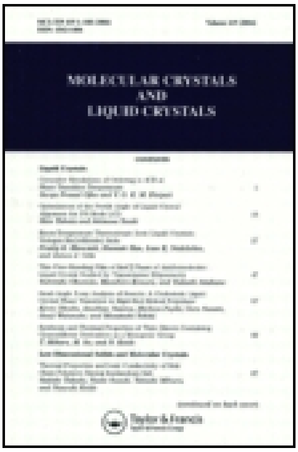

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Comparative Effects of the Fire Behaviours of Potassium Aluminium Sulphate and Potassium Sesquicarbonate on Flexible Polyether Foam

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The effects of potassium aluminium sulphate ($K_2SO_4 \cdot Al_2SO_4)_3 \cdot 24H_2O$) and potassium sesquicarbonate ($K_2CO_3 \cdot 2KHCO_3 \cdot 3/2\ H_2O$) as flame retardants on fire properties of flexible polyether foam was studied. Potassium sesquicarbonate performed better at increasing the ignition time and the amount of char formed and both factors improved with flame retardant concentration. However, the afterglow time, flame duration, burn length and flame propagation rate decreased with increase in concentration. The flame propagation rates of foam samples with alum were higher than the corresponding rates with potassium sesquicarbonate. This could be attributed to the nature of their decomposition products at pyrolysing/flaming temperature. Thermogravimetric analyses showed that the flame retardants delayed the onset of degradation. The delay effect was higher with potassium sesquicarbonate (akanwu) than with potassium aluminium sulphate (alum). Again, the delay effect was affected by the flame retardant concentration.

Keyword Fire; flame retardant; ignition time; polyether foam

Introduction

Fire is a worldwide problem which claims lives and causes significant loss of properties. Most of the immediate surroundings of man consist of polymeric materials that are combustible materials, and their burning often poses a serious threat to human health and the environment. Fire retardants are chemical compounds or mixture of compounds that, when added to or incorporated chemically into polymers, serve to slow down or hinder ignition or growth of fire [1,2]. Flame retardants generally either decrease ignition susceptibility or lower the flame propagation once the ignition has occurred. It can be incorporated into a material either as a reactive component or as an additive component. As a reactive, they are incorporated into the polymer structure of the plastics, for example, when polyurethane and polyamides are retarded with red phosphorus. Flame retardants are classified into three types namely: non-durable, semi-durable and durable, based on durability or fastness to light, heat, chemicals etc. [3].

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Inherent flame–retardant polymers, with flame retardant elements or groups chemically bonded into the molecular chains, (i.e., not physically added to the polymer matrices) have been investigated [4]. Some researchers formulated flame retardant polyurethanes containing phosphorus compounds that react with isocyanate. For example, flame retardant polyurethane foam (PUF) has been prepared with diethyl N,N′-diethanolaminomethylphosphate and isocyanate [5]. Phosphorus containing polyurethane has been synthesized by a novel reaction of phosphorus containing diisocyanates and diols [6].

Organic flame retardants result in the generation of a toxic smoke which has adverse health effects on those exposed. There has been much concern in particular about the emission of polybrominated dibenzo furans (PBDF) and polybrominated dibenzo dioxins (PBDD) during manufacture, use and combustion of brominated flame retardants. In brominated flame retardants, nearly all the bromine is converted to gaseous HBr which is a corrosive and powerful sensory irritant unless suitable metal oxides and carbonates are present [7]. Several researches have been carried out on the use of synthetic flame retardants. Some of these synthetic flame retardants are not readily available in the country and moreover their products and by-products are toxic. As a result, it becomes necessary to look for less toxic, lower-cost and readily available local raw materials. The raw material chosen were potassium aluminium sulphate (alum) and potassium sesquicarbonate (akanwu). One of the major driving forces behind this research is the need to address the environmental consequences and health hazard associated with the use of synthetic flame retardants. Therefore, the aim of this work is to look for economically and environmentally friendly flame retardants for the production of flexible polyether foam in our industries.

Materials and Methods

The raw materials used for the production of foam were obtained from Winco foam Nigeria Ltd, Awka. Potassium aluminium sulphate(alum) used as flame retardant was sourced from Anambra State Water Corporation, Awka, while potassium sesquicarbonate (akanwu) was procured from Head Bridge Market, Onitsha, Anambra State, Nigeria.

Preparation of the Novel Flame Retardant

The novel flame retardants were milled into fine powder using a manually operated corona lever machine, Landers and YCIA S.A model. The powder was sieved to pass through laboratory test sieve of 63 μm USA Standard Testing Sieve, ASTM E.11 Specification and kept in air tight polyethylene bags.

Preparation of Flexible Polyether Foam Samples

The measured quantity of the novel flame retardant were added to the polyol in a mixing bowl and stirred vigorously, followed by sequential addition of other raw materials such as silicone, stannous octoate, 2-dimethylamino ethanol (DMAE) and water [3]. The mixture was stirred and toluene diisocyanate (TDI) was finally added and stirred continuously until when there was a sign of rising, then the mixture was immediately poured into the mould. The foam was allowed to solidify for about 9 minutes in the mould before being removed. It was left for 24 hours for total curing after which it was removed from the mould and tested. Foam formulations using the two novel flame retardants are shown in Table 1.

Table 1. Foam formulation using the two novel flame retardants

Raw material	Pph%	FS_0(g)	FS_1(g)	FS_2(g)	FS_3(g)	FS_4(g)	FS_5(g)
Polyol	100	500	500	500	500	500	500
TDI	54.8	274	274	274	274	274	274
Water	4	20	20	20	20	20	20
Amine	0.14	0.7	0.7	0.7	0.7	0.7	0.7
Silicone	0.8	4	4	4	4	4	4
Stannous Octoate	0.16	0.8	0.8	0.8	0.8	0.8	0.8
Alum	Varied	0	0.5	1.0	1.5	2.0	2.5
Akanwu		0	0.5	1.0	1.5	2.0	2.5
	Percentage	0%	0.1%	0.2%	0.3%	0.4%0	0.5%

Note: Pph% = part per hundred, $FS_{0\,=}$ Foam samples.

Characterization of the Foam Samples

The following fire characteristics of the foam samples were analysed: ignition time, burn length, flame propagation rate, flame duration, char formation, afterglow and add-on [8–10]. Thermo gravimetric analyses of the foam samples were also carried out.

Results and Discussion

Since flexible polyurethane foam is used in mattresses, cushions of furniture, automobiles, general upholstery; clothe interlining and packaging, considerable efforts have been made to develop non-flammable foams as well as to understand the mechanism of flame retardation and propagation. Polyurethane foam burns as long as a source of flame is present but stops burning when the flame is removed, that is, it is said to be self-extinguishing [10]. Burning occurs when the external heat source increases the polymer temperature to a point where it begins to decompose and release combustible gases. Once gases ignite, the temperature increases until the release of combustible gas is rapid enough for combustion to be self-sustaining provided oxygen is available to support the combustion process.

The results in Fig. 1 show that ignition time increases as the concentration of flame retardant increases. Ignition time is the time taken by the sample to catch fire. The sample increases in temperature as it receives and redistributes the heat by conduction when the external heat source transfers heat to the foam sample. As the temperature of the material increases, decomposition reactions occur which release volatile combustible products. A combustible mixture is formed with air and ignition occurs if sufficient heat is supplied [11].

The ignition time of the neat polyurethane samples was low but increased with increase in flame retardant concentration. At 0.1–0.5% loading there was a considerable increase but the ignition time of potassium sesquicarbonate was higher than that of alum. The higher ignition time for potassium sesquicarbonate indicates a higher retarding effect on the foam samples than alum.

Burn length determines the distance from the original sample edge to the farthest point showing evidence of damage due to combustion [12]. The results of burn length are shown in Fig. 2. It decreases as the concentration of the flame retardant increases. At 0%, the foam sample gave the highest burn length because of the absence of a flame retarding effect. At

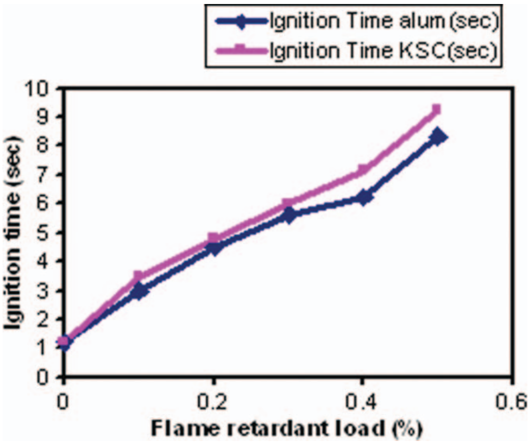

Figure 1. Effect of flame retardants on ignition time.

0.1–0.5%, foam samples incorporated with potassium sesquicarbonate had a much lower burn length than alum.

Flammability can be reduced by using compounds such as hydrated alumina $Al_2O_3.3H_2O$ that evolve water endothermically to cool the pyrolysis zone. The results in Fig. 3 show that flame propagation rate decreased as the concentration of the flame retardant increases. The flame propagation rates of foam samples with alum are higher than the foam samples with potassium sesquicarbonate due to the nature of decomposition products at pyrolysing temperature. Also it can be seen that the flame propagation rates of foam samples containing alum are higher than the foam samples with potassium sesquicarbonate. This could be attributed to their nature of decomposition products at pyrolysing/flaming temperature.

$$\underset{\text{(Alum)}}{K_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O} \xrightarrow{\Delta} K_2SO_4 + Al_2O_3 + 3SO_3 + 24H_2O$$

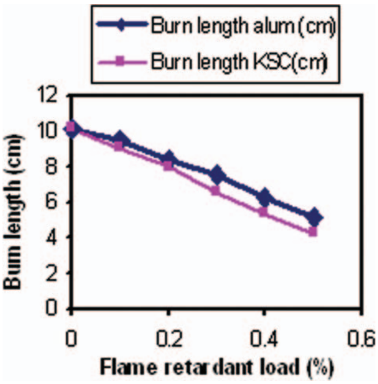

Figure 2. Effect of flame retardant on burn length.

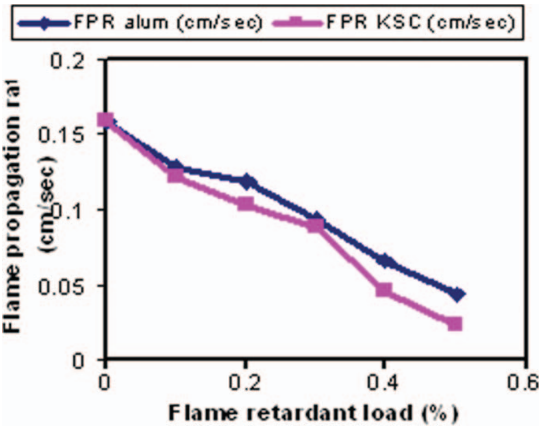

Figure 3. Effect of flame retardants on flame propagation rate.

$$\underset{\text{(Akanwu)}}{K_2CO_3{\cdot}2KHCO_3.{}^{3}\!/\!_{2}H_2O} \xrightarrow{\Delta} K_2O + 2KHCO_3 + CO_2 + {}^{3}\!/\!_{2}H_2O$$

Thus, the reduction in flame propagation rate when compared to the control may be due to two principal factors; evolution of water and non-combustible gases which cool the flame as well as dilute the concentration of flammable pyrolysis products. The component in potassium sesquicarbonate e.g. potassium oxide acts in the condensed phase as an excellent heat conductor, deflecting heat from the burning surface.

The result in Fig. 4 shows that as the concentration of flame retardant increased, the flame duration decreased. At 0% concentration, the foam sample gave the highest value of flame duration. At 0.1–0.5% loading the foam sample incorporated with potassium sesquicarbonate gave a lower result of flame duration when compared to the foam samples incorporated with alum. The reason for this was because of the components in potassium sesquicarbonate which tends to reduce the time of flame duration. These components such

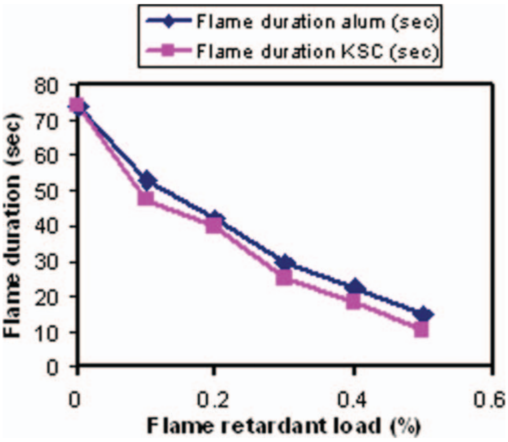

Figure 4. Effect of flame retardants on duration of flame.

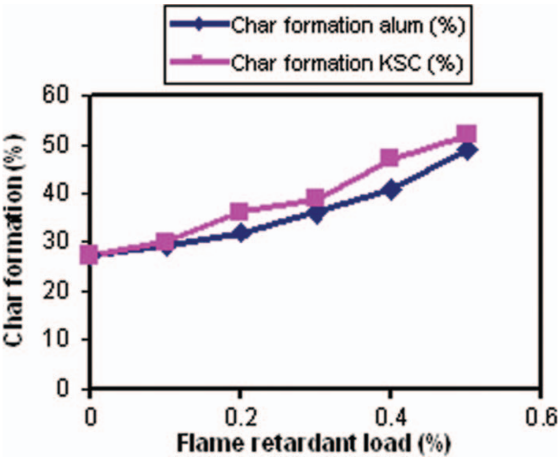

Figure 5. Effect of flame retardants on char formation.

as water vapour, hydroxides and carbonates have a stronger effect than sulphate and oxides in the alum.

Results in Fig. 5 show that as the concentration of flame retardant increases, char formation increases. From literature, flame retardant promotes char formation which acts as a physical barrier to flame and inhibits the volatilization of flammable materials [13].

Polymer decomposition by heat entails firstly, pyrolysis, and then oxidation/combustion process. At high temperature (700°C) pyrolysis tends to proceed more violently with more disorderly disruption of chain structures to form flammable volatiles and with less condensation of carbonaceous entities to form char.

From Fig. 6, it can be seen that at different concentrations, potassium sesquicarbonate gave a lower value of afterglow time than alum probably because of the increased char formation which consequently reduces the afterglow time. The results of add-on show that as the concentration of flame retardant increases, add-on increased since both of them are soluble in water. Add-on is the quantity of flame retardant absorbed during the production

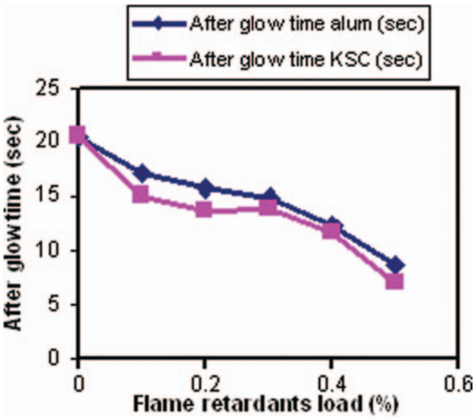

Figure 6. Effect of flame retardants on afterglow time.

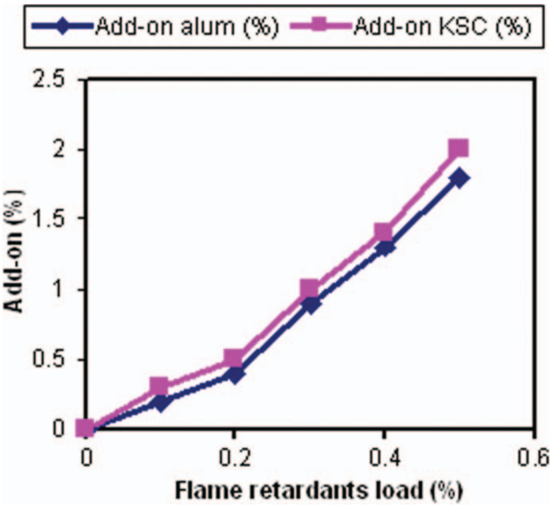

Figure 7. Effect of flame retardants on Add-on.

of foam sample. The results in Fig. 7 show that potassium sesquicarbonate absorbed more.

Thermal Behaviour

Thermogravimetric analysis was used to investigate the effect of potassium aluminium sulphate and potassium sesquicarbonate on the thermal behaviours of flexible polyether foam samples. The test was carried out on the samples prepared with different concentrations of flame retardants and was studied as a function of weight loss with the increase in temperature and the results are shown in Table 2. In case of 0.1% potassium aluminium sulphate, the first decomposition took place between the temperature ranges of 50°C to 230°C with slight loss in weight of about 0.5 mg and is almost uniform in all concentrations of flame retardant; the weight loss may arise from evaporation of residual moisture or solvent. When compared to the initial decomposition temperature for potassium sesquicarbonate, it is 60°C, i.e. slightly higher and weight loss lies between 0.20 to 0.4 mg. This initial decomposition temperature is slow. Initial decomposition temperature (IDT) and final decomposition temperature (FDT) for different concentrations of potassium aluminium sulphate have been found to be 50°C and 540°C while than of later are from 60°C to 555°C. The second decomposition temperature starts from 231°C to 410°C and this is sharp. At higher temperature, weight loss may be as a result of the decomposition polyether foam and the average is between 16 and 23 mg for different of concentration of potassium aluminium sulphate, and between 15 and 20 mg for potassium sesquicarbonate as deduced from thermograms, while the weight loss for the control (0%) is 17.5 mg. The weight loss for the third decomposition region for the control sample is 0.2 mg, that of alum is from 0.2 to 0.4 mg while that of potash is between 0.2 and 0.5mg which indicates that at third decomposition region for potash much weight is lost. Residual weight is an accurate reflection of char formation.

In differential thermal analysis (DTA), the results of the degradation profile of the foam samples prepared with the two flame retardants is shown on Table 3. Also, it is observed that

Table 2. Results of TGA showing changes in weight loss (mg) with increase in temperature (°C)

Temperature decomposition stage	Weight loss of control sample (mg)	Weight loss of foam treated potassium aluminium sulphate (mg)					Weight loss of foam treated potassium sesquicarbonate (mg)				
	0%	0.1%	0.2%	0.3%	0.4%	0.5%	0.1%	0.2%	0.3%	0.4%	0.5%
First decomposition temperature (5–280°C)	0.5	0.5	0.2	0.5	0.3	0.2	0.4	0.2	0.2	0.4	0.2
Second decomposition temperature (281–420°C)	17.5	17.0	23.0	17.5	23.0	20	17,0	15.5	17.5	20.0	20.0
Third decomposition temperature (421–560°C)	0.2	0.3	0.2	0.2	0.2	0.3	0.3	0.2	0.2	0.5	0.5

Table 3. Effect of flame retardants on degradation profile

	Thermo-gram	Pure sample	Treatment with Alum					Treatment with potassium Sesequicarbonate				
Event	parameter	(0%)	0.1%	0.2%	0.3%	0.4%	0.5%	0.1%	0.2%	0.3%	0.4%	0.5%
Max. Temp (°C)	Stable up to	306.84	304.84	305.31	239.82	314.67	306.76	306.47	305.48	307.73	302.02	304.78
On set of thermal degradation time (min)		3.02	6.40	7.68	2.80	8.78	7.87	9.48	8.93	2.60	12.13	10.63
1st step degradation Temperature (°C)	Start temp	62.22	112.19	134.72	66.10	152.58	136.86	165.76	157.83	64.77	201.53	182.44
	Mid temp	306.84	304.25	306.31	239.82	314.42	306.75	306.47	305.48	307.73	302.04	304.78
	End temp	356.98	328.04	358.83	338.59	340.42	369.04	358.88	338.55	354.07	361.81	359.32
2nd step degradation Temperature (°C)	Start temp	370.14	372.82	434.64	—	—	—	−458.44	—	—	—	—
	Mid temp	431.67	397.99	470.51	408.81	472.43	—	546.07	388.68	—	—	—
	End temp	486.66	481.06	537.42	513.64	525.86	514.72		471.85	523.51	474.85	478.48
Duration of degradation in (min)		22.33	22.68	26.33	24.56	29.30	31.32	27.57	23.63	31.80	28.58	28.72
1st step Energy req.(uV)	Start Energy	−19.01	−8.73	−15.98	−12.39	−13.72	−18.19	13.68	−4.60	−17.98	15.94	14.14
	Mid Energy	12.07	19.84	23.22	11.82	23.72	21.31	18.22	27.52	18.58	10.26	20.28
	End Energy	46.40	22.28	12.95	55.19	49.81	17.73	40.98	56.25	24.15	32.12	22.58
2nd step Energy req.(uV)	Start Energy	24.23	−0.73	32.75	—	—	—	—	—	—	—	—
	Mid Energy	33.14	17.50	79.07	29.64	24.44	—	100.77	388.68	—	—	—
	End Energy	72.11	20.97	43.06	58.35	29.04	94.12	55.64	73.30	47.33	114.85	110.19

in addition to exothermic peaks there are also endothermic peaks at different temperatures. The thermal degradation time of samples treated with various concentrations of potassium sesquicarbonate (with 0.1% it was 9.48 min) were greater than those treated with potassium aluminium sulphate (with 0.1% it was 6.40 min) except at 0.3% where that of alum was greater. Again, foam samples treated with potassium sesquicarbonate required more energy to degrade than ones treated with potassium aluminium sulphate, at 0.1% it was 55.64 min and 20.97 min respectively.

Conclusion

The following conclusions could be drawn on the possibility of using alum and potassium sesquicarbonate as flame retardants in the production of polyurethane foam. The nature of the flame retardant chemical constituent affected the flammability properties of the polyurethane foam studied with potassium sesquicarbonate performing better than potassium aluminium sulphate. However, the results of the TGA analyses also revealed that polyurethane foam filled with potassium sesquicarbonate as flame retardant required a higher activation energy than alum for the pyrolysis / combustion of the samples. Also, the onset of degradation time was more delayed in potassium sesquicarbonate than alum. Finally, these flame retardants, added at low concentrations, enhanced the flammability properties of the polyurethane foam better than at higher concentrations.

Acknowledgments

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