

Spectroscopic and thermogravimetric studies of homogeneous materials from PU/PMMA/SiO₂

Estudios espectroscópicos y termogravimétricos de materiales homogéneos a partir de PU/PMMA/SiO₂

RAMÍREZ-SALAS, Virginia ^{1†*}, ORDOÑEZ-PACHECO, Luis Daniel¹, ALARCÓN-RUIZ, Erika¹ and MORENO-MARTÍNEZ, Beatriz Eugenia¹

¹Instituto Tecnológico de Ciudad Madero/Tecnológico Nacional de México, Departamento de Ingeniería Química y Bioquímica

²Instituto Tecnológico de Nuevo León/Tecnológico Nacional de México, Departamento de Ingeniería Industrial

ID 1st Author: Virginia, Ramírez-Salas / ORC ID: 0000-0002-0548-8653, CVU CONACYT ID: 173197

ID 1st Coauthor: Luis Daniel, Ordoñez-Pacheco / CVU CONACYT ID: 844011

ID 2nd Coauthor: Erika, Alarcon-Ruiz / CVU CONACYT ID: 163514

ID 3rd Coauthor: Beatriz Eugenia, Moreno-Martínez / CVU CONACYT ID: 162379

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Abstract

Polymers of organic-inorganic origin are incompatible by nature and a proposal to solve this behavior is the formation of Interpenetrated Polymeric Networks (IPN) using coupling agents. Coupling agents make it possible to create a crosslinking between the phases present that provides better mechanical, optical and thermal properties. These materials are known as Hybrid Networks. To obtain optically transparent materials, individual networks of Polyurethane (PU), Methyl Polyacrylate (PMMA) and Silica (SiO₂) were used. Binary and ternary networks were synthesized using bulk polymerization incorporating SiO₂ up to 10% by weight. In this research, coupling agents such as Trimethoxysilyl Propyl Methacrylate (MSMA) and Isocyanotopropyl Triethoxy Silane (IPTS) were introduced to the ternary networks in order to reduce the phase separation that occurs in these systems. Fourier Transform Infrared Spectroscopy (FTIR) studies demonstrated the presence of functional groups of binary and ternary networks. On the other hand, the thermogravimetric tests (TGA) carried out on hybrid IPN's with coupling agents, presented greater thermal stability and better optical properties, providing the new IPN's with the opportunity to have promising applications.

Resumen

Los polímeros de origen orgánico-inorgánico son incompatibles por naturaleza y una propuesta para solucionar este comportamiento es la formación de Redes Poliméricas Interpenetradas (RPI) utilizando agentes acoplantes. Los agentes acoplantes permiten crear entre las fases presentes un entrecruzamiento que proporciona mejores propiedades mecánicas, ópticas y térmicas. A estos materiales se les conoce como Redes Híbridas. Para obtener materiales ópticamente transparentes, se trabajaron con redes individuales de Poliuretano (PU), Polimetil metacrilato (PMMA) y Sílica (SiO₂). Se sintetizaron redes binarias y ternarias empleando la polimerización en masa incorporando SiO₂ hasta en un 10% en peso. En esta investigación, se introdujeron agentes acoplantes como el Trimetoxisilil Propil Metacrilato (MSMA) y el Isocianotopropil Trietoxi Silano (IPTS) a las redes ternarias con el propósito de reducir la separación de fases que ocurre en estos sistemas. Los estudios de Espectroscopía Infrarroja por Transformada de Fourier (FTIR), demostraron la presencia de los grupos funcionales de las redes binarias y ternarias. Por otro lado, los ensayos termogravimétricos (TGA) realizados a las RPI's híbridas con agentes acoplantes, presentaron mayor estabilidad térmica y mejores propiedades ópticas, proporcionando a las nuevas RPI's la oportunidad de tener aplicaciones prometedoras.

Interpenetrated Networks, IPN's

Redes Interpenetradas, RPI's

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* Correspondence to Author (virginia.itcm.tecnm@gmail.com)

† Researcher contributing as first author.

Introduction

The first polymeric networks were synthesized in the 20th century (Kausar, 2019). Interpenetrated Polymeric Networks are defined as Polymers that comprise two or more networks that are at least partially entangled on a molecular scale without covalent bonds with each other and cannot be separated unless the chemical bonds are broken (Kumar et al. 2018). Commonly, RPI's are prepared from a mixture of two monomers or polymers that are miscible. However, in this work, a network of inorganic origin has been incorporated, using coupling agents to obtain homogeneous materials that have better optical, mechanical and thermal properties; The formation of IPN's is a valuable strategy to reinforce and optimize the properties of a polymer network by combining a second network in it (Liang and Deng, 2017).

The first synthesis of mineral materials from polymerization reactions using molecular precursors of the metal alkoxide type was carried out by Ebelmen in 1845, obtaining with some gems such as sapphire, ruby and emerald (Sanchez et al, 1996). This method of manufacturing materials is known as the "sol-gel procedure", arousing strong interest for renewal both in the university community and in the industry.

The presence of organic composites makes it possible to modify the mechanical properties, produce films and fibers, obtain by simple molding various geometric structures for integrated optics, control porosity and adjust the hydrophilic / hydrophobic balance of the network. For their part, inorganic composites can play various roles, such as: contributing to increase the mechanical and thermal stress of the material, allowing the refractive index to be modulated, as well as adding electrochemical, magnetic and electrical properties (Babonneau et al., 1996). That is why the RPI's that are formed from organic / inorganic composites achieve excellent optical, thermal and mechanical properties.

The networks are classified according to the Interpenetration mode: if both polymeric systems are partially, semi or fully cross-linked.

The analysis of the properties of PU, PMMA and SiO₂ is of vital importance, since PU has excellent elasticity, resistance to abrasion and damping properties (Kausar 2019); on the other hand, the crosslinked network of PMMA is an amorphous polymer that has high transparency and high mechanical resistance; finally, the SiO₂ network, thus allowing the obtaining of a highly cross-linked inorganic network in an organic matrix without risk of decomposition or degradation.

In work carried out by Ghosh, (et. Al.) 2018 synthesized biodegradable and intelligent RPI's from PU, silicone and polystyrene, which exhibited good mechanical properties, biodegradability, impact resistance, scratch resistance as well as good thermal stability.

For its part, Bonilla, 2005, synthesized ternary hybrid materials, where the silica network obtained was synthesized from TEOS using the sol-gel method incorporating up to 37% by weight of TEOS, which upon polymerization formed a network of SiO₂ improving the thermal stability of materials above 700°C.

In this work, interesting results were obtained with respect to hybrid networks. The presence of an inorganic network can be considered as a protection for the organic network, because it raises the thermal decomposition temperature of the polymer. The thermal transition temperatures of the PU / SiO₂ and PMMA / SiO₂ hybrids are similar to that of the pure polymer. If a crosslinking agent (coupling agents) is added, the phase separation is lower and therefore its thermal stability is greater.

Methodology (Bonilla, 2005)

Section 1. Synthesis

The synthesis of the binary and ternary networks is presented below:

a) PU / PMMA network, the NCO, OH, MMA and TRIM monomers were mixed (with a 50/50 weight ratio) and 0.5% by weight of BPO was added for the formation of the PMMA network; DBTL was added for the formation of the PU network;

b) PU / SiO₂ network, in ethyl acetate the monomers NCO, OH and TEOS were dissolved (for 5, 10, 15% by weight of SiO₂ in the final sample) and the PU catalyst, finally added the aqueous HCl solution;

c) PMMA / SiO₂ network, at the beginning of the reaction the monomer MMA used as solvent for the rest of the components was added. TRIM and TEOS were homogenized (5, 10, 15% by weight calculated). The initiator of the PMMA network was incorporated by magnetic stirring and finally the aqueous HCl solution was added;

d) PU / PMMA / SiO₂ network without coupling agents. From previous studies, the highest quantity of TEOS incorporated in binary systems was obtained, with a 45/45/10 ratio by weight, the monomers (NCO, OH, MMA, TRIM and TEOS) were mixed by adding the network initiator of PMMA, the catalyst for the PU and the finally, the aqueous solution in the sol-gel processes of the TEOS were also incorporated;

e) PU / PMMA / SiO₂ network with coupling agents, the coupling agents are \square -Isocyanate propyl triethoxy silane (IPTS) and 3-(trimethoxy silyl) propyl methacrylate (TSMA) as grafting agents for PU networks and PMMA, respectively, which were added at a maximum 4% by weight, for ternary networks.

Section 2. Characterizations

The RPIs that were formed were characterized by the techniques of: Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA). Fourier transform infrared spectroscopy (FTIR). The FTIR assays were obtained from a Perkin Elmer Spectrum One equipment with a resolution of 2 cm⁻¹ and 32 scans on KBr chip. On the other hand, the thermogravimetric analysis (TGA) was carried out in a TA Instruments Model SDT 2960 Simultaneous DSC-TGA equipment, with 20 mg of sample in an aluminum tray with a temperature ramp from Tamb to 800° C, with a heating rate 5° C / min in nitrogen atmosphere

Results

Section 1

Table 1 shows the results of the binary RPIs of PU / SiO₂ at different concentrations of TEOS. Table 2 shows the results of the PMMA / SiO₂ networks. Table 3 shows the results of the RPI's of PU / PMMA / SiO₂ at different concentrations of TEOS with and without coupling agents.

% in weigh		Appearance of the sample
PU	TEOS	
95	5	Translucent, flexible
90	10	Translucent, soft-rubbery
85	15	Translucent, rubbery
80	20	Appearance of the sample

Table 1 RPI's of PU / SiO₂ at different concentrations of TEOS

Own Source

% in weigh		Appearance of the sample
PMMA	TEOS	
95	5	Translucent, rigid
90	10	Translucent, rigid
85	15	Opaque, semi-rigid
80	20	Opaque-White, fragile

Table 2 RPI's of PMMA / SiO₂ at different concentrations of TEOS

Own Source

% in weigh					
PU	PMMA	TEOS	IPTS	TSMA	Ap
45	45	10	-	-	* Tr/Sr
41	41	10	4	4	* Tr/Sr

Table 3 RPI's of PU / PMMA / SiO₂ at different concentrations of TEOS and coupling agents (IPTS, TSMA), Ap. Aspect, * Translucent, semi-rigid (Tr / Sr)

Own Source

Section 2

Infrared spectroscopy (FTIR)

The results obtained from the FTIR tests are described below: i) Figure 1 FTIR spectrum for PU / SiO₂ binary RPIs: a) 95/5, b) 90/10 and c) 85/15% in weight; ii) Figure 2 FTIR spectrum for the PMMA / SiO₂ network: a) 95/5, b) 90/10 and c) 85/15% by weight; iii) figure 3 FTIR spectrum for the PU / PMMA / SiO₂ system in a range of 4000–500 cm⁻¹ and ternary with and without coupling agents ternary with and without coupling agents. In Figure 1, the infrared spectrum of the PU system network with 5, 10 and 15% by weight of SiO₂ is observed.

The presence of representative groups of PU and SiO₂ in the three spectra is remarkable. The three compositions of TEOS to form the silica network indicate that the inorganic network was formed in the polyurethane network; the representative bands of the inorganic network (SiO₂) at 1103-1079, 789-751 and 585-507 cm⁻¹. The band of the urethane group at 1468 cm⁻¹ corresponds to the N-H bending. The carbonyl group attached to the monosubstituted amine (-CO-NH-) at 1526 cm⁻¹. The bending and stretching of the carbonyl group (C = O) is at 1742 cm⁻¹.

The peaks representing the C-H asymmetric stretching are observed in the range of 2987-2822 cm⁻¹, corroborating their appearance at 1320-1362 cm⁻¹. In figure 2, the characteristic bands of the PMMA network show the stretching of the methyl groups (-CH₃) at 2994 and methylenes (-CH₂) at 2942 cm⁻¹, corroborating their appearance at 1470 cm⁻¹ and 1738 cm⁻¹ the carbonyl group band (C = O) is observed, assigned to the ester group of the PMMA chain. The characteristic peaks for the Si-O-Si bonds are at 1214-1120, 852-748 cm⁻¹ and 516-490 cm⁻¹; OH groups are found in the 3300-3700 cm⁻¹ and 950-1008 cm⁻¹ region.

Apparently, the three spectra of the samples do not show great changes, however, in figure 2 c) a shoulder is detected at 1640-1547 cm⁻¹ that is not observed in figures 2 a) and b) and is attributed to silanol groups in the medium, produced by the nature of the polyol and by the higher concentration of TEOS that favors the formation of these.

It should be mentioned that these materials improved their appearance by introducing coupling agents. For the synthesis of these networks, the same conditions of the binary networks were taken obtaining the ternary system resulting in semi-rigid IPN's, with a better formation of the inorganic network, which was observed in the TGA analyzes in section 2 showing a residual weight of 10% in silica, this is attributed to the fact that the inorganic network and the coupling agents provide greater crosslinking to the system and consequently greater thermal stability.

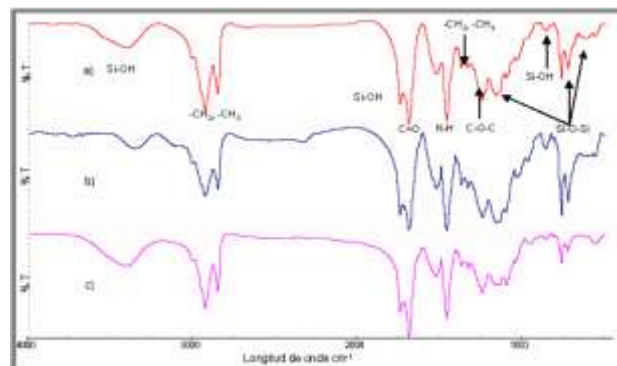


Figure 1 FTIR spectrum for the PU / SiO₂ network: a) 95/5, b) 90/10 and c) 85/15% by weight

Own Source

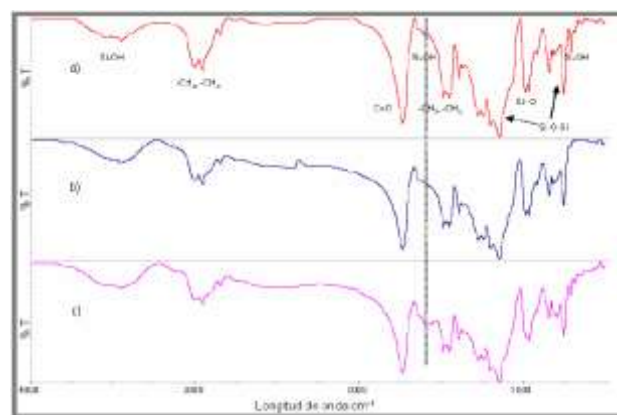


Figure 2 FTIR spectrum for PMMA / SiO₂ network: a) 95/5, b) 90/10 and c) 85/15% by weight

Finally, Figure 3 shows the infrared spectrum of the ternary network incorporating into the organic system an amount of TEOS of 10% of the total weight calculated for the network and 4% by weight of the coupling agents. The spectra shown represent the characteristic functional groups of the ternary network without agents and with coupling agents. In the region of 3200-3670 and 940-1002 cm⁻¹, of both spectra, are the bands attributed to the -OH groups, these originate from the OH's of the polyol and residual silanol.

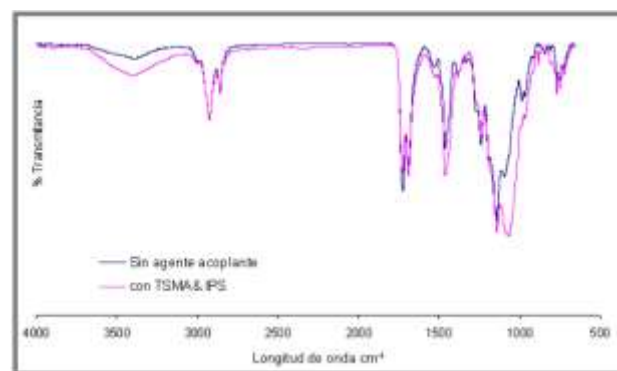


Figure 8 FTIR spectrum for PU / PMMA / SiO₂ system in TSMA and IPS

Thermogravimetric Analysis (TGA)

In thermogravimetry (TGA), for a cross-linked polymer, an increase in temperature causes the molecular motion to increase until the polymer molecules degrade. This process occurs in stages, when a substance is heated to different temperatures undergoes a series of transformations, which are attributed to changes in the mass of said substance.

The characterized samples correspond to the binary and ternary hybrid systems with and without coupling agents. Figure 4 represents the TGA of the PU / SiO₂ network with 95/5, 90/10, 85/15. Observing the characteristic behavior for the organic network considering that when reaching 500°C all the organic part has degraded and after this temperature the residual weight corresponds to a silica network.

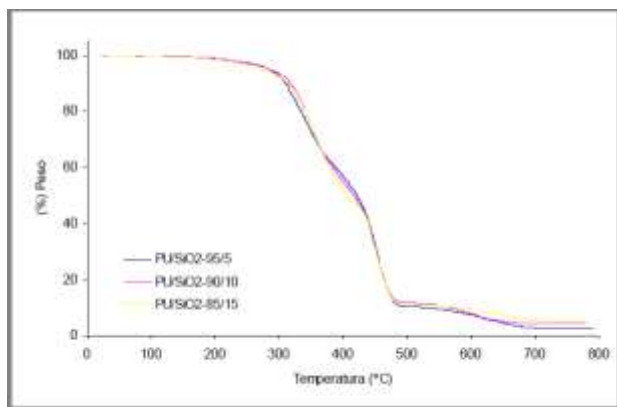


Figure 4 PU / SiO₂ binary network thermogram

Figure 5 shows the TGA thermogram of the PMMA / SiO₂ binary network, where the thermal stability of the sample is close to 800 °C. It can be seen that the curve that represents the IPN of PMMA / SiO₂ whose ratio is 90/10 presents a greater resistance to thermal decomposition, since all the organic part at a temperature close to 400 °C has decomposed; additionally, the optical properties of the sample were better compared to the samples whose PMMA / SiO₂ ratio is 95/5 and 85/15. With the above we can consider that above 500 °C is only the silica network.

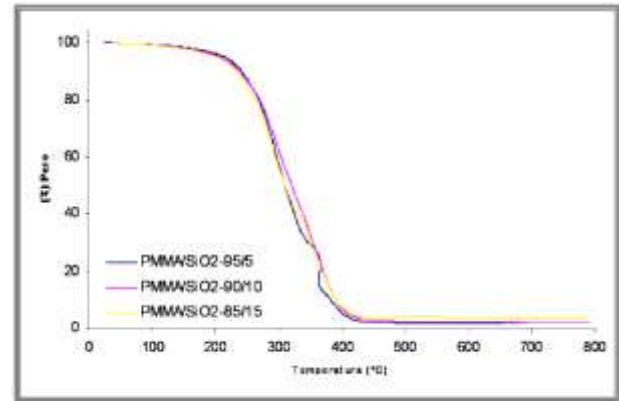


Figure 5 Thermogram of a PMMA / SiO₂ network

Figure 6 corresponds to a PU / PMMA / SiO₂ ternary thermogram, in this it is possible to appreciate the ternary network whose final concentration corresponds to 45/45/10 and 41/41 / 10-4% with IPTS and MSMA. It is observed that the loss in weight up to 200 °C is very small, this is attributed to the fact that the humidity in the material is very little, but from 245-378 °C there is a significant loss in weight; In this first stage, the soft segments of PU, CO₂ pyrolysis and PMMA can be decomposed in the two curves with and without agents. In a second stage, the ternary IPN that does not contain coupling agents presents a shoulder in a range of 378-464 °C that can be caused by the thermal decomposition of secondary organic products such as polyurea that it was possible to observe in the infrared spectra, the segments rigid PU, hydroxyl groups and complete decomposition of PMMA.

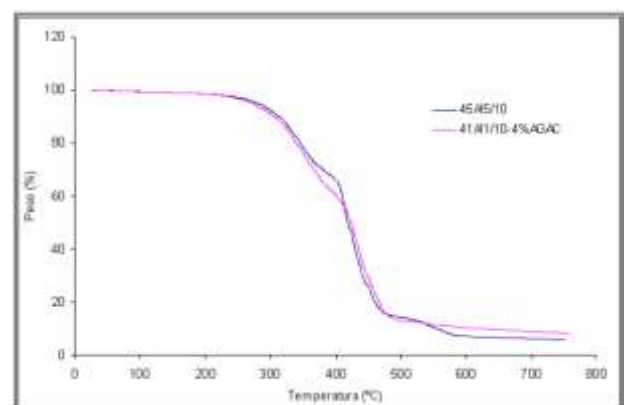


Figure 6 TGA of PU / PMMA / SiO₂ ternary networks

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Conclusions

In the FTIR studies, the representative groups of each system were observed, where the appearance of various bands attributed to silanol (Si-OH) indicate that a partial conversion of silica was obtained. The IPN synthesized without coupling agents presented its thermal stability very close to 800 °C with a residual weight of 7%, which is attributed solely to the SiO₂ network since it is considered that all the organic part decomposed around 500 °C .

However, the use of coupling agents increased said stability, manifesting a higher residual weight in the SiO₂ content of 10.58%, this is due to the fact that these agents contain within their chemical structure, Si-O groups that increase the active sites for generate the polymerization of the inorganic network in addition to TEOS, causing the network to obtain a higher residual weight of silica.

The tests carried out on the ternary IPNs revealed that by incorporating the three networks in a single system, they affect four important points: 1) formation of secondary products, 2) the thermal stability of the materials, 3) homogeneity of the systems and 4) mechanical properties.

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