Journal of Thermal Engineering, Vol. 5, No. 2, Special Issue 9, pp. 70-76, February, 2019
Yildiz Technical University Press, Istanbul, Turkey

EFFECTS OF KAOLIN ADDITIONS ON THERMAL BEHAVIORS OF RIGID POLYURETHANE FOAMS

B. Aydoğan[1], N. Usta[2,*]

ABSTRACT

Thermal insulation is very important issue in many industrial applications and different materials are preferred to satisfy the thermal insulation depending on the applications. One of the most important properties of the thermal insulation materials is low thermal conductivity. In addition, the cost of the material is another important factor. Among the thermal insulation materials, rigid polyurethane foams are used in automotive, transportation and building sectors due to lower thermal conductivity. Although the thermal conductivity of the rigid polyurethane foam is lower than those of many other thermal insulation materials, other thermal insulation materials may be preferred in some applications due to their lower costs. Therefore, different natural inorganic minerals have been added as fillers into the foams, mainly to reduce raw materials costs. In this study, kaolin, which is a cheap natural inorganic mineral, was incorporated into rigid polyurethane foams in 5, 10 and 15 % in mass. Effects of kaolin addition on thermal decomposition and thermal conductivity of rigid polyurethane foams were investigated. The results revealed that the incorporations of kaolin into the foams slightly increased the thermal conductivities of the foams. However, it was found that kaolin addition enhanced the thermal stability of rigid polyurethane foams.

Keywords: *Rigid Polyurethane, Kaolin, Thermal Conductivity, Thermal Decomposition*

INTRODUCTION

Different kinds of materials are used to satisfy thermal insulation in many industrial applications. There are mainly two important factors for choosing the thermal insulation materials. First factor is low thermal conductivity and second one is the price of the material. Rigid polyurethane foam (PUR) is preferred in many industrial applications such as automotive, transportation and building sectors due to its low thermal conductivity [1-4]. Although, the thermal conductivity of PUR is lower than those of many thermal insulation materials, PUR is not preferred in some applications due to its higher price. Therefore, natural inorganic minerals like clay, talk and calcite have been used as fillers in rigid polyurethane foam productions to reduce raw materials costs [5-7]. The particle size, chemical composition and amount of filler are important parameters affecting the thermal conductivity, mechanical and thermal stability of the foams [8]. In addition, there is an important issue related to usage of the rigid polyurethane foams. The thermal conductivity coefficients of the foams increase by time and it is called as thermal aging [9]. Therefore, thermal aging of the foams filled with inorganic minerals should be investigated.

Moreover, pure rigid polyurethane foams have low thermal stability and low resistance to fire. When they are exposed to the external heat flux, they are easily decomposed and combustible/non-combustible gases and smoke may be released [10-13]. The addition of natural mineral matters may enhance the thermal stability of the foams [14-17]. In this study, effects of 5, 10 and 15 wt. % kaolin additions on thermal degradation behavior and thermal conductivity coefficient of the rigid polyurethane foams (PUR) were investigated.

MATERIALS AND METHODS

Materials

Isocyanate (PMDI 92140) and polyol (Evopur-1122-28) which are the raw materials of the rigid polyurethane foam were bought from TEKPOL Ltd. (Turkey). The densities of polyol and isocyanate at 25 ^{o}C are 1130 kg/m^3 and 1230 kg/m^3, respectively. Meanwhile, the viscosities of polyol and isocyanate at 25 ^{o}C are 300 mPa.s and 210 mPa.s, respectively. OMYA Mining Ltd. (Turkey) generously supplied the kaolin which is mainly composed of 77.96 % SiO_2, 19.39 % Al_2O_3, 1.01 % CaO, 0.45 % MgO. The average particle size (d_{50}) of the kaolin is about 4 μm.

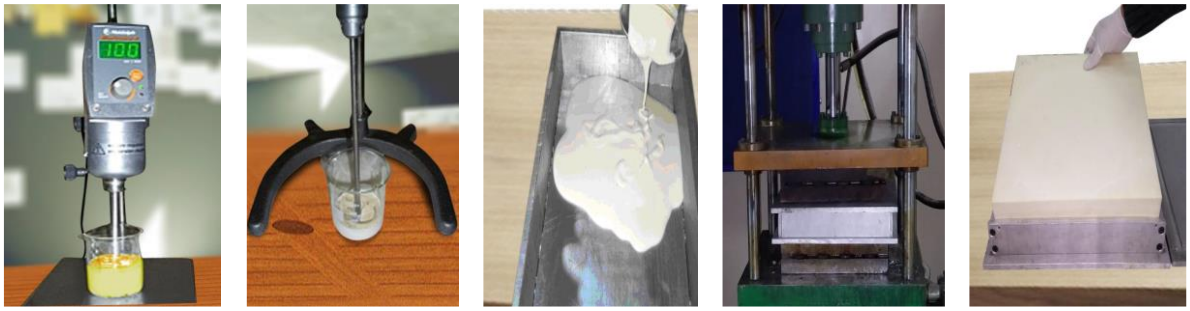
This paper was recommended for publication in revised form by Regional Editor Bekir Şener
[1]Department of Electrical and Energy, Voc. Sch.Tech. Sci. Mehmet Akif Ersoy University, Burdur, TURKEY
[2]Department of Mechanical Engineering, Energy Division, Pamukkale University, Denizli, TURKEY
**E-mail address: n_usta@pau.edu.tr*
Orcid id: 0000-0002-7928-5867, 0000-0002-5909-027X
Manuscript Received 7 November 2017, Accepted 27 March 2018

Sample Production

Initially, kaolin (KAO) which was dried at 100 °C for 24 hours to remove the moisture was added into the polyol and homogenization of the kaolin-polyol mixture was performed by using a mechanical homogenizer (Heidolph Silent Crusher M Model) running at 20,000 rpm for 5 min. Then the isocyanate was added into the kaolin-polyol mixture and they were stirred by using a mechanical stirrer (Heidolph Overhead Stirrer RZR 2020) running at 3,000 min^{-1} for 12 s. The amounts of the polyol and the isocyanate were reduced as the amount of kaolin addition to keep the density of the foam at 40 ± 0.5 kg/m^3. The mixture was poured into the aluminum mold which was pre-heated at 40 °C. The aluminum mold was kept under the press at 40 °C for 25 min. The sample was removed from the mold and waited in the production laboratory for 24 hours in order to satisfy completion of the curing process of the foam. The detailed information about the samples is given in Table 1 and the sample production stages are shown in Fig.1.

Table 1. PUR and PUR/KAO composites

Sample name	PMDI 92140 Polyol (%)	Evopur-1122-28 Isocyanate (%)	Kaolin (%)	Total (%)
PUR	45.9	54.1	-	100
PUR+05KAO	43.6	51.4	5	100
PUR+10KAO	41.3	48.7	10	100
PUR+15KAO	39.0	46.0	15	100



(a) (b) (c) (d) (e)

Figure 1. Sample production stages (a) Homogenization of polyol-kaolin (b) Mixing of isocyanate and polyol-kaolin (c) Pouring of the mixture into the mold (d) Curing in a heated press (e) Removing the sample from the mold

Thermogravimetric Analysis (TGA)

Thermogravimetric analyzes are important tests to understand the structural and thermal properties of polymeric materials [18]. Perkin-Elmer Diamond TG/DTA was used to perform thermogravimetric analysis of the samples. Ceramic pans were used in the tests which were performed between 40 and 800 °C at a heating rate of 20 °C/min. High purity nitrogen gas was purged at a flowrate of 200 mL/min to provide the inert environment in the oven of the equipment. The sample mass was adjusted as 10 ± 1 mg in the tests. The real time mass loss and derivative mass loss were recorded via PYRIS software of Perkin-Elmer Inc. during the experiment.

Thermal Conductivity

Kyoto QTM-500 which can measure the coefficient of thermal conductivity of thermal insulation materials within 5 % accuracy was used to measure the thermal conductivity coefficients of the foams according to ASTM C1113 [19]. The thermal conductivity coefficient of each foam sample was determined as the average of three measurements.

Average Cell Size Determination

An optical Nikon SMZ 1500 Stereo microscope which was connected to a computer was used to examine the morphology of the foam samples. The images were analyzed and the cell sizes of the foams were measured according to ASTM D 3576-04 [20]. The cell size of each foam sample was determined as the average of five measurements.

RESULTS AND DISCUSSION

Thermal decomposition behaviors of the samples were investigated with the thermogravimetric analysis. Figure 2 shows TG and DTG curves of PUR and PUR/KAO composites. In general, KAO additions did not significantly modify the decomposition mechanisms of PUR. There were three main decomposition mechanisms for both PUR and PUR/KAO composites. However, the main maximum decomposition temperature (T_{2max}) for the sample including 15 wt. % KAO was obtained as 362.99 ºC which is 4.45 °C higher than that of PUR (358.54 ºC). Meanwhile, the second maximum decomposition rate for PUR was obtained as 16.93 %/min. This value was 12.96 %/min for PUR+15KAO. Addition of the kaolin into the foam resulted in increasing of the maximum decomposition temperatures and decreasing of the maximum decomposition rates [21, 22].The particles of kaolin acted like a barrier and prevented the volatiles to leave from the foam and decrease the decomposition rate of the material. T_{50wt} was increased approximately 38 ºC with the addition of 15 wt. % KAO. In addition, KAO addition increased the residues at 800 ºC [9, 23, 24]. Although the residue at 800 ºC for PUR was 16.03, 15 wt. % KAO addition increased the residue to 28.33 %. The detailed results are given in Table 2.

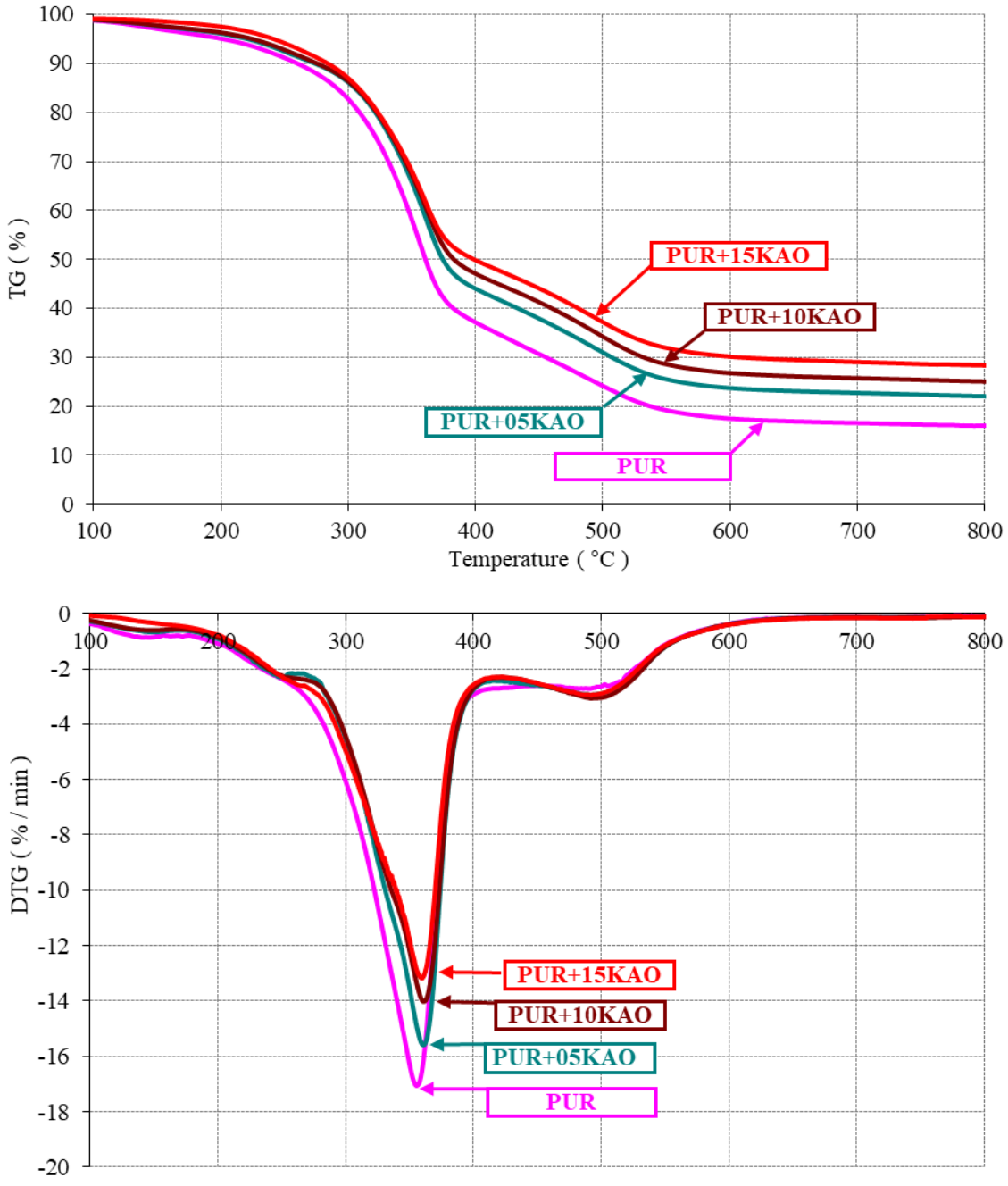


Figure 2. TG and DTG curves of PUR and PUR/KAO composites

The effects of kaolin additions on the average cell size of the foams were found and shown in Figure 3. The average cell size of PUR was determined as approximately 690 µm. The average cell sizes increased with the addition of KAO. The cell sizes of PUR+5KAO, PUR+10KAO and PUR+15KAO were approximately 800, 830 and 860 µm, respectively. Although the average particle size of KAO (d_{50}) was about 4 µm, kaolin particles broke down some of the cell walls. Therefore, average cell sizes were increased depending on the kaolin content in the foam.

Table 2. The detailed results obtained by thermogravimetric analysis of the foams

	SAMPLES			
	PUR	**PUR+05KAO**	**PUR+10KAO**	**PUR+15KAO**
$T_{\%5(m/m)}$ (°C)	201.70	220.66	224.91	241.38
$T_{\%10(m/m)}$ (°C)	260.13	273.69	275.75	283.99
$T_{\%50(m/m)}$ (°C)	360.36	374.37	383.07	398.81
T_{1maks} (°C) **R_{1maks} (%/min)**	143.29 -0.8218	157.34 -0,6287	159.07 -0,6081	163.5 -0.4042
T_{2maks} (°C) **R_{2maks} (%/min)**	358.54 -16.93	363.72 -15.50	364.39 -13.91	362.99 -12.96
T_{3maks} (°C) **R_{3mak} (%/min)**	497.48 -2.646	506.35 -2.827	507.29 -2.981	506.37 -2.803
Residue at 800 °C (%)	16.03	22.04	25.04	28.33

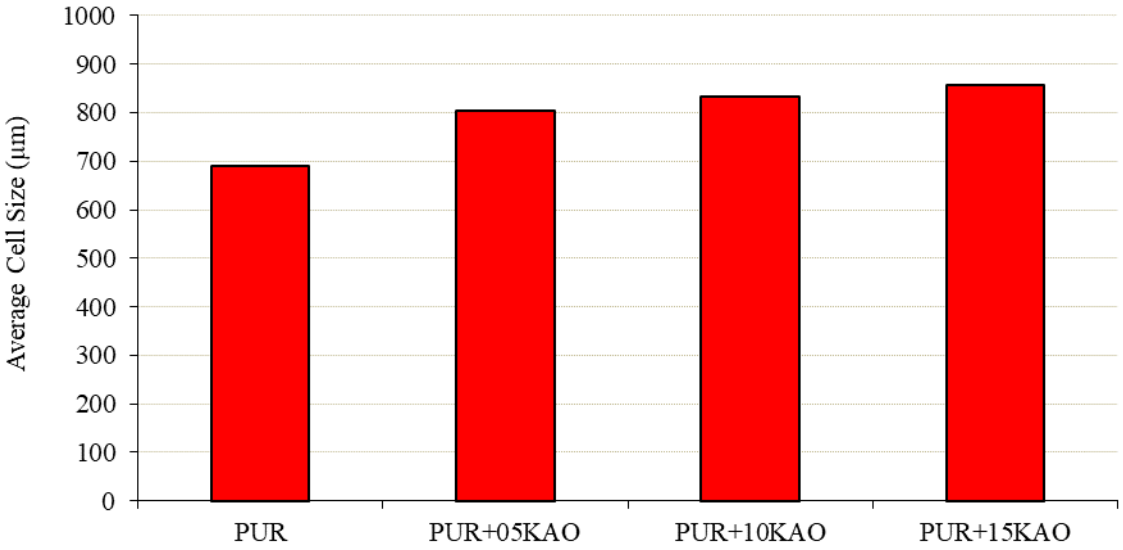


Figure 3. Average cell sizes of PUR and PUR/KAO composites

Figure 4 shows coefficients of thermal conductivity of PUR and PUR/KAO foams in first and fifty fifth days of the foam productions. Although 5 wt. % KAO addition into the rigid polyurethane foam did not significantly affect the thermal conductivity coefficient, 10 and 15 wt. % KAO additions increased it approximately 1.8 and 12.5 % for the first day. The increasing amounts of the coefficients were determined as 1, 8.2 and 10.6 % for 55th day. Thermal conductivity coefficient of rigid polyurethane foam mainly depends on cell size, closed cells content and the gas inside the cells [9, 22, 25]. Increases in the thermal conductivity coefficients of PUR/KAO composites may be explained with increasing cell sizes and decreasing the closed cell content of the foams due to breaking down of cell walls with kaolin particles.

CONCLUDING REMARKS

Effects of 5, 10 and 15 wt. % kaolin additions on thermal decomposition, average cell size and thermal conductivity of rigid polyurethane foams were investigated. It was determined that although the incorporation of

kaolin into the foam resulted in the enhancement of the thermal stability of the foams, it slightly increased the coefficient of thermal conductivity and the average cell size of the foam. As a result, it can be concluded that the kaolin can be used as a cheap filler up to 15 wt. % to decrease the production costs of rigid polyurethane foams without remarkable negative impacts in the thermal insulation of the foams.

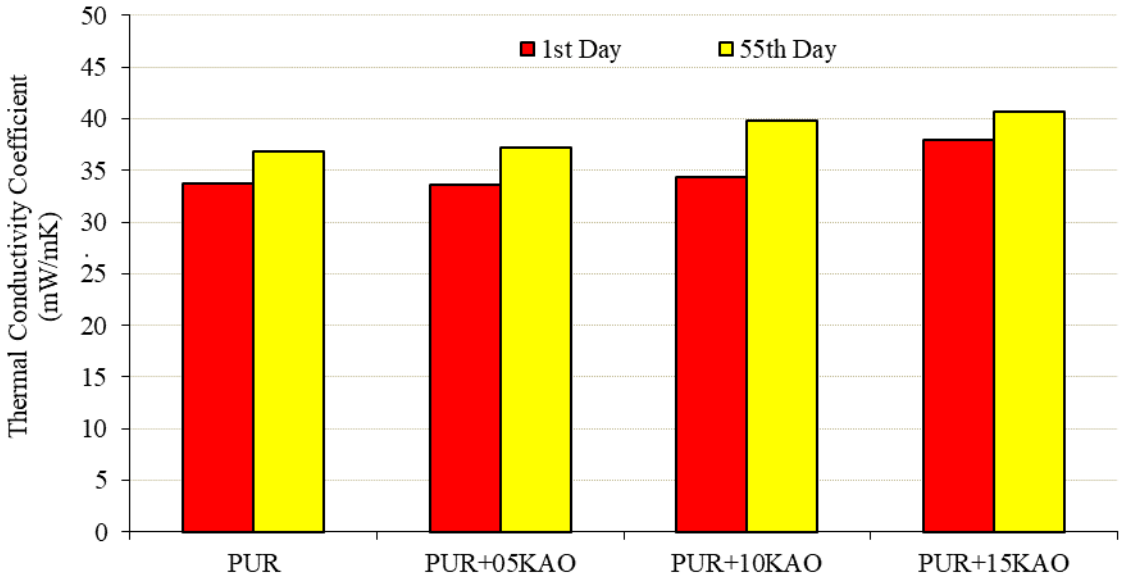


Figure 4. Thermal conductivity coefficients of PUR and PUR/KAO composites

ACKNOWLEDGMENTS

The authors would like to thank the Pamukkale University Scientific Research Council (BAP) for supporting this study under project contract No. 2014FBE026. Since the some of the equipment and materials were provided with the support of The Scientific and Technological Research Council of Turkey (TUBITAK) under project contract No. 108T246, the authors would like to thank TUBITAK.

NOMENCLATURE

DTG	Mass loss rate (%/min)
KAO	Kaolin
PUR	Rigid polyurethane foam
PUR+05KAO	95 % PUR and 5 % KAO
PUR+10KAO	90 % PUR and 10 % KAO
PUR+15KAO	% PUR and 15 % KAO
TG	Mass loss (%)
$T_{\%5(m/m)}$ (°C)	Temperature at 5 % mass loss
$T_{\%10(m/m)}$ (°C)	Temperature at 10 % mass loss
$T_{\%50(m/m)}$ (°C)	Temperature at 15 % mass loss
T_{1maks} (°C)	Maximum decomposition temperature in 1st stage
T_{2maks} (°C)	Maximum decomposition temperature in 2nd stage
T_{3maks} (°C)	Maximum decomposition temperature in 3rd stage
R_{1maks} (%/min)	Maximum decomposition rate in 1st stage
R_{2maks} (%/min)	Maximum decomposition rate in 2nd stage
R_{3mak} (%/min)	Maximum decomposition rate in 3rd stage
wt.	Weight

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