

Polyurethane Nanocomposite for Fireproof Applications to reduce toxic gases

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ABSTRACT

The polyurethane nanocomposite to reduce toxic gases is important to solve several industrial problems. We proposed novel rigid polyurethane based on nonmetallic nanoparticles for fireproof applications. On the other hand, we made synthesis, UV-VIS spectroscopy and Scanning Electron Microscopy characterization of polyurethane modified with nanostructures by a reaction process in-situ with flammability property. In addition the mechanical and flammability properties of rigid polyurethane were evaluated according to international test methods of burning for example using test ASTM D635. The ignition and toxic smoke expansion for nanozinc composite versus control polyurethane was also investigated. This could be new and functional polymer for construction and useful for other industries as textile, automotive or medical sector.

Keywords: Nanocomposite, Polymers, Flame retardancy, innovation.

INTRODUCTION

Rigid polyurethane has a wide range of applications such as insulation, packaging, among others, due to their excellent properties. However, as most organic materials are moderately flammable and the flame propagation is very fast; increasing the risk of fire, limiting their use in case of fire [1]. For example in the United States of America, there were 374,000 fires reporting in 2012, causing 2,385 deaths and economic losses of more than 7.1 billion dollars.

However the biggest problem occurs with toxic gases from combustion, those gases harmful is the main cause of deaths nearly 75% related to fire due to gases generated during the burning time. Death by inhalation of smoke is

usually really fast. On the other hand, some flame retardant (FR) additives are needed, among which halogenated compounds are the most widely used, and brominated additives are the main fire retardants. But during the combustion of flame retarding polymer based on these retardants, halogen acids are evolved, people would be exposed to these irritants and potential corrosion damage to equipment would occur. So much work has been done on halogen-free [2].

Polymer nanocomposites that are nanoparticles dispersed in a polymer matrix have garnered substantial academic and industrial interest since their inception [3]. Polymer nanocomposites for flammability applications are attractive because the formation of a nanocomposite not only improves the fire properties but can also improve other properties (e.g., mechanical properties), and it has the potential to bring true multifunctionality to materials [4]. Pholnak's work proposed analysis a UV-Vis absorption on polyurethane coating filled with Zinc Oxide for economic large-scale production of composites [5].

The productive sector has detected a market niche for rigid polyurethane nanocomposite to manufacture products with applications on the construction sector; that can use on the roof or on walls, imitation stone or wood.

METHODOLOGY

Polyurethane nanocomposite was made by synthesis of several polyether resins. Different samples were prepared in two groups, the control polyurethane without nanoparticles and polyurethane with zinc oxide nanoparticles to create a specific stoichiometry for all raw materials. Also the

polyurethane stoichiometry involved different concentration percentage of zinc oxide nanoparticles.

The experimental procedure was determined by several steps as shown in Figure 1. The polyurethane nanocomposite was evaluated and characterized by UV-VIS technical spectroscopy and analytical methods such as Scanning Electron Microscopy (SEM). All this information helps to make the perfect stoichiometric polymer nanocomposite according with the customer requirements. In addition flammability tests were evaluated according to international methods of burning for example using test ASTM D635.



Figure 1. Methodology for polyurethane nanocomposite

Characterization of the Samples

UV-VIS Analysis for polyurethane nanocomposite and the control sample were performed with ultraviolet visible light and near infrared spectrophotometer Cary 5000 UV - VIS NIR equipment used to measure Absorbance and Reflectance percentage.

SEM Analysis was performed with a Scanning Electron Microscope Jeol model JSM-7800F to evaluate the composition and the size of zinc oxide nanoparticles.

RESULTS AND DISCUSSION

According to the experiment results the specific characteristics of nanomaterials can be used to obtain better chemical, biological and mechanical properties.

SEM analysis helps us to identify chemical composition and morphology as shown in figure 2 and figure 3.

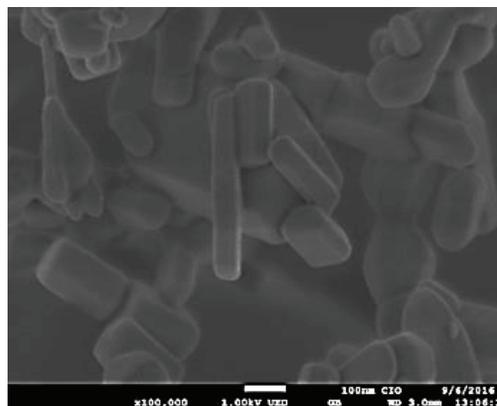


Figure 2. Micrograph of zinc oxide nanoparticles viewed by SEM

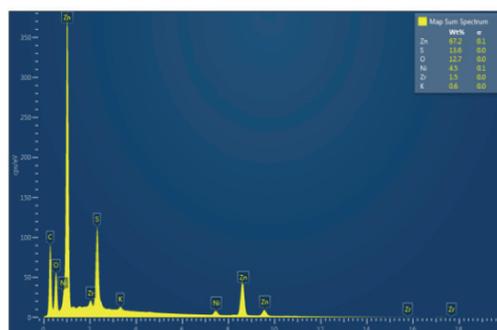


Figure 3. Chemical Composition of zinc oxide nanoparticles evaluated by SEM

UV-VIS Analysis of nanocomposite zinc- polyurethane is shown in Figure 4, the samples are observed with different concentrations above the control line of rigid polyurethane without zinc oxide nanoparticle or additives. At lower nanozinc concentration the absorption decrease and the color consistent was neutral.

The differences between polyurethanes are observed from the wavelength 200 nm to 400 nm. After 400 nm each sample has a different percentage of absorbance, due to the white color of the polymer.

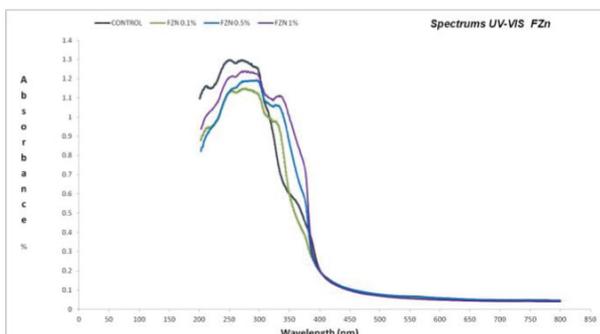


Figure 4. Absorption of Nanocomposite of Rigid Polyurethane characterized by UV-VIS

Figure 5 shows the results of reflectance for samples with different concentrations of zinc oxide nanoparticles. As can be observed, below the control line which corresponds to rigid polyurethane without zinc oxide nanoparticle or additives, the lower concentration of nanoparticles is located. The highest line corresponds to the increases of concentration in ZnO and present slightly reflectance, giving evidence that color of the polymer can affect the absorbance and reflectance of the polyurethane nanocomposite.

The differences between materials concentration are observed from the wavelength 200 to 400 nm, as well as the samples have similar curves after 400 nm.

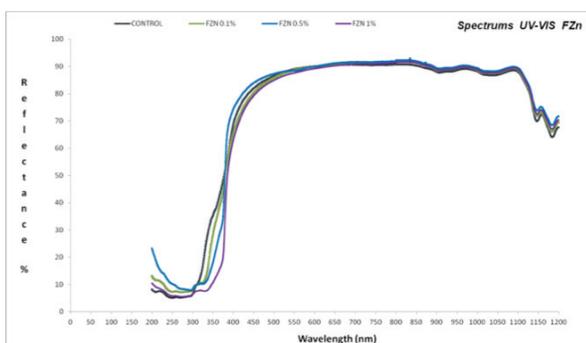


Figure 5. Reflectance of Nanocomposite of Rigid Polyurethane characterized by UV-VIS

Therefore the specific characteristics of nanomaterials can be used to obtain better chemical, biological and mechanical

properties. The efficient and effective uses of this allow proposing advanced industrial solutions. Polymeric materials are involved in most fires occurring in urban areas and transport, because they may begin the spread of fire.

The properties of flammability were evaluated by different standard test method for horizontal burning rate of polymeric materials using an Atlas horizontal flame chamber equipment certified for those proofs.

This standard measures describes the response of materials to heat and flame under controlled conditions, but does not by itself incorporate all factors required for fire hazard or fire risk assessment of the materials, products, or assemblies under actual fire conditions [6-8].

The methods include 3 specimens for every test; the sample size needed for the test is 300 mm of length, 100 mm of width and 10 mm of thickness. During 15 seconds the flame is direct applied on the sample. After that, the distance and time of burning was observed to know if the flame in these samples is self- extinguishing or not. As shown in Table 1 and Table 2.

The result of rigid polyurethane control after test, the polymer was self- extinguishing, with a little bit of smoke but a lot of flame melt, for this case is very dangerous if the material is using on construction as shown in Figure 6.

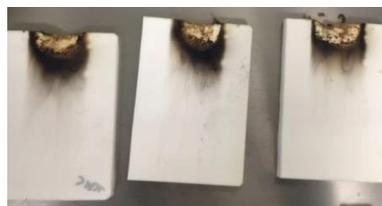


Figure 6. Rigid polyurethane control after test ASTM D635

The result of rigid polyurethane nanocomposite after test, the nanocomposite with ZnO was self- extinguishing, with a lot of smoke but a little bit of flame melt, in this case helps to reduce the spread of fire as shown in Figure 7.



Figure 7. Rigid polyurethane nanocomposite after test ASTM D635

Sample	Time of Burning	Smoke	Result
Ctrl PUR 1	Before 15 seg	Less	1
Ctrl PUR 2	Before 15 seg	Less	1
Ctrl PUR 3	Before 15 seg	Little bit	1

Ctrl = Control Polyurethane, 1= Self-extinguishing

Table 1: Control Polyurethane Results for test ASTM D635

Sample	Time of Burning	Smoke	Result
FZn PUR 1	Before 15 seg	Much more	1
FZn PUR 2	Before 15 seg	Less	1
FZn PUR 3	Before 15 seg	Much more	1

FZn= Polyurethane Nanocomposite with ZnO
1= Self-extinguishing

Table 2: Polyurethane Nanocomposite with ZnO Results for test ASTM D635

CONCLUSIONS

The polyurethane nanocomposite for fireproof applications was evaluated and characterized with UV-VIS spectroscopy, SEM and Atlas horizontal flame chamber equipment. The sample of polyurethane with zinc oxide nanoparticles produces more smoke and more combustion, but the advantage is that, there was less flame dripping with respect to the control sample. The results show that the incorporation of zinc oxide nanoparticles into the polymeric matrix produces the self-extinguishing flame property in the composite material.

The research of polyurethane nanocomposite could open new possibilities to resolve industrial problems. Therefore development and innovation of polymers nanocomposite could support to save lives and to understand properties for new materials for example mechanical (modulus, impact strength), thermal properties (not melt or sag under normal use conditions) and flammability properties (meet regulations depending on the fire risk scenario).

REFERENCES

- [1] Denghui Wu, Peihua Zhao, Yaqing Liu. "Flame retardant property of novel intumescent flame retardant rigid polyurethane foams". *Polymer Engineering & Science*, Volume 53, Issue 11, 2478–2485, November 2013, DOI: 10.1002/pen.23710.
- [2] X. Y. Pang, M. K. Song, Y. Tian, M. W. Duan, "Preparation of high dilatibility expandable graphite and its flame retardancy for LLDPE", *J. Chil. Chem. Soc.*, 57, N° 3, 2012,
- [3] Winey Karen and Vaia Richard, "Polymer Nanocomposites" *MRS bulletin*, Volume 32, April 2007.
- [4] Morgan A. B. and Wilkie C. A. "Flame Retardant Polymer Nanocomposites", Wiley, 2007, ISBN: 9780471734260
- [5] Pholnak C., Sirisathitkul C., Soontaranon S et al. "UV-Vis Absorption and Small Angle X-ray Scattering Spectra of Commercial Polyurethane Coating Filled with Zinc Oxide", *Natl. Acad. Sci. Lett.*, 2016, 39:125, doi:10.1007/s40009-016-0424-6
- [6] ASTM D5132 2011 "Standard Test Method for Horizontal Burning Rate of Polymeric Materials Used in Occupant Compartments of Motor Vehicles".
- [7] ASTM D4986 2010 "Standard Test Method for Horizontal Burning Characteristics of Cellular Polymeric Materials".
- [8] ASTM D635 2014 "Standard Test Method for Rate of Burning and/or Extent and Time of Burning of Plastics in a Horizontal Position".