Characterization of Polymer Nanocomposites with Thermal Analysis and Spectrum techniques

M. E. Mena[1, 3], R. F. Estrada[1], L. A. Torres[2], R. Tinajero[4] and L. Palafox[4]

[1] Universidad Iberoamericana Ciudad de México, Prolongación Paseo de Reforma 880, Lomas de Santa Fe, México, C.P. 01219, Ciudad de México. quenamena@gmail.com , rodolfo.estrada@ibero.mx

[2] Universidad Iberoamericana León, León, MX, adolfo.torres@iberoleon.mx

[3] Desarrollos y Acabados en Poliuretano, S.A. de C.V., León, MX

[4] Ciatec AC, León, MX

ABSTRACT

Polymer nanocomposites have attracted attention in materials science because they exhibit different properties from those of their counterpart polymer microcomposites. Were performed a Thermogravimetric Analysis (TGA) of polyurethane nanocomposite in order to establish the thermal stability and their mode of thermal degradation on the internal nanostructure before and after combustion. In addition, Energy Dispersive Spectroscopy (EDS) allowed one to identify the chemical information of each element detected and their relative proportions. SEM analysis was a surface morphology method for characterization of nanocomposites or nanomaterials. It could use to determine particle size, morphology and elements chemical composition. Further, these techniques provide information to help derive meaningful relationships between nanostructure and macro scale properties.

Keywords: Nanocomposite, Characterization, TGA, SEM, EDS, polyurethane, flame resistance.

INTRODUCTION

Polyurethane foam products do not ignite spontaneously. Moreover, polyurethane never ignites spontaneously under a usual foam manufacturing conditions where it is made from mixing two components: the polyol component and the isocyanate component [1]. Recently polymer nanocomposites have attracted extensive attention in materials science because they exhibit quite different properties. The dispersion and distribution of the nanomaterials into the polymeric matrix depends the compatibility between nanomaterials and the matrix as well as formulation stoichiometry and production method [2]. An important characteristic is the size of nanoparticles, their effects increase because of their scattering on the total surface area per unit volume [3].

Thermogravimetric (TGA) is a technique used for materials characterization mainly coal, clays, and polymers. It is used to study the reactions of decomposition of materials, in the determination of the characteristics of volatilization and kinetic parameters, such as the activation energy and the pre exponential factor, as well as the influence of temperature and heating rate on the development of thermal decomposition reactions and reaction mechanisms [4-5].

In the thermogravimetric analysis, the weight loss of a sample is registered to the extent that the temperature is increased, up to temperatures of 1200 ºC, under controlled conditions of heating speed and different reaction atmospheres; obtaining in this way, the curves called TG or thermograms [6]. Nanoclay phase into PU matrix increases the thermal stability, and affects the total heat of degradation, which suggests a change in the degradation reaction mechanism.

Scanning Electron Microscopy (SEM) is an analysis capable of producing high-resolution images of the surface of a sample using electron-matter interactions [7]. This equipment can determine the particle size, morphological comparison and chemical composition of raw materials. Also for polymer matrix can help to measure pore diameters of their structure and to understand the internal nanostructure before and after combustion. EDS is not a surface analysis technique, but is a qualitative analysis to understand the chemical information of each element detected by the spectrums analysis on the sample [8].

Development and innovation of new materials as polymer nanocomposites have been tested and demonstrated useful/safe human application. Therefore, new materials can use for the furniture and construction industry with the property fireproof to avoid the propagation of the fire, as well as providing fire safety and improved properties for a wide range of consumer goods. Flammability property is a potentially strong area of opportunity to innovate on functional nanocomposites. The nanocomposite could be applied to automotive, ship industry or construction market as well as can be used on soles for safety shoes or industrial boots for firefighter, oilman, and any other industries.

METHODOLOGY

Polyurethane nanocomposite was made by synthesis of several polyether resins. Specimens were prepared in two rigid foams groups, control polyurethane without nanoparticles and polyurethane with titanium dioxide nanoparticles.

The thermal degradation of the materials was determined on a TA Instrument model TGA Q-500 V6.3 Build 189 using a heating rate of 10 °C/min up to 850 °C under an atmosphere of argon.

EDS analysis and SEM images were obtained with a Scanning Electron Microscope Jeol model JSM-7800F operating at 10 kV.

Samples Preparation

TGA sample weight was 9.6860 mg for polyurethane nanocomposite with titanium oxide nanoparticles and polyurethane control weight was 12.4190 mg.

Thermogravimetric analysis time roughly is an hour and a half, time in which the sample is losing weight. Initial temperature was at 24 °C shown on Figure 1.

Figure 1.Sample of polyurethane control located on TGA instrument

SEM analysis used samples with 10 mg of weight. Specimens were prepared an hour before to avoid humidity when completely sealed because they must be in high vacuum. Solid samples should be 5 mm wide by 5 mm long by 1 mm thick.

Characterization of the Samples

SEM analysis contributed to identify chemical composition and morphology for titanium dioxide nanoparticles, for example purity for TiO_2 nanoparticles was more than 99% with a little residue of silica as a result of synthesis as shown in figure 2 and figure 3. Micrographs in SEM showed that the nanoparticles are not spherical; however this is not a restriction to find ignition property.

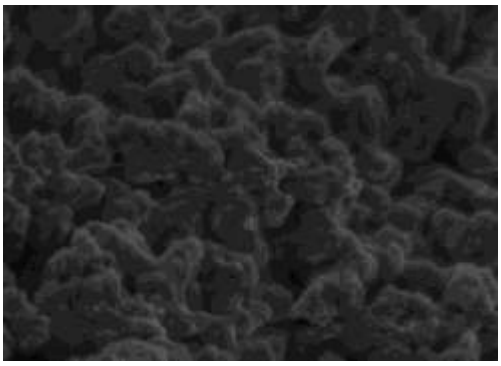

Figure 2. SEM micrograph of titanium dioxide nanoparticles.

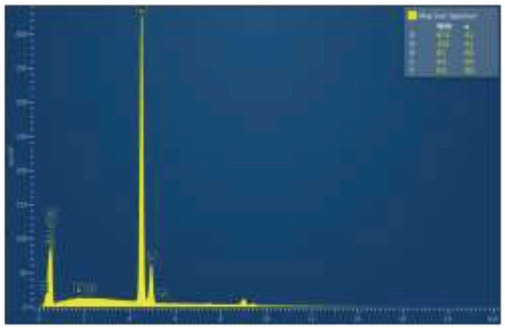

Figure 3. EDS analysis for chemical composition on oxide titanium nanoparticles.

RESULTS AND DISCUSSION

We investigated the characterization of polyurethane nanocomposites based titanium dioxide nanoparticles to search a fire resistance property. The TGA thermograms exhibited that polyurethane control had more resistance on degradation temperature than in comparison with polyurethane nanocomposite TiO_2. The dotted line is a control thermogram and continuous green line is the nanocomposite thermogram shown on figure 4.

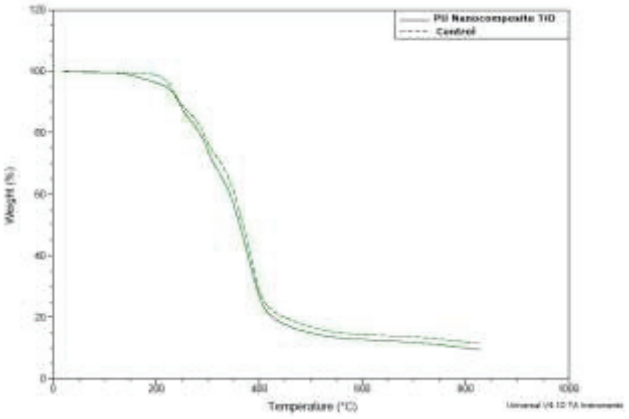

Figure 4. TGA of polyurethane nanocomposite with titanium dioxide nanoparticles and TGA polyurethane control from room temperature to 850°C at a heating rate of 10°C/min.

Polyurethane thermogram had three transitions of weight loss. The first range is of 24 °C until before 232 °C resulting chemical compounds, the main weight loss is between 300 °C to 480 °C which is the polyurethane based polymer polyether; in the range of 500 °C to 850 °C, the sample no longer loses weight, but in the end appeared an inorganic residue shown on figure 5.

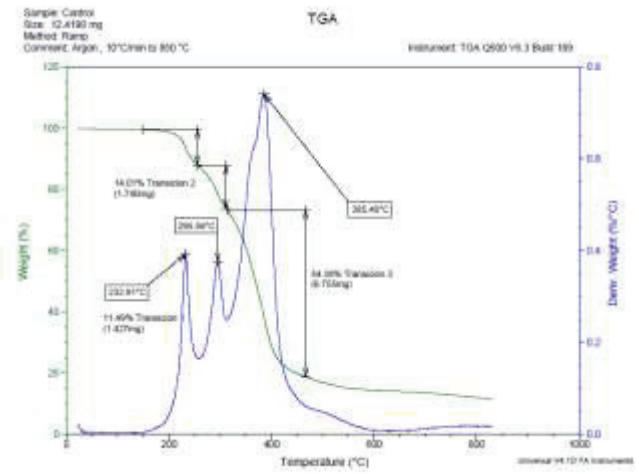

Figure 5. Thermal degradation of polyurethane control by TGA.

The thermogram of polyurethane nanocomposite of TiO_2 of polyurethane had five transitions of weight loss. The first range is of 24 °C until before 179 °C , second transition is of 240°C until before 305°C both resulting chemical compounds. Transition 3 and four occurs on the range of 300 to 325°C. The main weight loss is on transition 5 with 47.835% of loss weight between temperatures 350 °C to 420 °C which is the polyurethane based polyether; in the range of 450 °C to 850 °C, the sample no longer loses weight, but in the end an inorganic residue remained shown on figure 6.

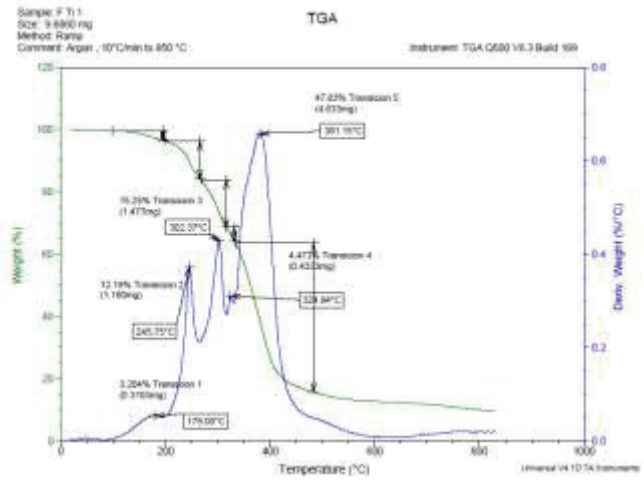

Figure 6. Thermal degradation of polyurethane nanocomposite with titanium dioxide nanoparticles by TGA.

The results of the present paper demonstrated that thermogravimetric analysis shows an unexpected three-stage process of degradation on polyurethane control in the temperature range of 232 – 386 °C. In addition, thermogravimetric analysis shows an unexpected four-stage process of degradation of the rigid polyurethane nanocomposite with titanium dioxide nanoparticles in the temperature range of 245 – 381 °C.

Moreover, the derivate weight is useful to understand the percentage of weight loss, as a result polyurethane control lost 11.49 wt% on it fist transition similar to transition 2 with 14 wt%, however the major degradation occurs on transition 3 with 54.39 wt% characteristic of polyurethane. Recorded peaks of thermal degradation on polyurethane nanocomposite demonstrate that transition 3 and 4 are different from polyurethane control, with 19.72 wt%, also the major weight loss resulted on transition 5 with 47.83 wt%

Finally, pore diameters for polymer matrix could measure to understand the internal nanostructure before and after combustion. SEM analysis shows a micrograph of top section morphology of unburned polyurethane nanocomposite with titanium dioxide nanoparticles at 100 µm resolution, using mathematical analysis we can determinate the pore diameters average, for this sample, pore diameter average is 50.55 µm shows on figures 7. Polyurethane after burned lost oxygen as a result the micrograph doesn't show pores on it morphology shown on figure 8.

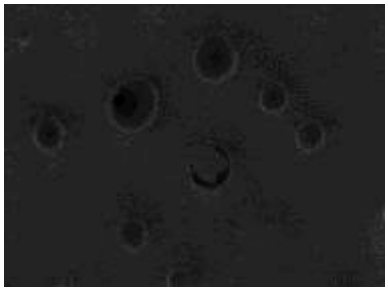

Figure 7. SEM micrograph showing a top section morphology of unburned polyurethane nanocomposite with titanium dioxide nanoparticles.

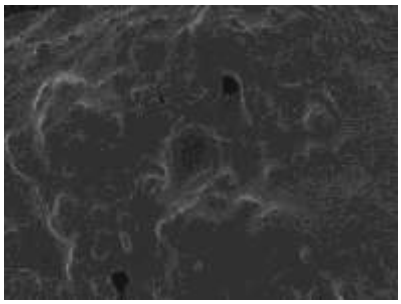

Figure 8. SEM micrograph showing a top section morphology post burn polyurethane nanocomposite with titanium dioxide nanoparticles.

CONCLUSIONS

It is observed that the degradation of the polyurethane occurs between 200 – 400°C. The weight loss at temperature below 190 °C has been attributed to volatile compounds and impurities imbedded in the surface of the polyurethane. Thermograms exhibited that polyurethane nanocomposite has greater thermal degradation than polyurethane conventional or control. However, nanocomposite appeared on transition 4 at 324.94°C as shown on thermograms, this polyurethane nanocomposite had five important transitions, two more transitions than polyurethane control.

Characterizations of nanocomposites are functional tools for application of nanotechnology R&D industrial strategies. TGA, SEM and EDS analyses become complimentary techniques useful for characterization nanocomposites or nanomaterials. Polyurethane rigid nanocomposites could be applied on construction or automotive industry looking for safety and sustainability products.

Nanotechnological applications will continue growing, research and innovate on polyurethane fireproof nanocomposites deepen the understanding of fire as well as fire prevention, contributing as a relevant and important industry development

REFERENCES

[1] Q & A on Fire and Fire Prevention of Rigid Polyurethane Foam, Japan Urethane Industry Institute (JUII), 2011.

[2] Kargarzadeh H., Ahmad I., Thomas S. and Dufresne A., Microscopic Analysis of Cellulose Nanofibril (CNF) and Cellulose Nanocrystal (CNC) Based Nanocomposites, Handbook of Nanocellulose and Cellulose Nanocomposites, 365-392, 2017.

[3] Nilufer Erdem, Aysun A. Cireli, Umit H. Erdogan, Flame Retardancy Behaviors and Structural Properties of Polypropylene/Nano-SiO_2 Composite Textile Filaments, Journal of Applied Polymer Science, 111(4), 2085-2091, 2008.

[4] Yaman S., "Pyrolysis of biomass to produce fuels and chemical feedstocks", Energy Conversion and Management, 45, 651–671, 2004.

[5] Carrier M., A. Loppinet-Serani, D. Denux, J.M. Lasnier, F. Ham-Pichavant, F. Cansell, C.A. and Monier, "Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass", Biomass and Bioenergy, 35, 298-307, 2011.

[6] ASTM E1131Standard Method for Compositional Analysis by Thermogravimetry, 2008.

[7] Rangel N. Alva H., Romero J., Rivera J., Álvarez A., Garcia E., "Synthesis and characterization of reinforced materials composite of polyurethane porous/ hydroxyapatite", Rev. Iberoam. Polim., 8(2), 99-111, 2007.

[8] Goldstein, J., Newbury, D.E., Joy, D.C., Lyman, C.E., Echlin, P., Lifshin, E., Sawyer, L., Michael, J.R., Scanning Electron Microscopy and X-Ray Microanalysis, 2003.