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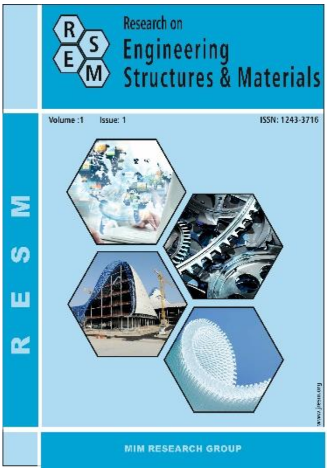

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Research Article

Cone calorimeter evaluation on fire resistance of rigid polyurethane foams filled with nanoclay / intumescent flame retardant materials

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Abstract

Natural minerals like calcite, clay, kaolin and dolomite are used as fillers up to 15 wt % in productions of rigid polyurethane foams to reduce production costs and enhance the fire resistance. In general, only filler additions do not significantly enhance the fire resistance of the foams. Therefore, different flame retardant materials are added together with the fillers. In this study, effects of 10 wt % nanoclay/5 wt % an intumescent flame retardant additions on combustion behaviour of rigid polyurethane foam were investigated by cone calorimeter tests. Heat release rate, total heat released, ignition time, smoke production and carbon monoxide emissions of neat and nanoclay/intumescent flame retardant filled polyurethane foams were examined. The experimental results showed that 10 wt % nanoclay/5 wt % the intumescent flame retardant addition significantly improved the fire resistance.

1. Introduction

Rigid polyurethane foams are used in thermal insulation applications due to their low thermal conductivities [1]. However, they can easily ignite and burn when they exposed to a heat source. Therefore, it is required to enhance thermal decomposition and fire resistances of the foams [2]. One of the methods used for these purposes is addition of different fillers and/or flame retardant materials into the foams [3]. There are different kinds of flame retardant materials added into the foams. The effects of flame retardants may change depending on their chemical compositions. The effects of some flame retardant materials like metal hydroxides can be seen with addition of high content of them. However, in this case mechanical properties may be worsened. Therefore, different studies have been focused on alternative flame retardants like intumescent flame retardants which generates a char layer building up a barrier between the oxygen and the material and this char layer protects the underlying materials from the flame [4, 5].

The effects of nanoclay/intumescent flame retardant additions on the thermal conductivity, the cell size, the thermal degradation and the fire resistance (UL 94 burning test) of the rigid polyurethane foams were presented in the previous study of the authors [6]. This study is an extension of the previous study. Since UL 94 burning test could give only limited information about the fire resistance of the foams, cone calorimeter tests were performed to investigate in detail the effects of nanoclay and nanoclay/intumescent flame retardant additions on the fire resistance of the foams. In this study, only the effects of 10 wt % nanoclay/5 wt % intumescent flame retardant addition on fire resistance of the foam were presented.

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2. Materials and Methods

2.1. Materials

The main components of polyurethane which are polyol (Evopur 1122-28) and isocyanate (PMDI 92140 – polymeric diphenyl methane diisocyanate) were purchased from TEKPOL Technical Polyurethane Ltd. (Turkey). The density and viscosity of the polyol are 1130 kg/m^3 and 300 mPa.s, respectively (at 25 ^{o}C). Meanwhile, the isocyanate is characterized by 31.2 % of NCO groups, with the density and viscosity of at 25 ^{o}C, 1230 kg/m^3 and 210 mPa.s, respectively. Nanoclay (NCL) was purchased from Nanoclay Ltd. (Turkey) and the average particle size (d_{50}) of the nanoclay was 50 nm. It is composed of 53.28 % SiO_2, 20.67 % Al_2O_3, 6.13 % Fe_2O_3, 2.82 % MgO and 1.71 % CaO. Ammonium polyphosphate (APP, n >1000) which was purchased from FR-MASTER was phase II and the average particle size (d_{50}) of APP was about 8 µm. Pentaerythritol (PER) was kindly supplied by Marmara Chemistry Company - Turkey and has average particle size below 75 µm.

2.2. Sample Preparation

APP, PER and NCL were dried in an oven at 100 °C for 24 hours to remove the humidity from them. The intumescent flame retardant (IFR) was obtained by mixing APP and PER. The mass ratio of APP/PER was adjusted as 2/1 [5]. The amount of raw materials was reduced as the amount of NCL/IFR to keep the density of the foam at 40 ± 0.5 kg/m^3. The detailed information about the sample content was given in Table 1. NCL/IFR were poured into the polyol and a rotor-stator type of mechanical homogenizer (Heidolph Silent Crusher M Model) with a speed up to 26.000 rpm was used for dispersion. Then an ultrasonic homogenizer is used to disperse the nano particles [7]. NCL/IFR filled polyol and isocyanate were stirred with a mechanical stirrer at 3000 min^{-1} for 12 s and then the mixture was poured into the mold. The mold was put under the pre-heated press to keep the temperature at 40 ± 2 ^{o}C for 30 min. The samples were kept in the laboratory conditions for 24 hours to complete curing process after removing the samples from the mold. The samples were put into the conditioning device at the temperature 23 ± 1 ^{o}C and relative humidity 50 ± 3 % for 48 hours before the experiments.

Table 1 Formulations of PUR and PUR/NCL/IFR

Sample Name	Polyol (%)	Isocyanate (%)	NCL (%)	IFR (%)	Total (%)
PUR	46.0	54.0	-	-	100
PUR+10NCL+05IFR	39.1	45.9	10	5	100

2.3. Cone Calorimeter

The fire behaviours of the samples were investigated by a cone calorimeter manufactured according to ASTM E-1354 [8] and ISO-5660 [9] standards. The samples were cut into 100 x 100 x 50 mm and wrapped in aluminium foil before the fire tests. The sample was exposed horizontally to an external heat flux of 35 ± 1 kW/m^2. All samples were tested three times and cone calorimeter data were reported as average values. The mass loss, temperatures, smoke and CO were recorded with the special software simultaneously in 1 s increment. In addition, heat release rate (HRR) and total heat released (THR) were calculated from the measurements. The detailed information was given in related standards [8, 9].

3. Results and Discussion

Heat release rate (HRR) is one of the most important parameters to characterize fire resistance [10]. The heat release rate curves of neat and NCL/IFR filled foams were given in Fig. 1. Both of them showed similar characteristics of thermally thick charring (residue forming) samples. However, it is seen that PUR burned fast and the HRR of PUR reached to the peak value of 117.6 kW/m^2 in 55 s. Although NCL/IFR addition did not significantly affect the ignition behaviour of the foam (time to ignition) and burning of the foam in 35 s, it slowed down flame propagation and decreased the HRR. Maximum HRR of the foam decreased to 106.8 kW/m^2 with NCL/IFR addition. Meanwhile, the HRR values of NCL/IFR filled foam were lower than that of neat PUR during rest of the time. Similar enhancement was also reported by other researchers [11, 12]. Intumescent flame retardant decomposes and produces a char layer. This char layer can partially hinder the decomposition of the material and reduces the heat release rate [5, 6].

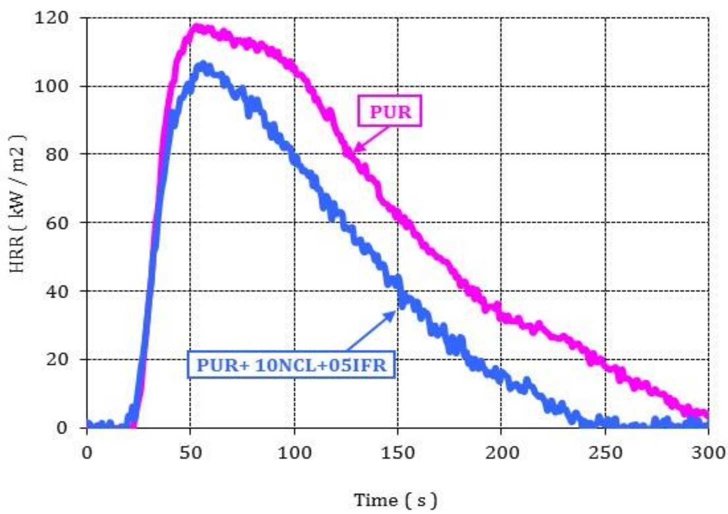

Fig. 1 Heat release rates of PUR and PUR/NCL/IFR

Fig. 2 shows total heat released (THR) curves of PUR and PUR/NCL/IFR nanocomposite. It can be clearly seen that addition of NCL/IFR substantially decreased the THR value. THR values of PUR and PUR/NCL/IFR were 15.9 MJ/m^2 and 11.2 MJ/m^2 in 300s, respectively. The reduction of THR value with the addition of NCL/IFR can be explained with the barrier effect of the char generated from NCL and IFR [5, 13].

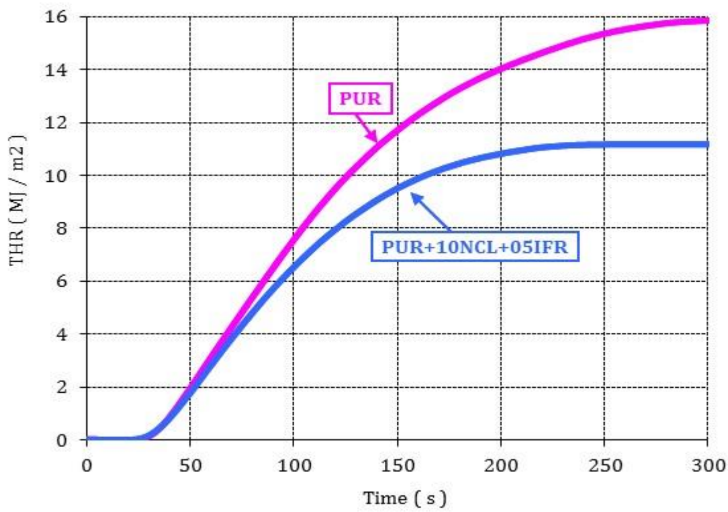

Fig. 2 Total heat released of PUR and PUR/NCL/IFR

CO and smoke generated by burning of rigid polyurethane foams are major causes of poisoning during fires [14]. The productions of smoke and CO which are generated due to the incomplete burning of the foam mainly depend on the properties of the foams and the fire intensity. In general, smoke and CO which are generated with the thermal decomposition of the foam in the condensed phase passes through the carbon layer and then smoke builds up into smoke particles in the gas phase [15]. In addition, CO generation may continue in smoldering combustion stage after flame ceases.

Smoke (extinction coefficient) and CO productions of PUR and PUR/NCL/IFR were given in Fig. 3 and Fig. 4, respectively. As it can be seen from the figures, CO and smoke trends in 300 s are similar. Although NCL/IFR addition did not significantly decrease the peak values of smoke and CO, it resulted decreases in smoke and CO generation during the rest of burning times. The reduction in smoke and CO may be explained with the low combustible material content in the NCL/IFR filled foam, fuel lean conditions in the certain periods and the intumescent effect of IFR which is defined as formation of a reinforced and cohesive char layer on the foam surface. This char layer provided an effective barrier against, oxygen, heat and combustible gases. It is thought that the presence of nanoclay additionally favored the formation of char layer limiting the mass loss and increasing the thermal stability of the foam [16, 17].

In other words, NCL/IFR addition affected the condensed phase and substantially prevented generation of smoke and CO in condensed and gas phases of the combustion. Although smoke generation was completely diminished with the addition of NCL/IFR in 200 s, CO generation appeared at low levels. Meanwhile, it should be pointed out that NCL/IFR addition also affected the smoldering combustion stage resulting in less CO generation after ceasing of the flame.

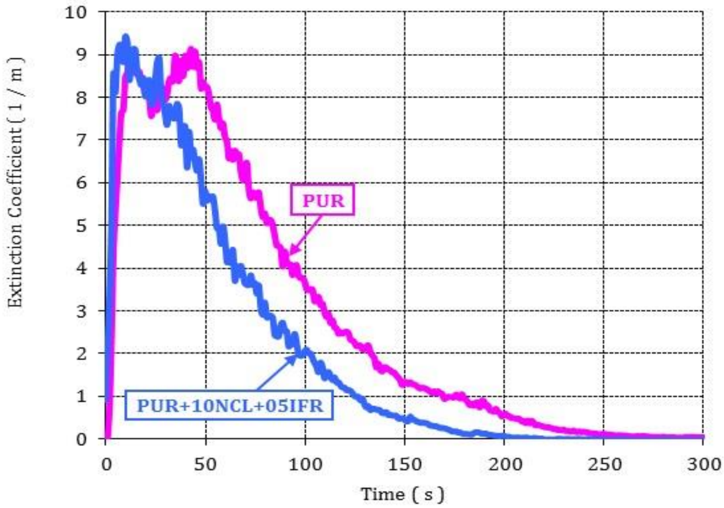

Fig. 3 The extinction coefficients of PUR and PUR/NCL/IFR

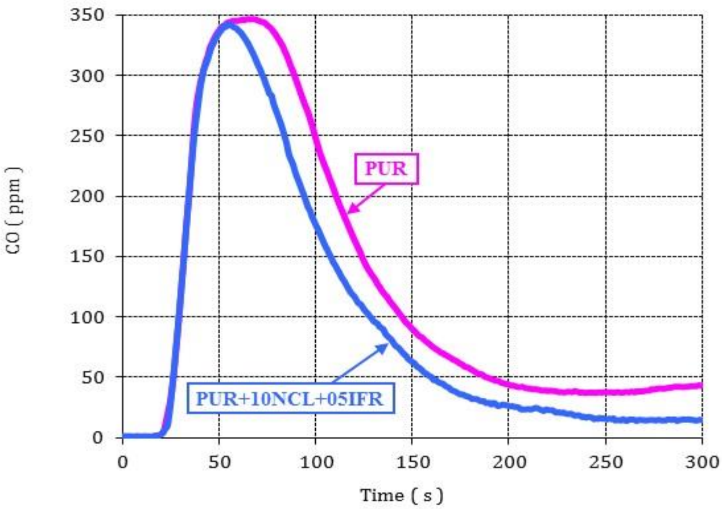

Fig. 4 CO emissions of PUR and PUR/NCL/IFR

5. Conclusions

The effects of NCL/IFR additions on fire behaviour of the rigid polyurethane foams were investigated by using a cone calorimeter. The experimental results indicated that NCL had a good synergistic effect with the IFR in the rigid polyurethane foams in terms of better fire resistance. 10 wt % NCL and 5 wt % IFR additions decreased maximum HRR and THR approximately 9.2 % and 29.6 %, respectively. Although NCL/IFR filled rigid polyurethane foam initially showed similar trend for smoke and CO emissions with the neat PUR and this resulted in closer peak values, the smoke and CO emissions of the NCL/IFR filled foam sharply decreased under those of the neat foam and generate lower smoke and CO emissions during the rest of burning times. Therefore, it is advised to use fillers with flame retardants to enhance the fire resistance and decrease smoke/CO generations of the rigid polyurethane foams.

Acknowledgments

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