liquid nitrogen, fractured and then coated with Au under vacuum. The micrographs were obtained employing a Philips 505 scanning electron microscope, at accelerating voltage of 25 kV. The TPA radial distribution in the spheres was measured with an energy dispersive X-ray analysis system (EDAX), attached to the microscope, with an ultra-thin window detector.

2.2.4. Sample leaching

The spheres containing TPA were twice washed in toluene at reflux for 8 h, in order to leach the acid that is not firmly attached to the matrix. The tungsten content was determined in the washing liquids with an IL 457 spectrophotometer of simple channel and double beam, equipped with a monochathode lamp, using a wavelength of 254.9 nm, and acetylene–nitrous oxide flame in volumetric ratio 14:11.

2.2.5. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)

The measurements were carried out with Shimadzu DT 50 equipment. The analysis was performed under nitrogen atmosphere, using 10 mg of sample, and a heating rate of $10^\circ\text{C min}^{-1}$. Aluminum cells were utilized, and the temperature range was between 30 and $500\text{--}550^\circ\text{C}$.

3. Results and discussion

The tungstophosphoric acid structure consists of a central tetrahedral PO_4 group surrounded by four W_3O_{13} groups, com-

posed of three edge-sharing WO_6 octahedra, that are linked between each other by corner-sharing oxygen atoms. Four different oxygen atoms can be distinguished, indicated by a–d subscripts. There are four $\text{P-O}_a\text{-W}$, where the oxygen atom links the central phosphorus with tungsten atoms of the structure, twelve $\text{W-O}_b\text{-W}$ that are linking corners of different W_3O_{13} groups, twelve $\text{W-O}_c\text{-W}$ that link the octahedra in each edge-sharing W_3O_{13} group, and twelve W=O_d named terminal oxygen.

The main characteristic FT-IR bands of bulk TPA are placed at 1080, 982, 888, and 793 cm^{-1} (Fig. 1), and are attributed to the stretching of the P-O_a , W-O_d , $\text{W-O}_b\text{-W}$, and $\text{W-O}_c\text{-W}$ bonds, respectively [15]. The FT-IR spectra of the samples prepared by immobilizing TPA in a blend of PVA, and PEG of 400 Da molecular weight (PLW20, PLW40) are also shown in Fig. 1. These samples presented the characteristic bands of bulk TPA, overlapped to the support bands (PLW00 spectrum). However, the band placed at 982 cm^{-1} showed a splitting, which evidences the existence of an interaction between the terminal oxygen of the Keggin compound and the polymeric matrix. A similar splitting was reported for the partially substituted cesium salts of TPA [16,17]. For PVA- WO_3 hybrids, a strong interaction between PVA chains and WO_3 was proposed by Yano et al. [18]. Due to the nature of both the polymeric matrix and the tungstophosphoric acid, the interaction can occur between the Keggin $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anions and protonated hydroxyl groups of the support (C-OH_2^+).

Comparing the spectra of the PLW20 and PLW40 samples with that of the lacunary $[\text{PW}_{11}\text{O}_{39}]^{7-}$ phase (Fig. 1), whose characteristic bands are placed at 1100, 1046, 958, 904, 812, and 742 cm^{-1} , we can establish that this species is not present. The first two bands are assigned to the P-O_a stretching that, unlike for TPA, is splitted into two components, as a result of the symmetry decrease of the central PO_4 tetrahedron, because the lacunary phase is obtained from TPA by loss of one octa-

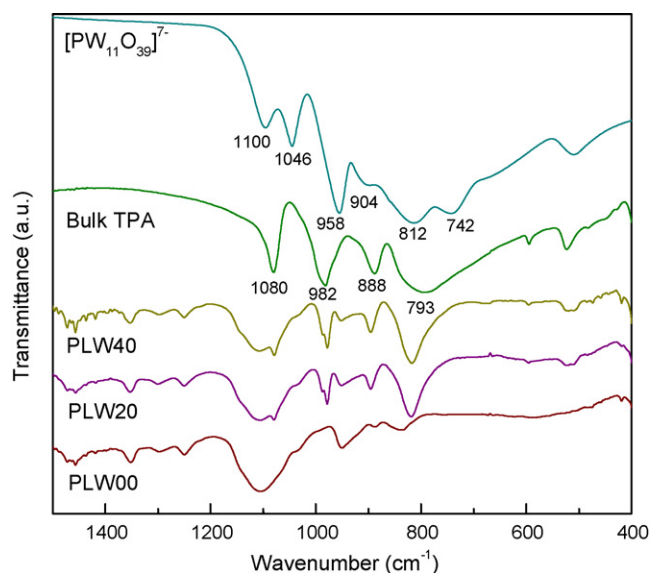


Fig. 1. FT-IR spectra of the samples prepared using PEG of 400 Da molecular weight, and different TPA content, bulk TPA, and $[\text{PW}_{11}\text{O}_{39}]^{7-}$.

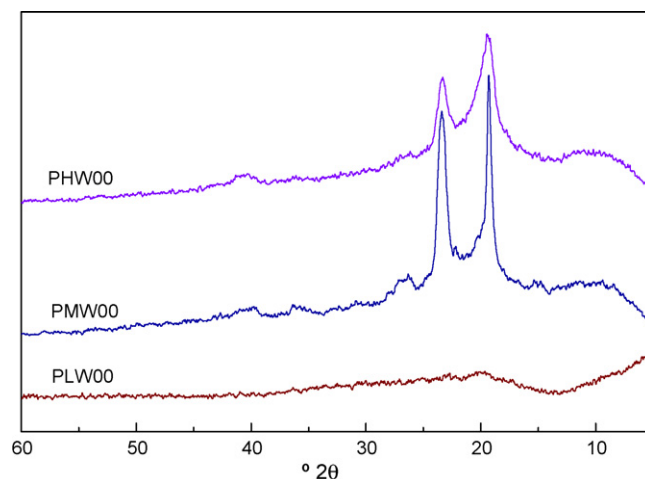


Fig. 2. XRD patterns of the matrices obtained with PVA, and PEG of different molecular weight.

hedron of the parent structure. Such splitting is not observed in our samples. It is evident that the existence of a TPA–matrix interaction did not affect the Keggin structure of the compound, which is maintained undegraded during sample preparation. A similar behavior was observed for the catalysts obtained using PEG of 2000 and 6000 Da molecular weight (medium and high, respectively).

The X-ray diffraction patterns of the PVA presented four wide peaks at 11°, 18°, 23°, and 42° 2θ , in agreement with a report in literature [19]. On the other hand, the solid PEG (PEG 400 is liquid) showed two main peaks at 19.3° and 23.4° 2θ . The patterns corresponding to PLW00, PMW00, and PHW00 matrices are shown in Fig. 2. It is observed that, with the exception of PLW00 matrix, a certain degree of crystallinity exists in the samples obtained without TPA addition. The presence of the characteristic PEG peaks, overlapped to those of PVA, could indicate that zones of the matrix exist where the cross-linking is not completely achieved for the samples prepared with the PEG of higher molecular weight, or with crystallites being spread between the amorphous zones of the matrix, as reported by Watase et al. [9].

The XRD pattern of bulk TPA dried at 70 °C ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$) showed several narrow peaks (Fig. 3), the pattern being characteristic of a body-centered cubic crystalline structure. The peaks of higher intensity are placed at 11°, 26°, and 34° 2θ .

The PLW40 sample showed a diffraction pattern where a broad band that extends from 15° to 40° 2θ indicates that the material has low crystallinity. The broad band is similar to that observed in the matrix pattern, thus TPA is present as a non-crystalline species or as crystallites small enough to give diffraction lines. The same behavior was observed for the PLW20 sample.

The same broad band is observed in the X-ray diffraction patterns of the matrices containing TPA, prepared with PEG of higher molecular weight (Fig. 4). However, peaks at low angles and small peaks overlapped to the broad band are observed for these samples, which could be assigned to TPA

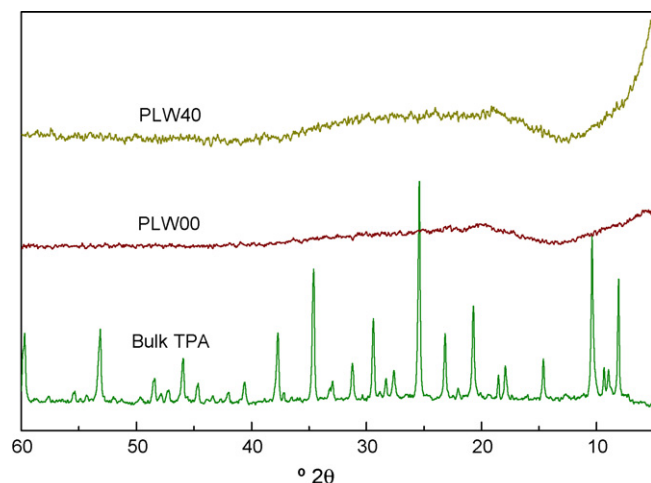


Fig. 3. XRD patterns of the PLW00 and PLW40 samples, and bulk TPA.

with a high hydration degree because it resembles the pattern of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 21\text{H}_2\text{O}$. Unlike samples obtained using PEG of 400 Da molecular weight (Fig. 3), the presence of TPA crystallites may be the result of a lower amount of OH groups in the matrices obtained with PEG of high molecular weight, available for the TPA anion-matrix interaction revealed by FT-IR.

Usually, the hydrogels formed by freezing–thawing method are strong and possess certain flexible character [20]. The micrographs obtained by SEM showed that the materials present a structure with channels (Fig. 5). This structure is adequate for the use of these matrices as support of active species employed in heterogeneously catalyzed reactions, because it allows the motion of reactants and products into and out of the matrix, without important diffusional restrictions. Appreciable changes in the structure, size or form of the channels were not observed when the PEG molecular weight was varied but, when TPA loading in the hydrogel is increased, a larger density of channels was observed.

The analysis of TPA distribution along the support radius was performed by EDAX, measured as tungsten content. A mainly

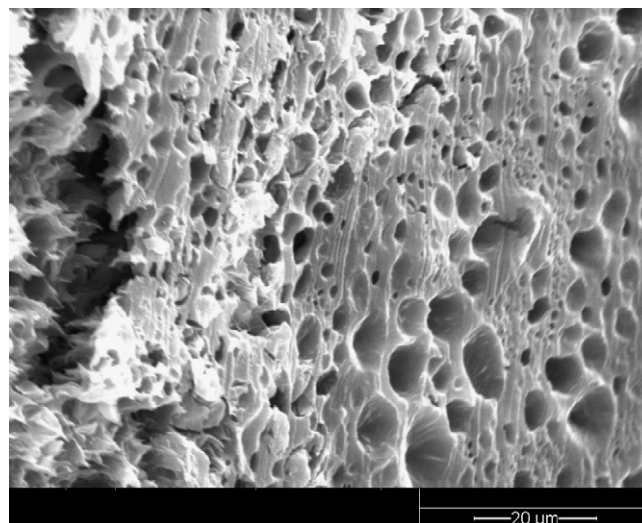


Fig. 5. SEM micrograph of the PLW00 sample, with a 1200× magnification.

homogeneous radial distribution is shown, with a slight increase in the surface.

On the other hand, the samples containing TPA were washed with toluene at reflux in order to study the ability of the matrix to retain the catalyst. Tungsten was not detected in the washing liquids by atomic absorption spectrometry, regardless of the different matrices employed as support. This result is indicative that TPA is firmly attached to the matrix.

The thermogravimetric analysis of the samples obtained with different TPA amounts in a matrix prepared with PEG of 400 Da molecular weight is presented in Fig. 6. Various steps are observed in the curves. A first process is taking place up to around 90 °C, and it is due to the loss of physisorbed water. In all the synthesized matrices, the weight loss was lower than 10% in this zone.

For the PLW00 sample, the second important weight loss began around 200 °C and is extended up to 400 °C, probably being the result of the loss by dehydration of OH groups from the

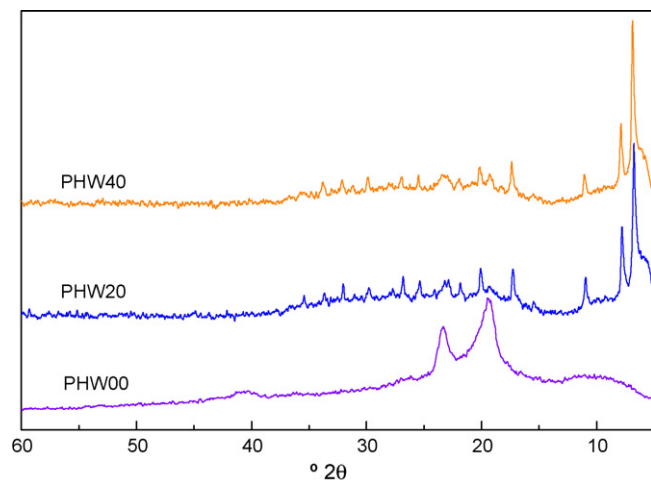


Fig. 4. XRD patterns of the samples obtained using PEG of 6000 Da molecular weight, and different TPA content.

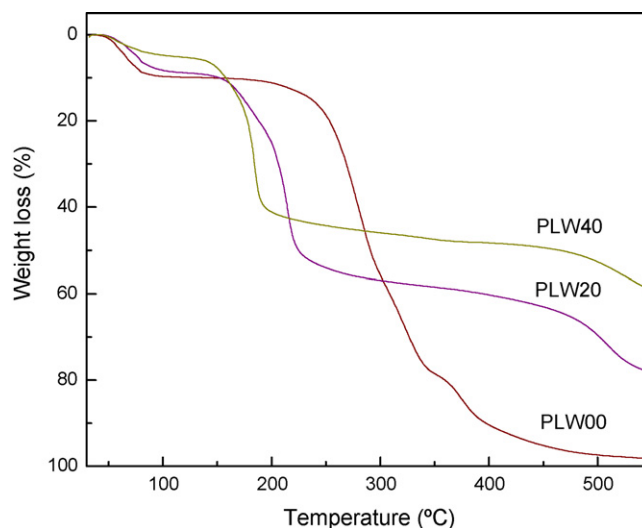


Fig. 6. TGA diagrams of the samples prepared using PEG of 400 Da molecular weight, and different TPA content.

Table 1

Degradation temperature of the samples obtained with different TPA concentration and PEG with different molecular weight

| TPA concentration (w/w%) | Degradation temperature | | |
|--------------------------|-------------------------|------------|----------|
| | Low PEG | Medium PEG | High PEG |
| 0 | 300 | 310 | 345 |
| 20 | 210 | 200 | 180 |
| 40 | 180 | 165 | 165 |

PVA and PEG chains. Overlapped to the dehydration, the degradation of the remaining solid begins in this temperature zone, with evolution of aldehydes, ketones, ethers, and water as final products [21]. For the matrices containing TPA, a shifting of this processes to lower temperatures is observed, and also the temperature range becomes narrower, when the TPA content increases. These results indicate that the matrix dehydration–degradation reactions are speeded up by the presence of inorganic compounds in the hybrid materials.

The temperature where the weight loss gradient in the TGA diagrams is maximum was defined as the degradation temperature of the material. For the matrices without TPA addition, it was observed that the degradation temperature is a function of the PEG molecular weight. It increases with the molecular weight, the temperature range being between 300 and 345 °C (Table 1), thus showing the effect of the PEG chain length in the matrix thermal stability.

In turn, the matrices containing TPA showed a lower degradation temperature range when the PEG molecular weight increases, but the thermal stability decreases with respect to the parent matrix as a result of the heteropolyacid addition (Table 1). This is in agreement with literature [22,23], where it is informed that the decomposition of different polymers is catalyzed by acid solids, and the premature start of the decomposition process of different polymers was correlated with the solid acidity. It is clear that a different effect is prevailing for these samples, becoming less important the PEG chain length. This fact can be explained taking into account that the existence of interactions between the Keggin compound and the matrix, through the –OH groups present in both PVA as well as PEG, decrease the physical interactions between both polymers, and the dehydration–degradation reactions are predominant.

The last step occurs above 400 °C, and can be related to degradation of organic compounds of high molecular weight that were not evolved before.

The DSC diagrams for the PVA–PEG matrices presented an endothermic peak at temperatures below 100 °C, assigned to the loss of physisorbed water, and four endothermic peaks of decomposition above 200 °C. For example in the PLW00, the first peak has its maximum at 84 °C, and the other peaks are placed at 208, 288, 358, and 422 °C (Fig. 7).

When TPA is added to the matrices, the DSC peaks placed below 350 °C, assigned to dehydration and degradation processes shifted to lower temperatures than those of the matrices without TPA, as can be observed in Fig. 7. This fact indicates that the association of the PVA and the PEG molecules in the structure was decreased due to the presence of TPA. The last

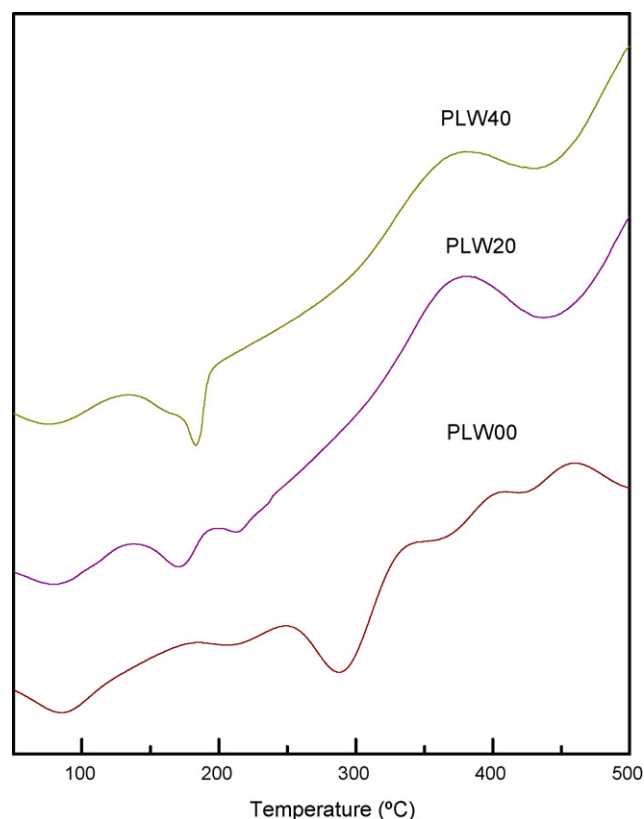


Fig. 7. DSC diagrams of the samples obtained using PEG of 400 Da molecular weight, and different TPA content.

degradation process is slightly shifted to higher temperatures. The results agree well with those obtained from TGA.

4. Conclusions

The ability of the polymeric matrix to anchor the tungstophosphoric acid without degradation of the heteropolyacid structure, due to interactions between them, was demonstrated through different characterizations. It was also shown that TPA is efficiently distributed in the matrix bulk. In addition, the existence of a channel network implies a qualitative increase in the textural properties of the materials obtained with respect to the bulk heteropolyacid.

A practical result of great importance is that TPA is firmly retained by the matrices, so the prepared materials can be used as catalysts in reactions in organic liquid phase, without solubilization of the active component. The thermal characterizations performed indicate that these materials would be used as catalysts in reactions carried out at temperatures lower than 160–200 °C, without degradation of the solids.

The feasibility of preparing new solid materials to be used in the field of heterogeneous catalysis may have great advantages, such as the simple and cheaper catalyst separation from the reaction media, among others. In order to search for eco-friendly technologies, the compounds with Keggin structure immobilized in the new polymeric blends are a good alternative for both the materials science and catalysis fields.

Acknowledgements

The authors thank G. Valle, M.E. Canafoglia, E. Ponzi, and N. Firpo for technical assistance, and ANPCyT for financial support.

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