

Evaluation of Mechanical and Thermal Properties of Polypropylene Modified with Nanostructured ZSM-5 Zeolite

R. Buitrago-Sierra^{1*}, J. Felipe Santa Marín^{1,2} and J. Geovanna Ordoñez¹

* robinsonbuitrago@itm.edu.co

Received: March 2018

Revised: July 2018

Accepted: January 2019

¹ Facultad de Ingenierías. Instituto Tecnológico Metropolitano, Medellín, Colombia.

² Tribology and Surfaces Group, National University of Colombia, Medellín, Colombia.

DOI: 10.22068/ijmse.16.2.12

Abstract: Polypropylene (PP) has been one of the most widely used polymers due to the versatility and cost benefits obtained with this material. In this work, composites of PP modified with nanostructured ZSM-5 (Zeolite Socony Mobil-5) zeolite were prepared and their thermal and mechanical properties were evaluated. Zeolites were synthesized by hydrothermal method and the crystallization time was modified to evaluate the effect of that parameter on zeolites properties. Scanning electron microscopy, thermal analyses, X-ray analysis, among others, were used to analyze the nanostructured particles. Composites were prepared by melt mixing in a torque rheometer and compression molding. After obtaining the composites, mechanical and thermal properties were evaluated. The results showed that some properties (surface area, and crystallinity) of zeolites depend on the crystallization time. Young's modulus and elongation at rupture of composites were modified when the zeolites were added to the polymer matrix. No significant modifications were found on thermal properties.

Keywords: Composites, Mechanical properties, Polypropylene, Thermal properties, Zeolites.

1. INTRODUCTION

The use of polypropylene (PP) has been increasing during the last years. The global production of PP in 2016 was about 56.4 MMT and for 2021 an increase up to 75 MMT is expected with an annual increase near to 5% [1]. Asia has the largest market and it is promoted by the automotive industry. As reported in 2009, the market size of polymer nanocomposites for industrial purposes is estimated to be 48 million pounds [2]. The markets for PP are dominated by flexible and rigid packaging (37%), followed by automotive, electric/electronic, and appliances (21%) [3].

Current efforts towards the achievement of improved properties in materials are related to composites. Composites are accepted as the future of materials. Polymeric materials are reinforced with natural or synthetic inorganic compounds to improve their physicochemical properties or just to decrease the cost of the raw material. Conventionally, reinforcements of polymer composites are done with particles or erfibers

[4], to improve mechanical properties (tensile strength, Young's modulus, etc), and resistance at high temperatures, electrical conductivity, resistance to gas permeability, biodegradability, flammability among others [5].

Polypropylene (PP) has been extensively used in packing, household items and especially in last decades in automotive industry given its versatility, low cost, recycling properties, and processability. However, the use of pure PP has been limited in the thermoplastic industry by its low modulus and impact resistance, especially at low temperature or high strain loads [6]. This issue has motivated the search for new PP composites with improved properties. On the other hand, zeolites are hydrated aluminosilicates formed by tetrahedrons of $[\text{SiO}_4]^{4-}$ $[\text{AlO}_4]^{5-}$ and these materials have multiple applications in soil remediation, agriculture, membranes, among others [7]–[9].

N. Bukit [10] studied the mechanical and thermal properties of polypropylene reinforced by calcined and uncalcined zeolite. The authors found that Young's modulus did not increase

when zeolites were added to polypropylene. However, tensile strength improved when zeolites were added to the polymer. Additionally, the authors stated that Young's modulus is linearly proportional with tensile strength. Nevertheless, the authors did not discuss the improvement mechanisms of mechanical properties.

Adloo et al. [11] report in a recent work, the improvement of electrical conductivity and flexural strength properties of PP bipolar plates by the use of PP composites and carbonaceous materials specifically graphite, graphene and carbon black, by modifying the properties of studied materials. Other PP composites using graphene structures have been widely used in the search of new applications or better performance of this kind of materials [12].

L. Zhang et al [13], studied the use of nanocomposites of polypropylene, showing the effectiveness of nano-SiO₂ to harden and strengthen the polymeric matrix. Similar results were reported in a recent work published by Watanabe and col [14] where polypropylene compounds were fabricated using silica nanospheres. The authors found that some mechanical properties were higher than those obtained with the raw PP studied polypropylene modified with silica nanoparticles. They identified several mechanisms of interaction of nanoparticles with composite [15]. On the other hand, since thermal properties are important to process polypropylene, the same authors studied melt temperature and other thermal properties. The authors found that all samples (with or without zeolites) melt at the same temperature and, the higher the amount of zeolite added, the higher the enthalpy of the sample.

In this work, composites of PP modified with nanostructured ZSM-5 zeolites were prepared and their thermal and mechanical properties were evaluated. The study was done to evaluate new materials with improved properties having in mind that zeolites are abundant and that polypropylene is a very common polymer in the industry. The synthesized and the obtained composites were studied by field emission scanning electron microscopy, X-ray diffraction, Nitrogen and CO₂ isotherms, thermo-gravimetric analysis, and mechanical tests.

2. METHODOLOGY

2.1. Synthesis of Zeolites

Zeolites were synthesized by the hydrothermal method reported by Narayanan and col [16]. Tetraethyl orthosilicate (TEOS, Si(OC₂H₅)₄, 98% of purity Sigma – Aldrich), was used as silicon source, aluminum isopropoxide ((C₃H₇)₃AlO₃) 98% of purity Sigma – Aldrich), a source of aluminum, as organic directing-structure agent Tetrapropylammonium Hydroxide ((TPAOH) 1M Sigma – Aldrich) was used while deionized water was added in all process steps. During synthesis, the crystallization time of zeolites was modified to evaluate the effect of that parameter on zeolites properties. The crystallization time was controlled in 24, 48 and 120 hours.

2.2. Characterization

Zeolites morphology was characterized in a JEOL 7100F FEG-SEM at the Microscopy Laboratory of Instituto Tecnológico Metropolitano (ITM), Medellín, Colombia. All images were obtained using secondary electron (SE) detector. Infrared (FTIR) analysis was done using a Shimadzu IRTracer-100 spectrometer. Spectra were acquired in ATR mode with 16 scans at a resolution of 4 cm⁻¹ over the 4000–600 cm⁻¹ spectral region.

X-ray diffraction (XRD) was used to verify the crystallinity of commercial and synthesized ZSM-5 zeolites. XRD patterns were obtained in a PANalytical X'Pert Pro diffractometer with Cu Kα radiation and a detector 2-D Pixcel. Spectra were taken from 0 ° and 120 ° at 1 degree per minute. Nitrogen and CO₂ adsorption and desorption isotherms at 77 K were obtained in order to determine the textural properties (surface area, micropore volume, distribution of pore sizes) of the synthesized and commercial zeolites. Tests were done using in a Micromeritics ASAP 2020 analyzer. Before the adsorption, samples were subjected to a degassing treatment in vacuum at 250 ° C for 5 hours in order to eliminate any initially adsorbed compounds on its surface.

Thermogravimetric and differential scanning calorimetry analyses were performed on a Q600 SDT TGA thermal analyzer (TA instruments).

During TGA analysis, nitrogen was used at a flow of 100 mL/min. A sample was weighed between 10 to 20 mg while sample was placed in the sample holder of the equipment, in this case, alumina capsules. For the analysis, a temperature ramp was used from room temperature to 50 °C in order to stabilize the environmental conditions of the sample and at this temperature, an isotherm was applied for 5 minutes. TGA / DSC analysis was done from 50 to 600 °C at a heating rate of 20 °C/min.

2.3. Composites fabrication

Low-density polypropylene was used for the matrix. Functionalization was done with maleic anhydride (95% Sigma – Aldrich) and as an indicator of the reaction dicumyl peroxide (98% Sigma – Aldrich) was added. The functionalization was done by placing 42 g of PP in rheometer chamber protected with a nitrogen atmosphere at 200 °C and after two minutes of melting time, 2.5 g of maleic anhydride and 0.25 g of dicumyl peroxide were added. The melted polymer was mixed for 3 minutes. After performing functionalization, tests were done to verify that the polymer was successfully functionalized following the procedure presented by Guzmán et al [17], and the results obtained by back titration showed that 5% of functionalization was achieved.

After polymer functionalization, composites were prepared by melt-mixing of PP (polypropylene) and the ZSM-5 particles using a Thermo Scientific torque rheometer equipped with a rotary mixer in a mixing chamber of 120 cm³. The process was done at 190 °C, with rotational speed of 60 rpm for 8 min.

Once the composite was obtained, samples were crushed in a rotary blade crusher to obtain pellets of functionalized polymer with zeolites. The pellets were located in a mold for 3 minutes at 220 °C. After that, a molding pressure of 10 MPa was applied to composites for two minutes at the same temperature. Subsequently, the upper mold was released to allow trapped gases to escape from the mold and finally, the molding pressure was applied again for one minute. Sample sheets of 300x80x4 mm were obtained and they were used to evaluate mechanical and thermal properties. After obtaining sheet specimens, tests samples for mechanical

evaluations were obtained by machining.

2.4. Physical-chemical characterization of composites

Infrared analysis (FTIR) was done to evaluate functionalized and composites. After obtaining the composites, samples were crushed and DSC tests were performed to determine transition temperatures, fusion and crystallization enthalpy. ASTM D3417 and ASTM D3418 standards were used to evaluate those properties. The topography of composites was evaluated using a scanning electron microscope.

Before mechanical testing, the samples were visually inspected. Size, color, porosity, and deformation were registered. Tensile tests according to ASTM D638 were performed in a Shimadzu AGX100 universal tester in polymers laboratory of Instituto Tecnológico Metropolitano. From tensile tests, ultimate tensile strength, tensile strain at tensile strength (as defined in ISO 527-1 Standard), and tensile chord modulus of elasticity were calculated. A strain range of 0,003 to 0,005 was used for chord modulus calculation.

3. RESULTS

3.1 Characterization of zeolites

Morphology and the microstructure of synthesized zeolites were obtained by SEM analysis. Particle size distribution was also determined from the SEM images using appropriate software for this purpose. Fig. 1, shows the SEM images and the particle size distribution of synthesized materials with different crystallization times and commercial zeolite. The results showed that the synthesized particles have a cylindrical shape. From the SEM images, it could also be observed that commercial zeolites have an elongated heterogeneous structure. Cuboidal structures are favored when organic templates as n-butylamine, ethylene diamine, and tetrapropylammonium hydroxide are used, in our case TPAOH was used as the template explaining the obtained structure [18].

The morphology obtained by the commercial zeolite is in agreement with the literature. It has been reported that, when the particle size is larger, the zeolites are more irregular and elongated

shapes are expected [19].

For synthesized zeolites, an increase in the particle size with the increase in the crystallization time was evidenced (see Fig. 1). The average particle size of synthesized zeolites after 24, 48 and 120 hours of crystallization are 174 nm, 210 nm, and 264 nm, respectively. Generally speaking, the distribution of the particle size increased with

the crystallization time. Additionally, when the crystallization time is shorter, the distribution is narrower. Similar results were presented by Baradaran and col [20], who reported an increase in the average particle size, with the increase in the crystallization time.

X-ray patterns of synthesized zeolites are presented in Fig. 2. In all cases, the presence of



Fig. 1. SEM images and particle size distribution histogram of synthesized and commercial zeolites.

a) ZSM-5 24h (40000X), b) ZSM-5 48h (30000X), c) ZSM-5 120h (30000X), d) commercial zeolite (30000X).

zeolite ZSM-5 was confirmed. The characteristic peaks at 2θ values of 7.9° , 8.8° , 14.7° , 23.1° , 23.7° , 23.9° and 24.4° are related to crystalline planes [101], [020], [301], [051], [303], [313] and [610] with spacing values of $d = 1.1$; 1.0 ; 0.60 ; 0.382 ; 0.385 ; 0.37 and 0.36 nm, respectively. These values were completely indexed with the structural pattern of ZSM-5 zeolite JCPDS 01 – 079 – 1638, in the database of the software X' Pert High Score, and they are in agreement with other reports for this material [21], [22]. The peaks observed for commercial samples were very similar to those reported by the synthesized zeolites.

Relative crystallinity was calculated by summing of peaks area between 23.0 and 24.5° . After that, the obtained value was compared with the sum of the same peaks for a pattern of 100% crystalline phase obtained from the software used for the analysis [23].

The crystallinity of synthesized samples was 38 , 55 and 67% for the zeolites with 24 , 48 and 120 h of crystallization time, respectively. Also, the average crystallite size calculated using the Debye-Scherrer equation was 28.4 , 33.9 and 43.8 nm, respectively. It must be emphasized that every particle shown in Fig 1 is composed of several crystallites and accordingly, the particle size did not correspond to the crystallite size. The obtained values are in agreement with the reported values by Narayan et al. [16], in analogous conditions. This result clearly evidences the importance of crystallization time in the morphology of synthesized materials. Summarizing, when crystallization time increased crystal size also tended to increase and these results are in agreement with the literature [20], [24].

In order to confirm the ZSM-5 structure, FT-IR analysis were conducted. Fig. 3, shows the spectra

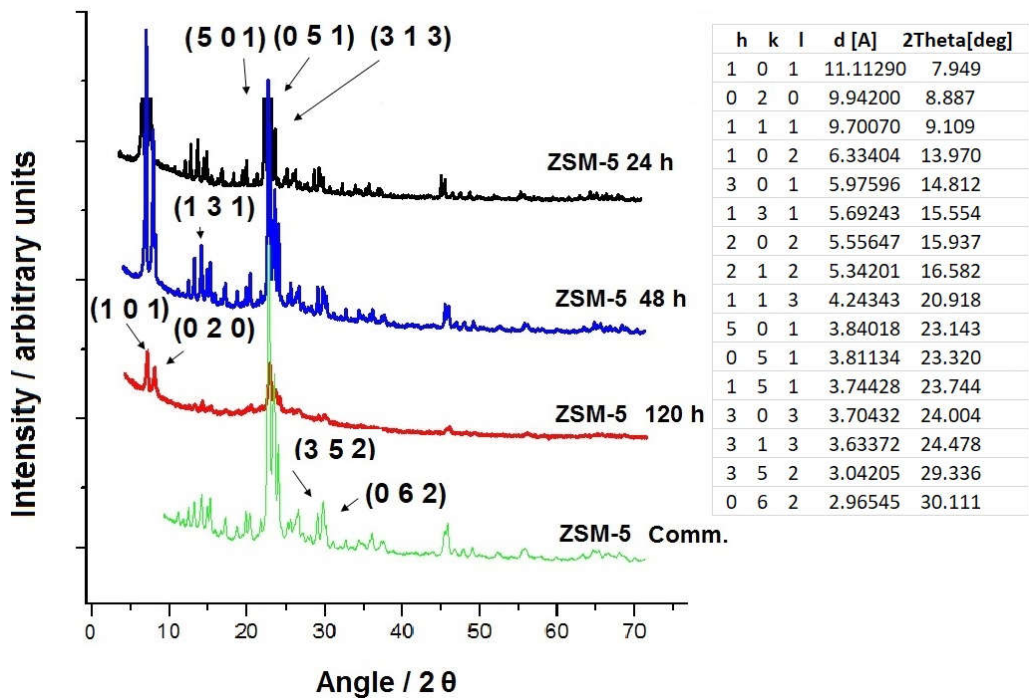


Fig. 2. XRD patterns of the ZSM-5 zeolites synthesized by the three distinct crystallization time.



Fig. 3. FTIR spectra of synthesized ZSM-5 zeolites and commercial zeolite.

of the synthesized zeolites and commercial one. From Fig. 3, it is possible to observe the typical vibration peaks of MFI-type zeolite. In the infrared spectrum two main regions are evidenced, the first one above 2500 cm^{-1} with a broadband present in all cases and with peaks at 3447 and 3640 cm^{-1} related to strongly bonded zeolitic water [22], the second region from 2000 cm^{-1} to 500 cm^{-1} , with the typical peaks at 543 and 792 cm^{-1} attributed to pentasil framework vibration and Si-O-Si symmetric vibration, respectively could also be observed. On the other hand, peaks at 1111 and 1226 cm^{-1} are assigned to asymmetric stretching of Si-O-Si [25]. In sample ZSM-5 24h peaks are not well defined, and the intensity ratio is quite low when it is compared to the bands of the other samples indicating that the molecules are not completely formed at this point.

Textural properties as surface area, pore volume, and average pore diameter were characterized by nitrogen and carbon dioxide adsorption isotherms.

In all cases, isotherms with type IV (IUPAC classification) typical of mesoporous materials with small hysteresis loops were obtained. Table 1 resumes the results obtained from this analysis. Textural characterization (Table 1) shows that synthesized zeolites have a pore volume between 0.18 and $0.24\text{ cm}^3/\text{g}$ with BET surface area between 261 to $337\text{ m}^2/\text{g}$, that is in agreement with values in other reports of the literature for HZSM-5 MFI type structures [26]. These results indicate that synthesized materials have an elevated microporosity and small inter-crystal mesoporosity probably due to the agglomeration of the crystals [27]. Table 1 resumes the main textural and structural properties obtained from BET and XRD analysis. In addition, the crystallite size described in table 1 is different from the particle size as explained before. The increment in the size of the pores resulted in a larger surface area.

Thermogravimetric analysis was done for all synthesized samples. From the TGA results (not

Table 1. Textural and structural properties of commercial and synthesized zeolites.

Sample	Crystallinity (%)	Average crystal-size (nm)	Average particle size (nm)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size diameter (nm)
24	38	28	174	261	0,18	3,8
48	55	34	210	337	0,22	8,3
120	67	43	264	308	0,24	7,6

shown), all samples showed a similar thermal behavior. Specifically, two thermal events were evidenced, a first weight loss in a range from 25 °C to 150 °C in all samples associated with physisorbed water and strongly adsorbed mainly physisorbed or chemisorbed. This result is in agreement with results obtained by the FTIR analysis where a strong vibration of water molecules adsorbed in the structure of the zeolites was identified. The amount of water uptake was very similar in all samples, and just small differences near 1% of weight loss were obtained for the water uptake of all the samples with different crystallization times.

A second thermal event was identified from 200 to 500 °C with a small decay in the weight of all the samples of just 2%, this decomposition is associated with the total removal of the organic template structure TPAOH in this case. In all cases, zeolites were thermally stable from 500 °C to 1000 °C [28].

Since the highest surface area was obtained for zeolites after 48 hours of crystallization time, those conditions were selected to study the effect of the addition of the nanostructured particles on the mechanical and thermal properties of the PP.

3.2. Physical-chemical characterization of composites

3.2.1. Mechanical characterization

Fig. 4 shows the results of Young's modulus. Modulus of elasticity of composites increased when it is compared to the pure polypropylene. The largest increase in elastic modulus was shown when the composite was prepared with 5 wt. % of zeolites. Young's modulus increased by 14% when it is compared to PP. When polypropylene is reinforced with commercial zeolites 822, the

improvement was observed only with an addition of 1 wt. % of zeolites. This behavior could be attributed to morphological characteristics of the commercial zeolite. As mentioned, the morphological characteristics of commercial zeolites differ from the synthesized zeolite. Crystal size, surface area, and elongated morphology could influence the interaction between the matrix and the reinforcing agent.

Furthermore, when 3 and 5 wt. % of commercial zeolite are added to the composite, Young's modulus tends to decrease. According to the literature, the formation of voids around the particles could reduce mechanical properties since the bonding between the zeolite particles and the polypropylene matrix is not satisfactory [29]. The improvement of Young's modulus has been reported before and it strongly depends on the morphological characteristics of the nanostructured particles used as a reinforcing agent. Size, concentration, shape, and dispersion of the nanostructured particles are parameters affecting the mechanical properties of composite materials [30], [31].

Fig. 5, shows a significant decrease in the strain at break of polypropylene with ZSM-5 zeolites compared to commercial pure polypropylene. The decrease in ductility evidenced for polypropylene / ZSM-5 matrix was obtained since the particles block the mobility of the polymer chains during deformation. According to Fig. 5, the strain at break tends to decrease with the increase in the amount of nanostructured particle added to the polymer. The particles also reduced the viscoelastic behavior of the polymer. Sarkar & Alexandridis, 2004 reported that viscoelastic behavior is the result of competition of two characteristics: free volume in the polymer due to a density profile inhomogeneous on the surface of the nanostructured particle and

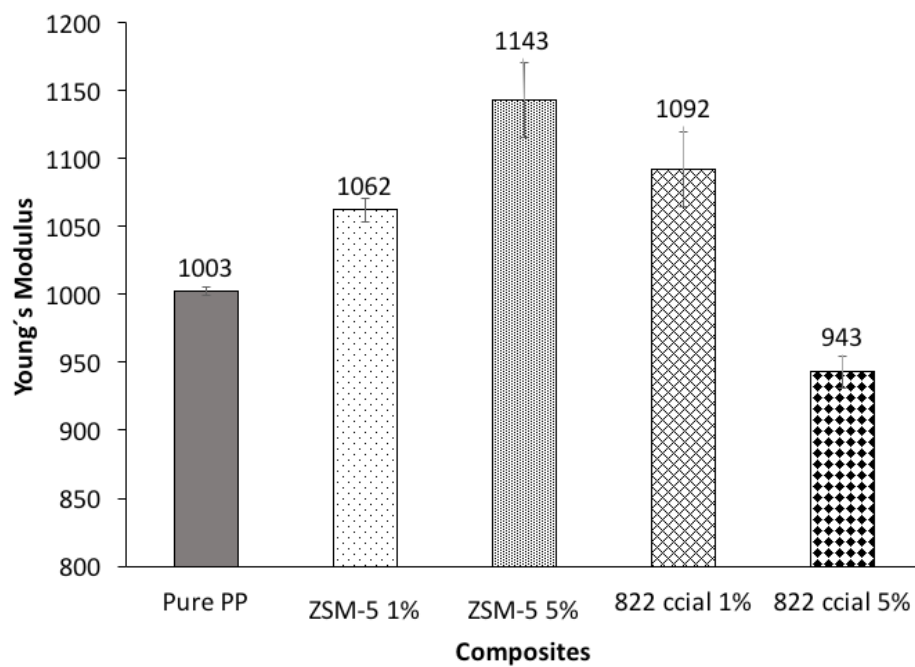


Figure 4. Young's modulus of modified zeolites and pure polypropylene.



Fig. 5. Strain at the break of modified zeolites and pure polypropylene.

also to the nanoparticle increasing the chain mobility and anchoring effects on the surface of the nanostructured particle or nanoparticle that partially block the movement of the chain [30].

3.2.2. Thermal characterization

In order to study thermal properties of the composites the polymer charged with the highest and the lowest percentage of commercial and

synthesized zeolite were studied by DSC analysis. Fig. 6, shows the final weight loss in all samples, this is an indicator that the right amount of zeolites was effectively incorporated to the polymer since in all cases the remaining weight corresponds to the percentage of load, taking into account the residual weight for the pure polyethylene.

Fig. 7, shows the degradation temperature of the composites with commercial and synthesized zeolites in different percentages against the pure polymer.

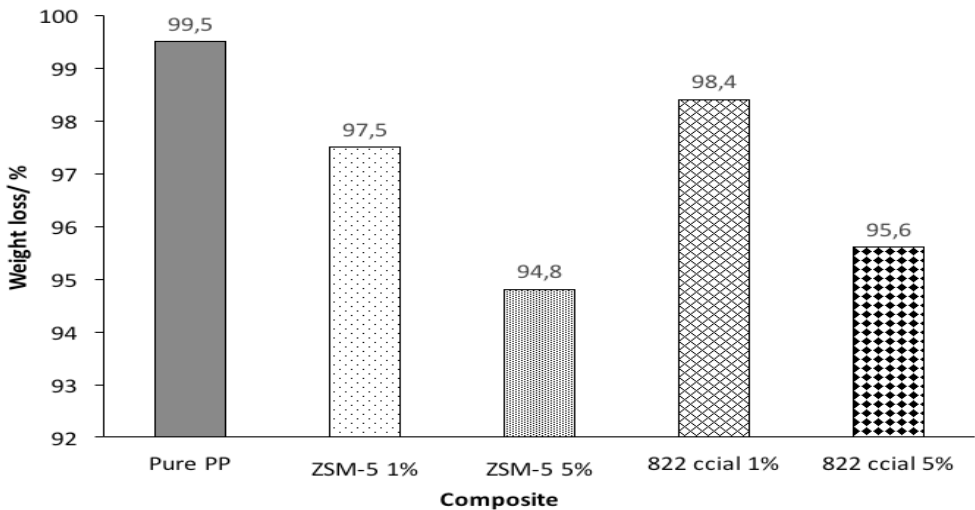


Fig. 6. Weight loss of the composites loaded with commercial and synthesized zeolites (1% and 5 wt. %).

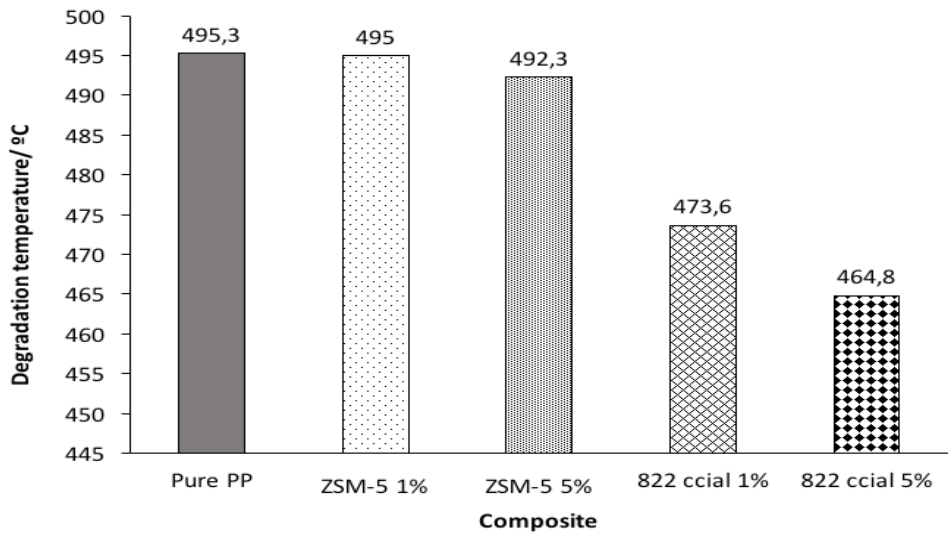


Fig. 7. Degradation temperature of the composites loaded with commercial and synthesized zeolites (1% and 5 wt. %).

Table 2. Composites most relevant thermal properties.

Material	Crystallization Temperature (T _c) °C	Fusion Temperature (T _m) °C	Crystallization Enthalpy (ΔH _c) J/g	Fusion Enthalpy (ΔH _m) J/g	Crystallinity percentage (xc)
PP + ZSM-5 1%	106,3	163,5	79,6	55,7	27,2
PP + ZSM-5 5%	107,1	164,5	78,8	55,1	28,0
PP + comm. 1%	107,1	164,0	85,1	59,9	29,2
PP + comm. 5%	105,8	164,4	81,8	59,5	30,3
PP	106,3	163,8	84,5	57,8	27,9

In all cases the degradation temperature was lower compared with the pure polymer, this effect was most noticeable with the increase of the load percentage, specifically for the samples with 5% of zeolite. From the thermograms (not shown) it was observed that the beginning of the thermal degradation was delayed when particles were added to the polymer, nevertheless the velocity of degradation is higher due to the catalytic effect of the zeolites [32]. This result could also be related to the morphology of zeolites, where the commercial zeolites with the elongated structure can favor the polymer degradation process.

Table 2, summarizes the most important values obtained by TGA-DSC analysis of the composite. From this table, it is clear that no significant changes in the thermal properties of the composites were obtained [30].

4. Conclusions

In this work, ZSM-5 “zeolites with different crystallization times were synthesized. An increase in the particle size and crystallinity for longer crystallization time was evidenced. Based on surface area and pore volume results, the sample with crystallization time of 48 hours, was found to be the best zeolites to study its effect on mechanical and thermal properties of the PP.

Composites of PP with synthesized and commercial zeolites were prepared for comparison. The highest Young's modulus was obtained for composite with 5 wt. % of synthesized zeolite. The strain at break was reduced when the particles were added to the polymer since the particles block the mobility of the polymer chains during deformation.

In all cases, degradation temperature of composites was lower compared to pure polymer and the effect is improved with the amount of zeolite added. This could be of great advantage in the recycling process. However, no significant modifications were found on the other thermal properties.

5. Acknowledgments

The authors would like to acknowledge to Grupo de Materiales Avanzados y Energía-MATyER of Instituto Tecnológico Metropolitano. Research project P14209 and Instituto Tecnológico Metropolitano are also acknowledged for financial support

REFERENCES

1. Global Polypropylene (PP) Market Report 2017”, Kevin Akeroyd, <http://www.prnewswire.com/news-releases/global-polypropylene-pp-market-report-2017-100-billion-market-size-demand-forecasts-industry-trends-and-updates-2016-2022---research-and-markets-300465031.html>.
2. Patel, H. A., Somani, R. S., Bajaj H. C., Jasra, R. V., “Nanoclays for polymer nanocomposites, paints, inks, greases and cosmetics formulations, drug delivery vehicle and waste water treatment. Bull.” Mater. Sci., 2006, 29, 133–145.
3. Bin Mazlan M. S. “Polypropylene organoclay nanocomposite,” Universiti Malaysia Pahang, 2010. 1-62.
4. Pavlidou, S., Papaspyrides C. D., “A review on polymer-layered silicate nanocomposites. Prog. Polym.” Sci., 2008, 33, 1119–1198.
5. Sinha Ray, S., Okamoto, M., “Polymer/layered silicate nanocomposites: A review from prepa-

- ration to processing. *Prog. Polym. Sci.*, 2003, 28, 1539–1641.
6. Zuiderduin, W. C. J., Westzaan, C., Huétink, J., Gaymans, R. J., “Toughening of polypropylene with calcium carbonate particles. *Polymer*.” 2003, 44, 261–275.
7. Reeve PJ, Fallowfield HJ. “Natural and surfactant modified zeolites: a review of their applications for water remediation with a focus on surfactant desorption and toxicity towards microorganisms.” *J. Environ. Manage.* 2018, 205, 253–61.
8. Eroglu N, Emekci M, Athanassiou CG. “Applications of natural zeolites on agriculture and food production.” *J. Sci. Food Agric.* 2017, 97, 3487–3499.
9. Tul Muntha S, Kausar A, Siddiq M. “A review on zeolite-reinforced polymeric membranes: salient features and applications. *Polym. - Plast. Technol. Eng.*, 2016, 55, 1971–1987.
10. Bukit N. “Mechanical and Thermal Properties of Polypropylene Reinforced by Calcined and Uncalcined Zeolite.” *Makara Teknol.*, 2013, 16, 121–128.
11. Adloo A, Sadeghi M, Masoomi M, Pazhooh HN. “High performance polymeric bipolar plate based on polypropylene/graphite/graphene/nano-carbon black composites for PEM fuel cells.” *Renew. Energy.*, 2016, 99, 867–874.
12. Huang CL, Lou CW, Liu CF, Huang CH, Song XM, Lin JH. “Polypropylene/graphene and polypropylene/carbon fiber conductive composites: mechanical, crystallization and electromagnetic properties.” *Appl. Sci.*, 2015, 5, 1196–1210.
13. Zhang S, Cao XY, Ma YM, Ke YC, Zhang JK, Wang FS. “The effects of particle size and content on the thermal conductivity and mechanical properties of Al_2O_3 /high density polyethylene (HDPE) composites.” *Polym. Lett.*, 2011, 5, 581–590.
14. Watanabe R, Kunioka M, Mizukado J, Suda H, Hagihara H. “Highly ductile polypropylene-based nanocomposites by dispersing monodisperse silica nanospheres in functionalized polypropylene containing hydroxyl groups.” *Polym.*, 2016, 99, 63–71.
15. Rong MZ, Zhang MQ, Pan SL, Lehmann B, Friedrich K. “Analysis of the interfacial interactions in polypropylene/silica nanocomposites.” *Polym Int.*, 2004, 53, 176–183.
16. Narayanan S, Vijaya JJ, Sivasanker S, Kennedy LJ, Jesudoss SK. “Structural, morphological and catalytic investigations on hierarchical ZSM-5 zeolite hexagonal cubes by surfactant assisted hydrothermal method.” *Powder Technol.*, 2015, 274, 338–348.
17. Guzmán M, Murillo EA. “Funcionalización de polietileno de baja densidad con anhídrido maleico en estado fundido.” *Polímeros*, 2014, 24, 162–169.
18. Sang S, Chang F, Liu Z, He C, He Y, Xu L. “Difference of ZSM-5 zeolites synthesized with various templates.” *Catal. Today.*, 2004, 93, 729–734.
19. Petushkov A, Yoon S, Larsen SC. “Synthesis of hierarchical nanocrystalline ZSM-5 with controlled particle size and mesoporosity.” *Microporous Mesoporous Mater.* 2011, 137, 92–100.
20. Baradaran S, Sohrabi M, Bijani PM, Royaei SJ. “Isobutane aromatization in the presence of propane as a co-reactant over H-ZSM-5 catalysts using different crystallization times J.” *Ind. Eng. Chem.*, 2015, 27, 354–361.
21. Fu T, Chang J, Shao J, Li Z. “Fabrication of a nano-sized ZSM-5 zeolite with intercrystalline mesopores for conversion of methanol to gasoline.” *J. Energy Chem.*, 2017, 1, 139–46.
22. Ayodele OB. “Structure and reactivity of ZSM-5 supported oxalate ligand functionalized nano-Fe catalyst for low temperature direct methane conversion to methanol. *Energy Convers.*” *Manag.*, 2016, 126, 537–547.
23. ASTM D5758-01(2015), “Standard Test Method for Determination of Relative Crystallinity of Zeolite ZSM-5 by X-Ray Diffraction, ASTM International,” West Conshohocken, PA, 2015.
24. Karimi R, Bayati B, Aghdam NC, Ejtemaei M, Babaluo AA. “Studies of the effect of synthesis parameters on ZSM-5 nanocrystalline material during template-hydrothermal synthesis in the presence of chelating agent”. *Powder Technol.*, 2012, 229, 229–236.
25. Yuan E, Zhang K, Lu G, Mo Z, Tang Z. “Synthesis and application of metal-containing ZSM-5 for the selective catalytic reduction of NO_x with NH_3 .” *J. Ind. Eng. Chem.*, 2016, 42, 142–148.
26. Gao Y, Wu G, Ma F, Liu C, Jiang F, Wang Y, Wang A. “Modified seeding method for preparing hierarchical nanocrystalline ZSM-5 catalysts for methanol aromatization”. *Microporous Mesoporous Mater.* 2016, 226, 251–259.
27. Wei Y, de Jongh PE, Bonati ML, Law DJ, Sunley GJ, de Jong KP. “Enhanced catalytic performance of zeolite ZSM-5 for conversion of methanol to dimethyl ether by combining alkaline treatment and partial activation.” *Appl. Catal. A Gen.*, 2015, 504, 211–219.
28. Wu G, Wu W, Wang X, Zan W, Wang W, Li C. “Nanosized ZSM-5 zeolites: Seed-induced synthesis and the relation between the physicochemical properties and the catalytic performance in the

- alkylation of naphthalene.” *Microporous Mesoporous Mater.*, 2013, 180, 187-195.
29. Pehlivan H, Balköse D, Ülkü S, Tihminlioglu F. “Characterization of pure and silver exchanged natural zeolite filled polypropylene composite films.” *Compos. Sci. Technol.*, 2005, 65, 2049-2058.
 30. Sarkar B, Alexandridis P. “Block copolymer–nanoparticle composites: Structure, functional properties, and processing.” *Prog. Polym. Sci.*, 2015, 40, 33-62.
 31. Buxton GA, Balazs AC. “Simulating the morphology and mechanical properties of filled diblock copolymers.” *Phys. Rev. E.*, 2003, 67, 031802.
 32. Özmihçi F, Balköse D, Ülkü S. “Natural zeolite polypropylene composite film preparation and characterization.” *J. Appl. Polym. Sci.*, 2001, 82, 2913-2921.