The Effects of Intumescent Flame Retardant Including Ammonium Polyphosphate/Pentaerythritol and Fly Ash Fillers on the Physicomechanical Properties of Rigid Polyurethane Foams

Ali Rıza Tarakcılar

Materials Science Division, Mechanical Engineering Department, Pamukkale University, Denizli 20070, Turkey

ABSTRACT: In this study, rigid polyurethane foams that contain up to 5.0 wt % fly ash (FA) being a by-product of thermal power stations and being cheap source were successfully produced using a polyurethane injection machine. The effects of FA content on the thermal conductivity, compressive strength, and flammability were investigated. The morphology of the cell was observed under a special microscope. The incorporation of FA in rigid polyurethane foams may dramatically decrease production costs and reduce environmental pollution. In addition, the effects of intumescent flame retardant composed of ammonium polyphosphate and pentaerythritol were examined in pure rigid polyurethane foams and FA-rigid polyurethane foams. It was found that 5.0 and 7.5 wt % intumescent flame retardant loadings enhanced the thermal stability and improved the flammability resistance of the foams. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2095–2102, 2011

Key words: polyurethanes; fillers; flame retardance; mechanical properties; thermal properties

INTRODUCTION

Polyurethane materials, which are produced through interaction between polyols and polyisocyanates by incorporating some additives such as catalysts, foaming agents, surfactants, flame retardants, and fillers, can be used in different sectors including thermal insulation and automotive sectors. Recently, studies related to the polyurethane and its composites have been increased to a large extent. Although flame retardants are used to enhance thermal properties of polyurethane materials,[1] fillers are mainly used in them with the primary goal of reducing production costs.[2] Meanwhile, fillers may improve some properties of polyurethane materials. However, care should be taken regarding the compatibilities of flame retardants and fillers with polyurethane materials and negative effects on their mechanical and thermal properties.

There are some minerals such as silica, clay, and calcium carbonate having been used in polyurethane materials.[3] In addition, fly ash (FA), a by-product from thermal power stations fuelled by pulverized coal, has been considered as a filler in different polymers.[4] It was reported that FAs improved thermal stability of some of polymer materials.[5] Fly ashes as fillers have not been much examined with respect to the production of polyurethane materials.[6] Because FAs are by-product from the thermal power stations, and they are cheap and produced in great amounts in various countries throughout the world. Although some amount of FAs find its way to industry, most of them remains unused in the vicinity of power stations generating environmental pollution.

There are different kinds of flame retardant materials such as alumina trihydrate,[7] expandable graphite,[8–12] alumina trihydrate and triphenylphosphate,[7] decabrominated dipheny ethane,[10] melamine polyphosphate and melamine cyanurate,[13] phosphorus-melamine-urea-formaldehyde,[14] and aluminum phosphinate[15] used in rigid polyurethane foams. Furthermore, the intumescent flame retardant systems have been considered in rigid polyurethane foams.[16] For example, ammonium polyphosphate (APP) as an intumescent flame retardant has been used for polyurethane materials.[8] Intumescent flame retardants including blowing agents work in the way that they decompose generating nonflammable gases resulting in the char that expands and

Correspondence to: Dr. A. R. Tarakcılar (tarakci@pau.edu.tr or alirizatarakcilar@gmail.com).

	Unit	Polyol component	Isocyanate component
Density (25°C)	g/cm^3	1.13	1.23
Viscosity (25°C)	mPa.s	240	210
NCO content	%	–	31.2

provides insulating crusts. This process protects the material from heat flux or flame acting as a physical barrier limiting the escape of volatile products toward the flame and the diffusion of oxygen toward the polyurethane.[8,17]

In this study, rigid polyurethane (PUR) foams used as an insulating material were taken into consideration. The PUR foams that contain up to 5.0 wt % FA and 5.0 wt % intumescent flame retardant including APP and pentaerythritol (PER) were successfully produced using polyurethane injection machine. The effects of the intumescent flame retardant and FA fillers on the physicomechanical properties of PUR foams were investigated.

EXPERIMENTAL

Materials

PUR foam raw materials which are Elastopor H H2011/4 as a polyol component and PMDI 92140 polymeric diphenylmethane diisocyanate as an isocyanate component were purchased from Elastogran BASF Group (İstanbul, Turkey) in industrial grade. Their technical specifications are listed in Table I.[18] The polyol component was provided as a system containing all necessary additives for the foaming process. A FA filler as a particulate filler was supplied by Kemerkoy Power Station (Mugla, Turkey). The chemical composition of the FA is listed in Table II.[19] The information about particle size of the FA is as follows: 97.9% of particles are less than 200 μm; 85.9% of particles are less than 90 μm; 69.5% of particles are less than 45 μm. APP (Exolit AP 423, $n > 1000$) was supplied from Clariant (İstanbul, Turkey). The crystal modification of APP was phase II. The average particle size (d_{50}) was approximately 8 μm. Pentaerythritol (PER) having particle size below 75 μm was supplied by MKS Marmara Chemistry Company (İstanbul, Turkey).

Sample preparation

The PUR foam samples were prepared by means of a real small scale PUR foam injection machine, which was designed and produced for laboratory purposes by Cersan Machines Limited Company (İstanbul, Turkey). The machine has two component tanks for polyol and isocyanate. Two components are poured into their tanks and they are mixed in a

mixer head which rotates approximately at 6000 rpm. The mixture is poured into preheated aluminum molds and the molds are put under a heated press to keep the temperature at 40°C for 30 min. As soon as curing process is completed under the press, the samples are removed from the molds and let to remain at the temperature 23 ± 1°C and relative humidity 50 ± 2% for 24 h in a conditioning device for complete curing. All samples are cut at different sizes for different tests.

In the present study, the stoichiometric proportion of the components was adjusted as 1/1.18 (polyol/ isocyanate). The amounts of components were adjusted to obtain PUR foams with the density of 40 ± 0.5 kg/m^3. Two different sizes of FA were considered in this study. First, the coarse FA particles supplied from power station was directly used as the filler in PUR foams. Second, the fine FA particles which were obtained by sieving below 25 μm were used as the filler. The FA concentration was varied from 1.0 wt % to 5.0 wt %. The amounts of polyol and isocyanate components were reduced at the same amount of FA to keep the density of the samples at 40 ± 0.5 kg/m^3.

An intumescent flame retardant which consists of APP as an acid source and blowing agent, and PER as a carbonific agent was used in the experiments for flame retardancy. APP and PER combination were examined at the mass ratio (2 : 1) as it was applied by Demir et al.[20] This combination as an intumescent flame retardant is referred to as AP in the article. The loadings of intumescent flame retardant were 2.5, 5.0, and 7.5 wt % of total weight of the raw materials. Heidolph Silent Crusher M Model homogenizer was used to disperse both the FAs and intumescent flame retardant particles into the polyol.

Compression test

The compressive tests were performed using an Instron 8801 computer controlled testing machine (model 8801) in accordance with the ASTM D1621-04a standard[21] at 23 ± 2°C and 50 ± 5.0% relative

TABLE II
Chemical Composition of the Fly Ash[19]

Chemical	Content (%)
SiO$_2$	26.25
Al$_2$O$_3$	12.72
Fe$_2$O$_3$	7.04
CaO	35.26
MgO	2.11
Na$_2$O	0.63
K$_2$O	0.38
SO$_3$	14.80
TiO$_2$	0.60
P$_2$O$_5$	0.21

humidity. The samples were cut to the size of 50 × 50 × 2.5 mm and the orientation of the compression was parallel to foam rise direction. The cross-head speed was maintained at 2.5 mm/min with a load cell of 500 kN. The load was applied until the sample was compressed to approximately 87% of its original thickness. Five replicates were tested for each sample and the results were averaged.

Thermal conductivity measurements

Thermal conductivities of the samples were measured using Kyoto QTM-500. Again five replicates were measured for each sample and the results were averaged. The thermal conductivities were measured with 3% accuracy.

Microscopy

The morphology of the PUR foam samples was examined with an optical Nikon SMZ 1500 Stereo microscope, which was connected a personal computer. The optical images were taken from different areas of each sample.

Viscosity measurements

The viscosity measurements of the polyol components blended with AP and FA were performed at 25°C by using an A and D Sine-wave vibro viscometer SV-10 that measures viscosity by detecting the driving electric current necessary to resonate the two sensor plates at a constant frequency of 30 Hz and amplitude of less than 1 mm. The measurements were recorded via special software running in a PC. The viscosities were measured with ±1% accuracy and the temperatures were measured with ±0.1°C accuracy.
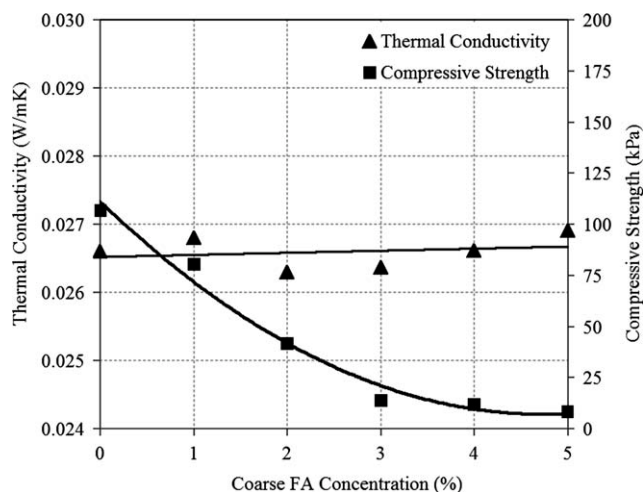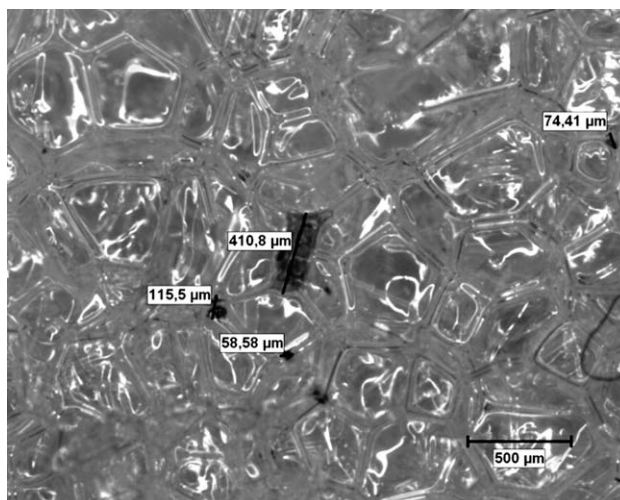

Figure 2 Optical microscopy picture of the cross-sectional surface of PUR + coarse FA (magnitude ×30).

Density test

The densities of PUR foam samples were determined by averaging the mass/volume measurement results of five specimens per sample.

Thermogravimetric analysis

Thermal gravimetric analysis (TGA) was performed to measure the thermal stability of PUR foam samples by using Perkin–Elmer Diamond TG/DTA. Aluminum pans were used to place the sample inside the heating chamber and the samples were heated up to 500°C at a rate of 10°C/min under nitrogen. The real time weight loss as a function of the temperature was recorded during the experiment.

Flammability test

The flammability tests of PUR foam samples were performed according to UL 94 standard.[22] The test specimens were 150 ± 5 mm long by 50 ± 1 mm wide and 10 mm thickness. Each specimen was marked across its width with three gauge marks at 25 mm, 60 mm, and 125 mm from one end. The methane burner with wing tip was adjusted to provide a blue flame 38 ± 2 mm high. The flame was applied for 60 ± 1 s and then removed from the sample. The burning time was determined from the first gauge mark to the flaming or glowing stops or passes of the third gauge mark. The burning distance was determined from the first gauge mark to the flaming or glowing stops, or up to the third gauge mark. The burning rate was calculated by means of the formula (burning distance/burning time).
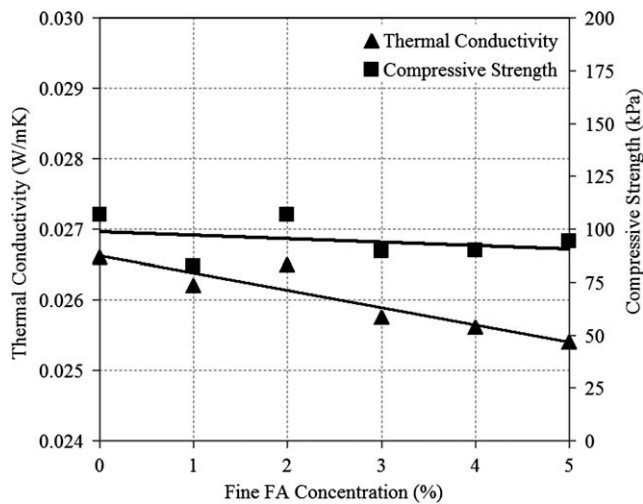

Figure 1 Effects of coarse FA concentration on thermal conductivity and compressive strength of PUR material.

Figure 3 Effects of fine FA concentration on thermal conductivity and compressive strength of PUR material.

RESULTS AND DISCUSSION

The compressive strength and thermal conductivity

The important properties for PUR foams used in the thermal insulation industry are thermal conductivity and compressive strength properties. Therefore, the effects of FAs as a filler and the intumescent flame retardant on these properties were investigated. The compressive strength and thermal conductivity properties of pure PUR foam and coarse FA-PUR foam composites are shown in Figure 1. Although the incorporation of coarse FA slightly increased the thermal conductivity, increasing the amount of FA concentration resulted in a dramatic reduction in the compressive strength. The main reason for the reduction may be explained with the size of the particles. It was assumed that the coarse FA particles collapsed the cell structure and ruptured cell walls.[7] The optical microscopy pictures of the cross-sectional surface of coarse FA-PUR given in Figure 2 supported this assumption. The coarse FA particles
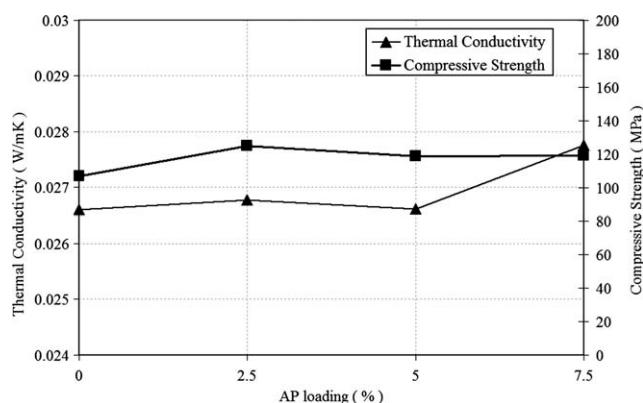

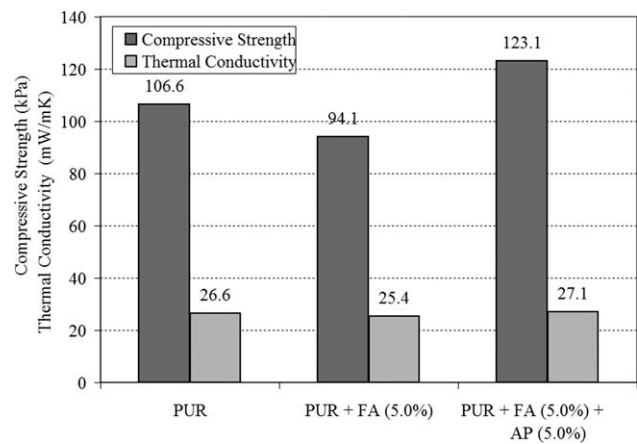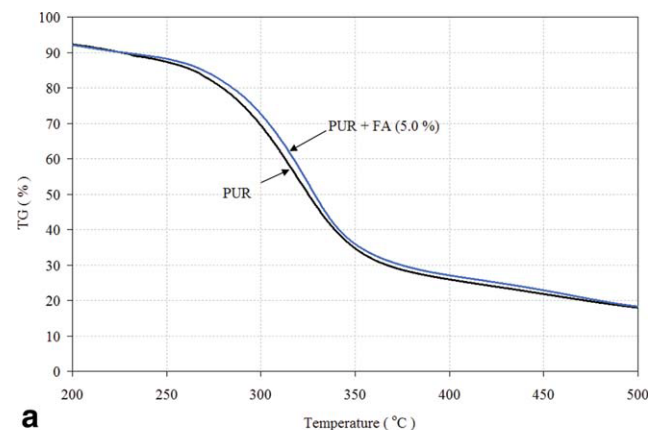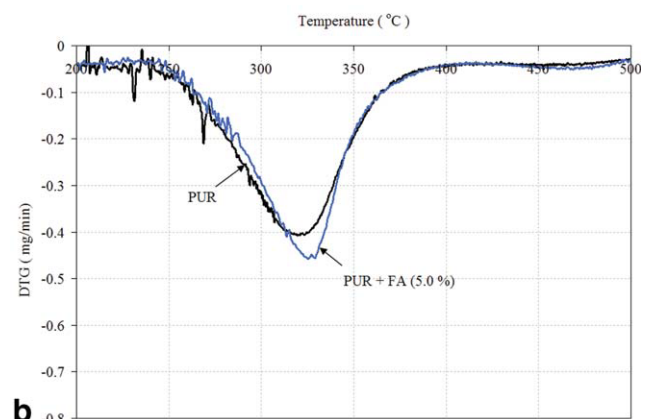**Figure 4** Effects of AP loadings on thermal conductivity and compressive strength of PUR material.

Figure 5 Effects of fine FA (5.0 wt %) and AP loading (5.0 wt %) on thermal conductivity and compressive strength of PUR material.

could not be fit into the struts; they simply lied between cell walls. The thermal conductivity of PUR foam depends on the foam density, the ratio of close to open cell, the cell size, the cell orientation, and the thermal conductivity of the gases in the cells and the filling materials.[23] In other words, the thermal conductivity of the PUR foam is the combination of

Figure 6 Effect of 5.0 wt % fine FA concentration on TGA (a) TG and (b) DTG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
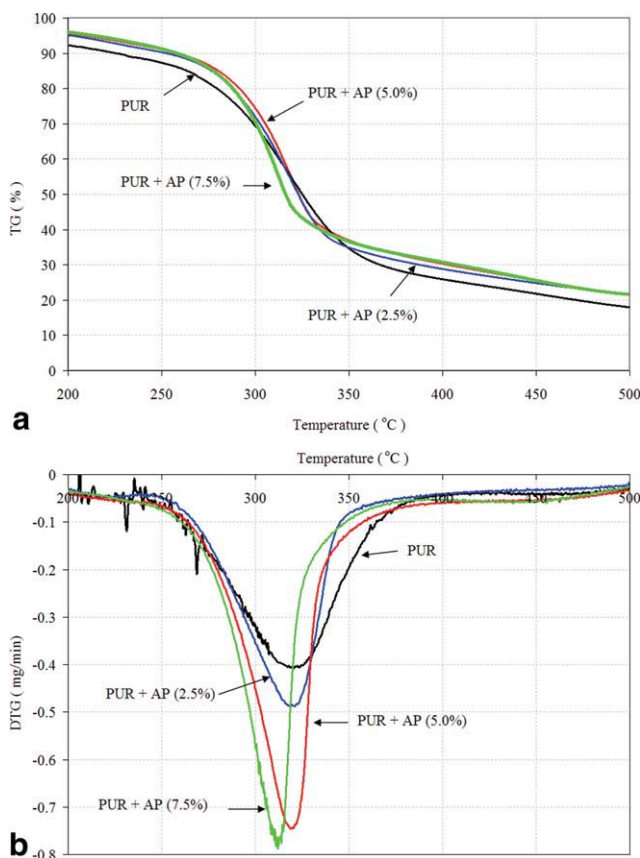
Figure 7 Effects of AP loadings on TGA (a) TG and (b) DTG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thermal conductivity of the solid phase, thermal conductivity of the gas inside the cells, thermal conductivity associated with radiation across the cells, and thermal conductivity due to convection within the cells.[16] The coarse FA particles as a solid material may lead to increasing thermal conductivity of the solid phase of the foam. Therefore, the size of the FA was reduced below 25 μm by sieving and the fine FA particles were used in the FA-PUR composite foam production.

The change of thermal conductivity and compressive strength with respect to the fine FA concentration are shown in Figure 3. The reduction in size enhanced both of the properties. Although the compressive strength was also reduced with fine particles, the reduction is fairly small. The beneficial effect of fine FA particles was seen in the thermal conductivity. The fine FA particles could be fit into the struts resulting in decreasing of the cell size. The thermal conductivity of the fine FA-PUR foam composite decreased with respect to the pure PUR foam because of the cell size decrease.[24]

The effects of AP loading on thermal conductivity and compressive strength of the materials are shown in Figure 4. Although the AP addition slightly increased the compressive strength, there was no

significant change in the thermal conductivity of the materials including 2.5 and 5.0 wt % AP. However, 7.5 wt % loading resulted in increase in the thermal conductivity. AP loading of 5.0 wt % was also introduced to the PUR foam-fine FA (5.0 wt %) composite foam. Although 5.0 wt % AP loading slightly increased the thermal conductivity, it resulted in increase in the compressive strength (Fig. 5).

Thermal behavior

The thermal degradation studies are closely related to investigating the flammability, burning, and flame retardancy of polyurethane materials. Figure 6 shows the thermal degradation of the pure PUR and fine FA-PUR foam, which includes 5.0 wt % fine FA. TG-DTG curves show only single step degradation in both the PUR foam and FA-PUR foam. There was no significant weight loss until the temperature reaches to 250°C for both PUR and FA-PUR.[25] The degradation steps of PUR and FA-PUR took place in the temperature range between 250 and 370°C. The incorporation of FA resulted in slightly an improvement of the thermal stability, comparing to the
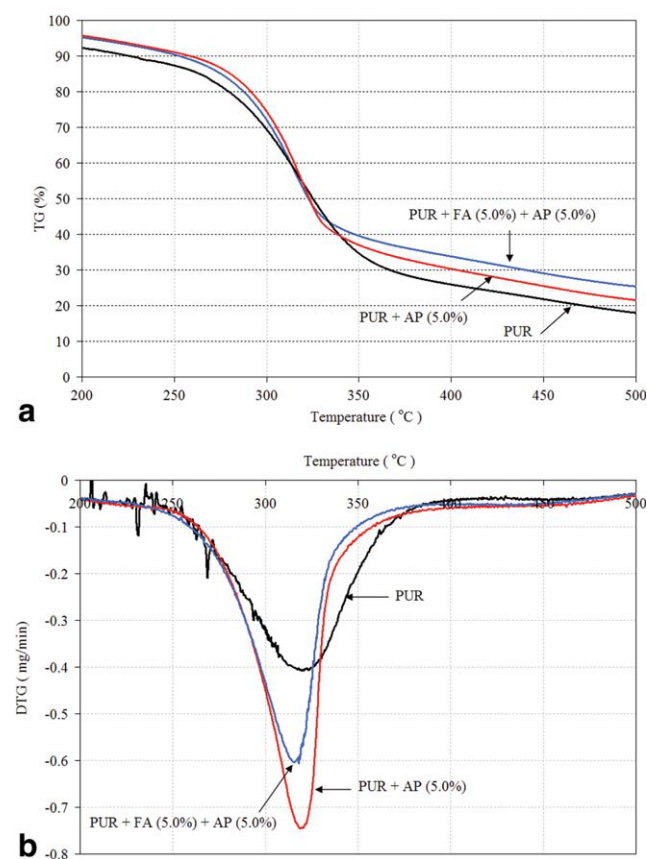

Figure 8 Effects of fine FA concentration (5.0 wt %) and AP loading (5.0 wt %) on TGA (a) TG and (b) DTG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
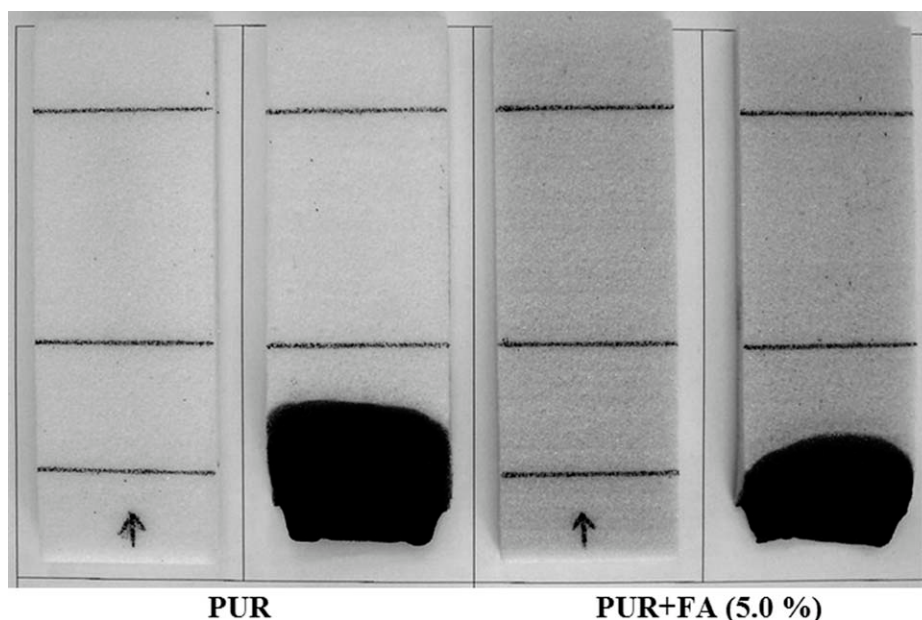
Figure 9 Effect of 5.0 wt % fine FA addition on the flammability.

curves of the pure PUR foam. The temperature at which the maximum weight loss rate occurred was shifted from 320 to 326°C with FA addition. This may be explained with a barrier effect of FA that delays the escape of volatile degradation products from PUR.

The effects of AP in the thermal degradation are shown in Figure 7. TG and DTG curves represent that the addition of AP reduced the temperature at which maximum degradation rate occurred but improved the thermal stability at high temperatures. The temperature of maximum degradation rate was decreased with an increase in AP loading when compared with that of pure PUR. The rate of decomposition rose with AP content increase. This may be explained with the specification of AP that produces phosphoric/polyphosphoric acids at the initial stage of degradation bringing about carbonization.[8] The char on the surface of PUR limited the mass loss. This means that the amount of residue of PUR with AP was higher than
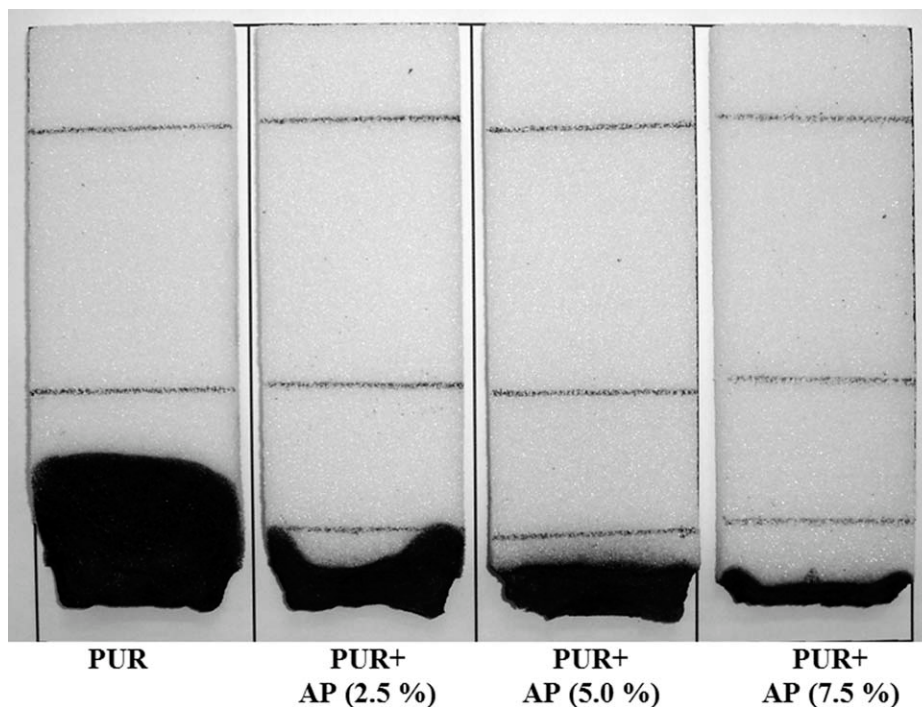

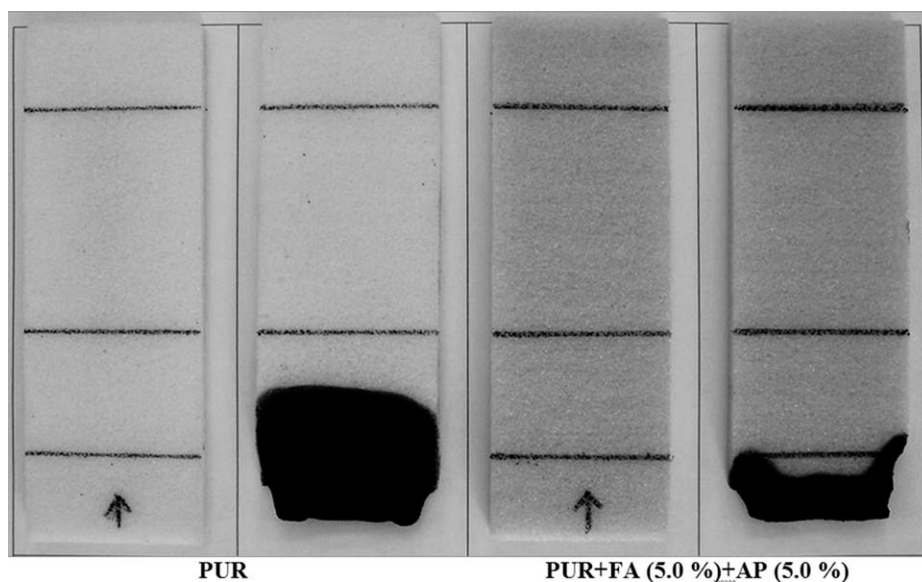**Figure 10** Effects of AP loadings on the flammability.

Figure 11 Effects of fine FA addition (5.0 wt %) and AP loading (5.0 wt %) on the flammability.

that of the pure PUR while the decomposition steps occurred in a narrow temperature range.

The best thermogravimetric performance was obtained using both the fine FA and the intumescent flame retardant. Also 5.0 wt % AP loading enhanced the thermal stability of the PUR foam-fine FA composites (Fig. 8). This may be explained with the synergistic effect of the fine FA particles and the intumescent flame retardant in PUR foam.

Flammability properties

Addition of 5.0 wt % fine FA improved the flammability resistance of the foams as seen in Figure 9. Although the flame passed the first gauge mark in the pure PUR foam at the burning speed of 40 mm/min, the flame was just able to reach the first gauge mark in PUR-FA foam.

The effects of AP loading on the flammability of PUR foam are shown in Figure 10. It can be said
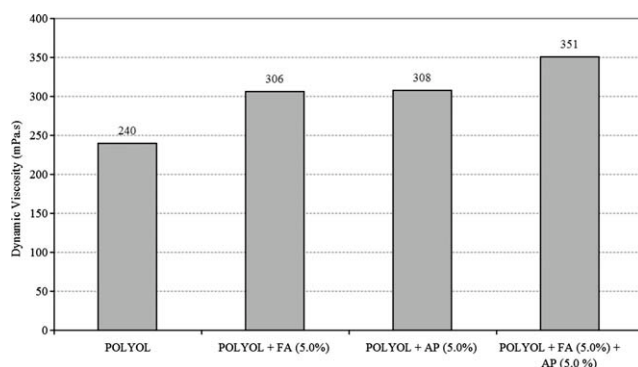
that AP loading obviously improved the flammability resistance of the foams of the materials. The flame could not reach the first gauge mark on the PUR foam loaded with AP. As the amount of AP increases in the materials, it was able to resist more to the flame. Figure 11 shows the effect of AP loading on the flammability resistance of the PUR-FA composite foam. The flame was not able to reach to the first gauge mark at all.

Viscosity

The viscosity is a very important factor to consider for the polyurethane production process. A high viscosity of polyol makes it difficult for the blending with the isocyanate. This results in less uniform foam forming. Figure 12 shows the effect of FA and AP content on the viscosity of the polyol. Addition of 5.0 wt % FA and loading of 5.0 wt % AP resulted in approximately 25% increase in the viscosity of polyol. If both of them are used together, the viscosity of the polyol system increased approximately 46%. The increase in the viscosity neither affected the functionality of the machine nor the production process of the foams. However, it should be noted that the increase in FA concentration more than 5.0 wt % caused stability issues in the machine.

CONCLUSIONS

The results of this study can be summarized as follows:

Figure 12 Effects of fine FA addition (5.0 wt %) and AP loading (5.0 wt %) on the viscosity of the polyol component.

1. The coarse FAs used in this study can not be used directly in PUR foam. Because the coarse particles reduce the compressive strength of PUR significantly.

2. The fine FAs (smaller than 25 μm) can be used up to 5.0 wt % in PUR foam production without any significant change in mechanical and thermal properties. The use of FAs reduces the production cost of PUR foams. More importantly, including FAs in a product prevents environmental pollution. The higher concentration more than 5.0 wt % could not be applied in the polyurethane injection machine.

3. The 5.0 wt % intumescent flame retardant composed of APP/PER (2/1), which is an effective flame retardant in pure PUR foam without producing negative effects on thermal conductivity and compressive strength. Increasing the intumescent flame retardant loading enhanced flammability resistance of the PUR foam but it raised the thermal conductivity.

4. It can be stated that the best thermogravimetric and fire performances were obtained using both FAs and the intumescent flame retardant because of their synergistic effect.

5. Adding FAs and intumescent flame retardant increased the viscosity of the polyol component.

6. Because all the sample preparations were performed via a small scale polyurethane injection machine, which has same working principle of its industrial counterparts, the results can easily be applied to industrial PUR foam production. The FA and the intumescent flame retardant contents may be increased in a one-shot method using a mixer. But the results may not be applied to industrial PUR foam production.

References

1. Chattopadhyay, D. K.; Webster, D. C. Prog Polym Sci 2009, 34, 1068.
2. Nikje, M. M. A.; Garmarudi, A. B.; Haghshenas, M. Polym Plast Technol Eng 2006, 45, 213.
3. Zatorski, W.; Brzozowski, Z. K.; Kolbrecki, A. Polym Degrad Stab 2008, 93, 2071.
4. Deepthi, M. V.; Sharma, M.; Sailaja, R. R. N.; Anantha, P.; Sampathkumaran, P.; Seetharamu, S. Mater Des 2051 2010, 31.
5. Soyama, M.; Inoue, K.; Iji, M. Polym Adv Technol 2007, 18, 386.
6. Rama, S. R.; Rai, S. K. J Compos Mater 2009, 43, 3231.
7. Thirumal, M.; Singha, N. K.; Khastgir, D.; Manjunath, B. S.; Naik, Y. P. J Appl Polym Sci 2010, 116, 2260.
8. Meng, X. Y.; Ye, L.; Zhang, X. G.; Tang, P. M.; Tang, J. H.; Ji, X.; Li, Z. M. J Appl Polym Sci 2009, 114, 853.
9. Ye, L.; Meng, X. Y.; Ji, X.; Li, Z. M.; Tang, J. H. Polym Degrad Stab 2009, 94, 971.
10. Ye, L.; Meng, X. Y.; Ji, X.; Li, Z. M.; Tang, J. H. Polym Degrad Stab 2009, 111, 2372.
11. Bian, X. C.; Tang, J. H.; Li, Z. M. J Appl Polym Sci 2008, 110, 3871.
12. Thirumal, M.; Singha, N. K.; Khastgir, D.; Manjunath, B. S.; Naik, Y. P. J Appl Polym Sci 2008, 110, 2586.
13. Thirumal, M.; Khastgir, D.; Nando, G. B.; Naik, Y. P.; Nikhil, K.; Singha, N. K. Polym Degrad Stab 2010, 95, 1138.
14. Singh, H.; Jain, A. K.; Sharma, T. P. J Appl Polym Sci 2008, 109, 2718.
15. Modesti, M.; Lorenzetti, A.; Besco, S.; Hrelja, D.; Semenzato, S.; Bertani, R.; Michelin, R. A. Polym Degrad Stab 2008, 93, 2166.
16. Modesti, M.; Lorenzetti, A.; Simioni, F.; Camino, G. Polym Degrad Stab 2002, 77, 195.
17. Liang, H.; Shi, W.; Gong, M. Polym Degrad Stab 2005, 90, 1.
18. BASF The Chem Company. Technical data sheet for Elastofoam I 4501/109 and Iso PMDI 92040 2005.
19. Personal Communication. Kemerkoy Power Station Mugla: Turkey, 2010.
20. Demir, H.; Arkıs, E.; Balkose, D.; Ulku, S. Polym Degrad Stab 2005, 89, 478.
21. ASTM D1621-04a Standard Test Method for Compressive Properties of Rigid Cellular Plastics; ASTM International: Conshohocken, PA, 2004.
22. UL 94 Standard, Test for Flammability of Plastic Materials for Parts in Devices and Appliances; Underwriters Laboratories Inc.: Northbrook, IL, 1996.
23. Thirumal, M.; Khastgir, D.; Singha, N. K.; Manjunath, B. S.; Naik, Y. P. Cell Polym 2007, 26, 245.
24. Silva, M. C.; Takahashi, J. A.; Chaussy, D.; Belgacem, M. N.; Silva, G. G. J Appl Polym Sci 2010, 117, 3665.
25. Li, X. B.; Cao, H. B.; Zhang, Y. J Appl Polym Sci 2006, 102, 4149.