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Properties of rigid polyurethane foams produced by the addition of phosphorus compounds

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Abstract
Water blown rigid polyurethane foam(RPUF) was prepared with ammonium polyphosphate(APP) dimethyl methylphosphonate(DMMP),and their compounded systems as fire retardant(FR) additives. The effect of these additives on the properties of RPUF such as physic-mechanical, morphological, LOI and smoke density were studied. The mechanical properties such as compressive strength and tensile strength of filled RPUF shows inferior properties as that of neat RPUF. In order to evaluate flame retardant properties of the filled RPUF with various amounts of FRs, limit oxygen index(LOI) and maximum smoke density(MSD) were measured. The flame retardant property of filled RPUF was improved with respect to the neat RPUF. The LOI of DMMP filled RPUF was higher than that of the APP filled RPUF, and their compounded systems display well synergy effects. However, the APP filled RPUF emanates less quantity of smoke as compared to the DMMP filled RPUF. Moreover, we can also see from their compounded systems, the higher loading of DMMP with APP filled RPUF, the less MSD release compared to DMMP filled RPUF.

1. Introduction

Polyurethane is regarded as a versatile polymeric material since it exhibits good properties for many purposes[1,2]. Demand for commercial use of polyurethane is dramatically increased recently. However, Polyurethanes are very combustible plastics. The Oxygen Index(OI) of PUF is in the range of 16-18[3,4]. Highly porous lightweight combustible foams tend to have fast flame-spread and high thermal emission[5]. Various fires have occurred,which caused huge losses to the lives and property safety.So their use is limited in some applications due to degradation under certain condions, easy flammability and lack of thermal stability[6-9]. Increasing demands for polyurethane foams and the bad fire behavior are the reason why many studies are devoted to flame-retardancy[10]. Moreover, the researches on flame retardant polymeric material are expected to be activated for worldwide flame retardant restriction and requirement of halogen free flame retardant. A way of achieving enhanced flame retardant activity is to add FR into the PUF or that are capable of a synergy between FRs. The use of phosphorus compounds as flame retardants for PUF has been reported for a longtime[11,12]. Many organophosphorus compounds are very effective solid-phase flame retardants when used with oxygen-containing polymers[13]. In this study, phosphorus flame retardants were used for improvement of flammability produced for RPUF. We added

DMMP, APP and their compounded systems as flame retardants into the polyurethane matrix with the amount of 10wt% to 30wt% based on the polyol. Both flame retardants contain high levels of P element, which may be char-promoting agent during the combustion process. The flame retardant properties were characterized by LOI and maximum smoke density(MSD).

2. Experimental

2.1. Material

The polyisocyanates (44v20, functionality 2.7, NCO content 32%)were obtained from Bayer polyurethane Co.LTD, Shanghai, China. Polyether polyols(OH content 450 mgKOH/g) were obtained from Third Oil Refinery of Tianjin Petrochemical Co., China. Flame retardant polyether polyol(Friol-7190, OH content 190 mgKOH/g) were obtained by XinRui Chemical Technology Co.,LTD， shanghai，China. Triethylene diamine(A33) obtained from Air Products & Chemicals Inc. and Dibutyltin dilaurate (T12) obtained from Beijing Fine Chemicals Co.Ltd. were used as catalyst. Polyether dimethyl siloxane(B8533) supplied by EVONIK Germany was used as a surfactant.1,4-Butanediol and Glycerol were both obtained from Sinopharm Chemical Reagent Co.Ltd.The former was used as chain extender and the latter was used as cross linking agent. Dimethyl Methyl Phosphonate(DMMP) was supplied by Qingdao Lianmei Chemical Co. Ltd. ,China. Ammonium polyphosphate(APP) was supplied by Jinan Jinying Tai Chemical Co.Ltd., China. Distilled water generated in our laboratory was used as a chemical blowing agent. All the chemicals were used as received.

2.2. Preparation of RPUF

The FR containing RPUF samples were prepared by one-shot and free-rise method. All the raw materials were first well mixed in a plastic beaker, then the FRs were added and finally a homogenous mixture was obtained by using a high speed mechanical stirrer. The temperature of the mixture, 44V20 and the mold were under control. The 44V20 was added into the beaker with vigorous stirring for 10s. The resultant mixture was immediately poured into an open mold to produce free-rise foam. The amount of 44V20 was calculated from their equivalent weights. For the completion of the reaction, excess 44V20(NCO/OH=1.05) was used. After preparation ,the foams were kept in an oven at 70℃ for 24h to complete the polymerization reaction. Different test samples of specific shapes were cut from cured foam.

2.3. Measurements

The density of the PUF samples was measured according to GB/T6343-1995. The size of the specimen was 50*50*50mm3 (lenth*width*thickness) and the average values of three samples were calculated.

The compressive strength of different RPUF samples at 10% strain in the direction parallel to foam rise were measured according to GB/T8813-2008 using a electronic universal testing machine(AMETEK LR30K,Britain), which the strain rate was fixed at 5mm/min. The average values of five samples were calculated.

Tensile strength tests were performed according to GB 9641—1988 with a electronic universal testing machine (AMETEK LR30K, Britain).Five or more specimens per material were tested and the mean value of each item was determined. The distance between points was defined as 50mm, and the drawing speed was defined as 5mm/min to obtain stress-strain curves.

The morphology and the size of various RPUF samples were observed using a Hitachi H-800 scanning electron microscope (SEM),at an accelerate voltage of 20KV. The surface of the samples used for SEM were gold-sputtered with a conductive layer before observation.

Limiting oxygen index(LOI) tests were measured according to GB/T 2406—1993 by using a oxygen index instrument (JF-3, made by Nanjing Jiangning Analtical Instrument Factory, China).The size of the specimen was $100*10*10$ mm^3. In order to overcome problems of poor repeatability of data, eight or more specimens for each sample were used.

The smoke density was measured according to GB/T 8627—2007 by using a smoke density chamber (JCY-2, made by Nanjing Jiangning Analtical Instrument Factory, China) The specimen size for the LOI measurement was $25*25*6$ mm^3. The maximum smoke density was measured from the peak maxima of the curve of the light absorption time. Total amount of smoke present in the chamber for 4 min time.

3. Results and Discussion

3.1. Physico-Mechanical Properties

PUF is a porous material. Its apparent density can reflect the internal structure of the hole. Foam density is a very important physical property which has great influence on the mechanical properties of the PUF14. Generally, the density is dependent on the degree of foaming which in turn depends on the type and amount of blowing agent. In this work distilled water was used as the chemical blowing agent and the amount of FR additives was varied. Table 1 shows the effect of density of RPUF filled with DMMP, APP and their compounded systems at different loadings. It is observed that the densities of RPUFs filled with DMMP and APP increase compared with unfilled RPUF. Roughly, the density of each RPUF is increasing as the loadings of the FR are higher. In the case of their compounded systems filled RPUF, there is also an increase in density initially. The increase in density of RPUF is probably due to the decrease in average cell size and formation of uniform cell structure as shown in Fig 1. The RPUF filled with DMMP has smaller average cell size and better uniformity than that of RPUF filled with APP and their compounded systems, which the density of RPUF filled with DMMP increases significantly in contrast to the other two.

Physic-mechanical property is another important parameter which decides the application of PUF. In this case, the effect of the phosphorus FR additives and their compounded systems on the compressive strength and tensile strength have been studied. In order to eliminate the effect of foam density, the specific compressive strength (compressive strength/density) and specific tensile strength (tensile strength/density) were used for comparison. Table 1 shows the compressive strength、specific compressive strength、tensile strength and specific tensile strength of the RPUF filled with the phosphorus FR additives and their compounded systems at different loadings. In general, incorporation of filler into PUF causes inferior physic-mechanical property15. It is clear from Table 1 that the specific compressive strength of filled RPUF decreases with reference to neat RPUF except DMMP: APP-10:20. We can also see that the specific tensile strength of filled RPUF decreases compared to the initial density except APP-10. The decrease in mechanical properties may be due to the formation of voids in cell structure and the rupture of cell walls as shown in Fig.1. Generally, the APP filled RPUF shows better mechanical stability in specific compressive strength and specific tensile strength as compared to that with DMMP and their compounded systems. The APP alone filled RPUF shows less decrease in mechanical properties. This may be attributed to its low hygroscopicity、good dispersibility and close to neutralization. The liquid DMMP can release some acidic substances when mixed with polyether mixture, which can plasticize the polyurethane foam, and even shrink severely when the loadings are higher. As a result, the mechanical properties is decreased 16.

As can be seen from SEM images (Fig 1a),the blank sample is polyhedron shape, and has big size in pore diameter、regular shapes and homogeneous distribution. In comparison with the pure RPUF, it is observed from Fig 1b that the RPUF which is added DMMP becomes smaller in mean cell size and its opening rate increases. We suggest that the decrease in physic-mechanical property of filled RPUF may be due to the smaller cell size and the increasing cell rupture. Shutov[23] reported that the compressive strength and tensile strength of most PUF decreased with the cell size decreasing when the conditions such as the chemical structure of the polymer matrix, thickness were similar. The result obtained about opening rate and the mechanical properties from Liang Shuen 24 shows that the compressive strength of open-cell foam is lower than that of closed-cell foam under the same situation. Our result is well corroborated with these two conclusions. In the case of the APP filled RPUF (Fig 1c),it seems that the introduction of APP causes small changes in the cell size and the opening rate. It is determined that the introduction of APP causes limited worsening of mechanical properties. When DMMP and APP are added together, we can see from Fig 1d that there are many smaller and roughly the same size with the neat RPUF cells generated. We can suggest that the mechanical properties should between DMMP and APP filled RPUF. The cell morphology analyses had good correlation with the experimental results obtained from the physico-mechanical properties .

Table 1. *Effect of phosphorus compounds on the physic-mechanical properties of RPUF.*

FR loading(php)	**0**	**DMMP 10**	**DMMP 15**	**DMMP 20**	**DMMP 25**	**DMMP 30**
Density(kg/m^3)	41.87	52.03	47.39	56.34	59.32	60.82
Compressive strength at 10% strain(MPa)	0.33	0.39	0.22	0.40	0.20	0.18
Specific compressive strength[MPa/(g/cm^3)]	7.9	7.5	4.6	7.1	3.4	3.0
Tensile strength(MPa)	0.25	0.24	0.24	0.21	0.18	0.19
Specific tensile strength [MPa/(g/cm^3)]	6.0	4.6	5.1	3.7	3.0	3.1

FR loading(php)	**0**	**APP-10**	**APP-15**	**APP-20**	**APP-25**	**APP-30**
Density(kg/m^3)	41.87	41.93	45.45	46.75	46.84	46.70
Compressive strength at 10% strain(MPa)	0.33	0.32	0.32	0.34	0.30	0.35
Specific compressive strength[MPa/(g/cm^3)]	7.9	7.6	7.0	7.3	6.4	7.5
Tensile strength(MPa)	0.25	0.30	0.26	0.27	0.24	0.25
Specific tensile strength [MPa/(g/cm^3)]	6.0	7.2	5.7	5.8	5.1	5.4

FR loading(php)	**0**	**DMMP ：APP (5:25)**	**DMMP ：APP (10:20)**	**DMMP ：APP (15:15)**	**DMMP ：APP (20:10)**	**DMMP ：APP (25:5)**
Density(kg/m^3)	41.87	48.44	45.16	51.80	46.25	50.58
Compressive strength at 10% strain(MPa)	0.33	0.30	0.38	0.27	0.30	0.17
Specific compressive strength[MPa/(g/cm^3)]	7.9	6.2	8.4	5.2	6.5	3.4
Tensile strength(MPa)	0.25	0.25	0.24	0.19	0.27	0.17
Specific tensile strength [MPa/(g/cm^3)]	6.0	5.2	5.3	3.7	5.8	3.4

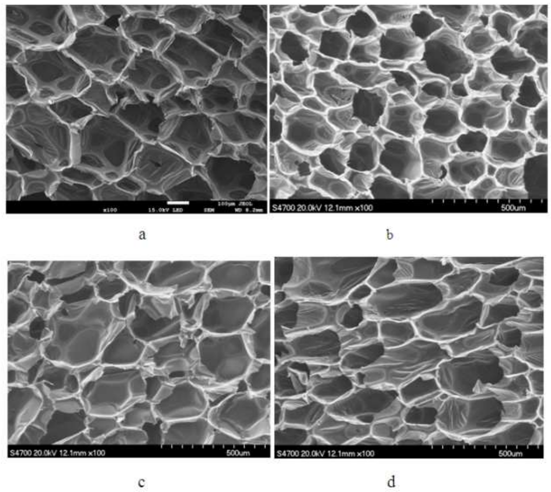


Fig 1. Microphotographs of RPUF with different phosphorus FRs under 100 magnification (a) neat;(b) DMMP-30php;(c) APP-30php; (d)DMMP: APP-15:15.

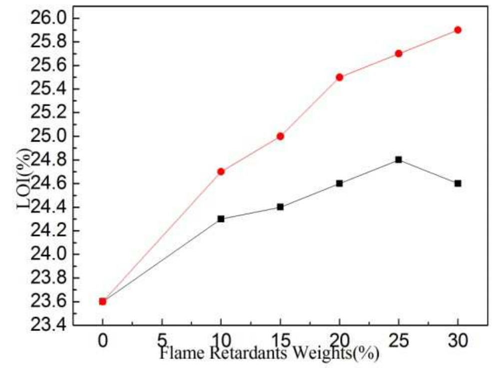
3.3. Flame Retardant Behavior

The fire behavior has been studied by means of oxygen index test and smoke density chamber. The effect of DMMP、APP and their compounded systems as FR on the flame retardant properties of filled and unfilled RPUFs were studied in comparison with neat RPUF. The result of the LOI values of RPUFs is shown in Fig 2. The higher LOI value represents the better flame retardancy25. We can see that the LOI values of RPUFs increase with the increase of DMMP, where the maximum LOI is about 25.9 in presence of fairly high DMMP amounts(30%). The APP filled RPUF also improved LOI, but it is not as effective as DMMP. The maximum LOI is only 24.8 when the filling amount was 25%.The increase in LOI revealed the resistance of the material to the inflammability. Phosphorus plays an important role in flame resistance. Generally the higher phosphorus content, the relative flame retardant property will be better. Phosphorus's combustion would form a char layer, which would cover the broken polyurethane foam structure. The char layer can isolate the polyurethane from oxygen and heat[26].

In general, the effective FR should have degradation temperature close to that of neat polymer matrix[17]. The decomposition temperature of DMMP is greater than 187℃, and the PU decomposition temperature is 170-200℃. So DMMP can perform a good flame retardant effect.

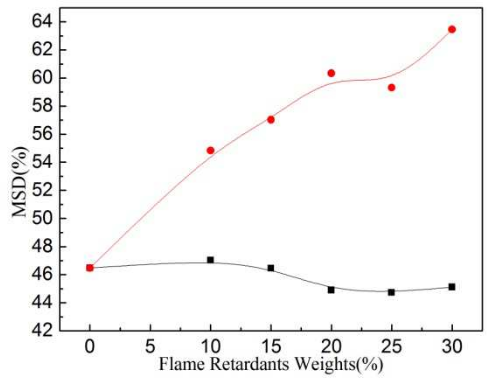
As to APP, the ammonia and other noncombustible gases decomposed from APP diluted the oxygen concentration surrounding RPUF. Meanwhile, it formed an intumescent char that can act as a barrier to heat, air/O_2, and pyrolysis products[25, 27]. There existed a synergistic effect between nitrogen and phosphorus in APP, which played the role both in the gas phase and in the condensed phase[28]. So when we mixed DMMP and APP together, it will generate better flame retardancy.

When we ignited the polyurethane foam, scorch and dark smoke are visible, which is believed to be caused by combination of thermal and oxidative decomposition of the foam. The maximum smoke density(MSD) results about the filled and unfilled RPUF are shown in Fig 3. It is clearly observed that APP performes much better than DMMP in smoke density. The smoke density decreases slightly with APP compared with neat RPUF. This indicates the APP has smoke suppression performance. Because the intumescent char layer prevented the smoke escape, and then reduced the smoke release[29, 30]. However, the output smoke density of DMMP/RPUF is much higher than unfilled RPUF. This is due to the phosphorus oxyacid DMMP decomposed. The covering phosphorus oxyacid is vitreous and sticky, which lead to incomplete combustion. So the smoke is more.



Properties: ●-DMMP, ■-APP

Fig 2. Curves of the RPUF's LOI values changing with the flame retardants contents.



Properties: ●-DMMP, ■-APP

Fig 3. Curves of the RPUF's MSD changing with the flame retardants contents.

Solid FR increases the viscosity, while liquid FR decreases. When the two are combinated, the viscosity can be adjusted. What's more, there existed a synergistic effect between the different FRs, which can improve the flame retardancy. The LOI and SMD of the compounded systems at different ratio are shown in Table 2. It can be seen significant improvements are observed in LOI of the compounded systems filled RPUF. The LOI can be as high as 26.7 when the ratio of DMMP and APP is 1:1 and 5:1, which demonstrated that DMMP has a good synergistic effect with APP.

Moreover, we can see their MSD from Table 2 that the higher loading of DMMP with APP filled RPUF, the less MSD release compared to DMMP filled RPUF.

Table 2. *The LOI and MSD of the compounded systems at different ratio.*

Mass Ratio (DMMP/APP)	1:5	1:2	1:1	2:1	5:1
LOI	25.8	25.6	26.7	26.0	26.7
MSD	49.25	49.90	50.69	53.92	59.10

4. Conclusions

In this paper, we prepared the RPUFs with DMMP, APP and their compounded systems. The mechanical strength of the filled RPUF shows lower than that of neat polyurethane. From the results of LOI, the filled RPUF shows better flame retardation over neat RPUF, which means the flame retandant property is improved. DMMP has higher LOI value than APP filled RPUF, which seems to be more effective in flame retardant. APP performed much better than DMMP in smoke density. APP has smoke suppression performance. There existed a synergistic effect between this two different FRs, which can improve the flame retardancy.

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