

## FLAME RETARDING IMPROVEMENT OF NYLON 6,6 COMPOSITES WITH ZEOLITE

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### Abstract

*In this research, the effects of types and contents of zeolite were investigated on flammability of Nylon 6,6. Different zeolite types such as 3A, 4A and 5A at the content of 5, 10 and 15% by weight were compounded with Nylon 6,6 by using twin-screw extruder. Flammability of samples was characterized with limiting oxygen index (LOI), vertical burning test (UL94) and thermogravimetric analysis. LOI of Nylon 6,6 composites with zeolite 5A was higher than Nylon 6,6 composites with zeolite 3A and 4A, respectively. Testing UL94 of virgin Nylon6,6 showed dripping as classified V-2 type while Nylon6,6 composites with 15% wt of zeolite 3A, 4A, 5A had no dripping which was classified as V-0 type. Moreover, the addition of zeolite in Nylon6,6 led to relatively lower thermal degradation compared to neat Nylon 6,6 especially for the case of Nylon 6,6 with zeolite type of 4A.*

### 1. Introduction

Nylons are widely used in many applications, such as textile industry and motor vehicle. Numerous types of Nylons are used i.e., Nylon 6, Nylon 6,6, Nylon 6,10. Nylons 6,6 is superior in many applications due to its outstanding dimensional stability, higher melting point and more compact molecular structure and excellent abrasion resistance. In textile industry, Nylon 6,6 is used for several products such as carpet, rope and curtain. These products are the formation of melting drip during burning which leads to spread of fire. The researchers have planned to study on flame retardant property of Nylon 6,6 by adding flame retardant. Flame retardants defined as chemical compounds that modify pyrolysis reactions of polymer or oxidative reactions implied in the combustion by slowing down or by inhibiting them. The flame retardant can act in various ways i.e. physically or chemically. Many types of flame retardants are used in consumer products. They are mainly phosphorus, antimony, and boron-containing compounds and halogen. However, halogen has been undergoing restricted because of the increasing concern about the possible hazard to the environment. Therefore, phosphorus-based and intumescent flame retardant system had been attracted more attention for flame retardant treatment of Nylon [1].

Zeolite is an alternative material for using as the flame retardant for improving flame retardant property of polymers [2-4]. Zeolites are the most favorable host materials due to their highly ordered pore systems, channels and cages of different dimensions and shape and the surface with negatively charge-balanced with exchangeable cations. Zeolite could absorb heat of combustion within their pores to reduce burning and enable a silicon compound to form on the polymer surface.

In this research, the effects of types and contents of zeolite were investigated on flammability of Nylon 6,6. Different zeolite type such as 3A, 4A and 5A and content 5, 10 and 15% by weight and along with Nylon 6,6 were compounded by using twin-screw extruder. Then, the composites were molded by using injection molding machine. Flammability of samples was characterized with vertical burning test, limiting oxygen index, thermogravimetric analysis. Moreover, morphological property of the samples was investigated by scanning electron microscope.

## 2. Experimental

### 2.1 Materials

The polymer used was Nylon6,6 provided by BASF. The additives were zeolite (type 3A, 4A and 5A) supplied by Grandbiz trading company. The unit cell of type 3A, 4A and 5A zeolite is classified by chemical formula:  $M[(AlO_2)_{12}(SiO_2)_{12}].27H_2O$ , where  $M = K, Na$  and  $Ca$ , respectively. Pore size of zeolite 3A, 4A and 5A are approximately 3, 4 and 5 Angstrom, respectively. Acetone was used for moisture elimination from zeolite.

### 2.2 Compounding

Zeolites were mashed by ball mill and were screened by grinder for size 75 – 150 nm. Then, zeolites were soaked in acetone and continuously stirred for 2 hrs. Zeolites were dried at 70 °C for 24 hrs. and Nylon 6,6 were dried at 100 °C for 24 hrs. Different zeolite type such as 3A, 4A and 5A and content 5, 10 and 15% by weight along with Nylon 6,6 were mixed by high speed mixer. The composites were compounded by using twin-screw extruder. Then, the composites were molded by using injection molding machine.

### 2.3 Characterization

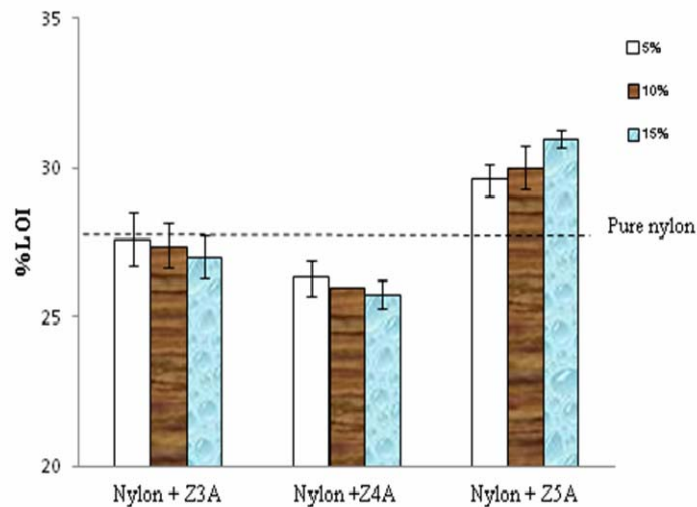
*Flammability test*, Standardized size samples according to UL-94 were undergone the vertical combustion test. The limiting oxygen index (LOI) test method for measuring the minimum oxygen concentration to support the candle-like combustion of composites was determined according to ASTM D-2863. The minimum concentration of oxygen in a mixture of oxygen and nitrogen flowing upward in a test column that supported combustion was measured under equilibrium conditions of candle-like burning. The gas flow rate in the column was adjusted to  $4 \pm 1$  cm/s.

*Thermo-gravimetric analysis*; Thermogravimetric were carried out by TGA7 Perkin-Elmer Thermal analyzer. Sample weight was in the range 3-10 mg. All samples for thermo-gravimetric were measured from 50 °C to 800 °C at the heating rate of 10 °C/min. Nitrogen was used as a carrier gas with a constant flow rate during analysis.

Scanning electron microscopy; SEM analysis was carried out on MX2000 of Camtrac company to investigate the dispersion of flame retardant in Nylon6,6 matrix.

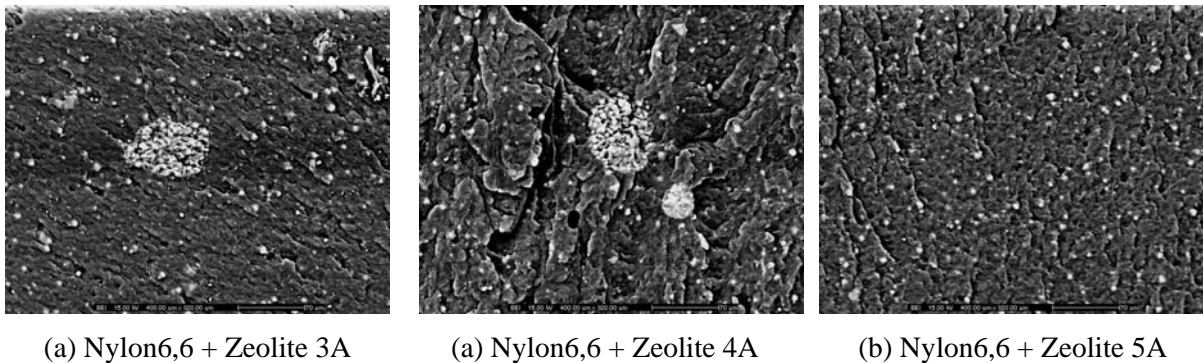
### 3. Results and discussion

From Figure 1, LOI of Nylon6,6 composites with zeolite 5A is higher than Nylon composites with zeolite 3A and 4A, respectively. When nylon 6,6 composites were exposed to heat of combustion, those radicals were released during the decomposition process. They could be trapped on the surfaces which were comprised of silica and alumina elements. Rationally, those radicals on such surface are much less reactive than free chain radicals.



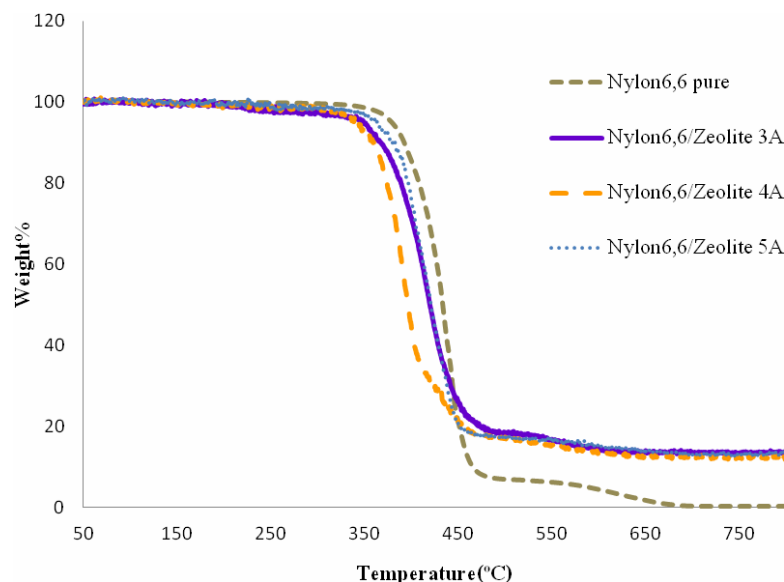
**Figure 1.** LOI of Nylon6,6 composites with different type of zeolite; zeolite 3A, zeolite 4A and zeolite 5A with content of 5%, 10% and 15%.

Zeolite 5A has the biggest pore diameter (5 Angstrom) comparing with the pore size of zeolite 3A (3 Angstrom) and zeolite 4A (4 Angstrom) cause more heat absorption. Moreover, it could be explained by zeolite dispersion in Nylon6,6 matrix. Zeolite 5A particles are dispersed very well throughout Nylon6,6 matrix as seen in Figure 2. While zeolite 3A and 4A particles are likely to agglomerate because it may be the interaction between particle-particle which is stronger than polymer-particle. And these interactions could be the influence from polarity and ion exchange. Therefore, Nylon6,6 composites with zeolite 4A illustrated the lowest LOI value.



**Figure 2.** SEM micrograph of Nylon6,6 composites with 15% wt of zeolite

Testing UL94 with pure Nylon 6,6 showed dripping as V-2 type while Nylon6,6 composites with 15% wt of zeolite 3A, 4A, 5A had no dripping classified as V-0 type. It could be explained by zeolite structure composed of aluminum-silicates mineral. Char formation could be occurred on the surface of composites during combustion as seen from TGA results of residue as shown in Figure 3. However, addition of zeolite in Nylon6,6 lead to low thermal degradation but not significantly for zeolite type of 3A and 5A.



**Figure 3.** Weight loss measurement carried out under air condition of Nylon6,6 composites with 15% wt of zeolite by TGA thermogram.

#### 4. Conclusions

Zeolite could act as flame retardant for Nylon 6,6 especially zeolite 5A. Pore diameter is the key point for absorbing the volatile radicals during the combustion process. Moreover, it could cause relatively high surface areas at which Nylon 6,6 matrix could interact with and thus dispersed quite well into polymer matrix. Char could be formed on the surface to obstruct oxygen and heat reaching the polymeric material.

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