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An Experimental Study on the Incombustibility of Polymer Mortar

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Abstract

One of the fields using unsaturated polyester (UP) resin is the polymer concrete industry. UP resin is being popularly used as a replacement of conventional concrete in making of various precast products due to improved strength and durability. However, the most serious problem in using UP resin in this field is combustibility of the material. Since it contains carbon, it is difficult to expect for polymer concrete to be incombustible. But it is well known that the combustibility can be controlled to some degree. In this study, polymer mortars were made using a UP resin as binder, a calcium carbonate as filler, and a silica sand as fine aggregate. Incombustibility characteristics were investigated for polymer mortar specimens, which were made with different contents of flame retarder and UP resin, 5 % to 12.5 % and 12 % to 24 %, respectively. The results showed that an optimum range of flame retarder contents to various UP resin contents could be determined.

Keywords: unsaturated polyester resin, polymer mortar incombustibility, flame retarder

1. Introduction

While the unsaturated polyester UP resin is good in chemical resistance, abrasive resistance, electrical insulation, impact resistance and freeze-thaw resistance, it is not good against heat and ultraviolet ray. However, theories on the subject of the development of flame retarder and the technique of mixing have been established in domestic and foreign countries to compliment this weakness. Also, the experimental method and the evaluation standard on incombustibility are regulated by IEC (International Electrotechnical Commission), UL (Underwriters Laboratories Inc.), JIS (Japanese Industrial Standards), ASTM (American Society of Testing Materials), KS (Korean Standard), and so on.

However, it was very difficult to find research documents on the incombustibility and the technique of mixing flame retarder of polymer concrete and polymer mortar, which uses UP resin as a binder.

This study evaluated the capacity of incombustibility of the polymer mortar according to the contents of flame retarder and binder. In order to obtain the optimized contents of flame retarder, experiments was performed to verify the incombustible characteristics of polymer mortar by setting the contents of binder, UP resin, as 12-24 % and varying the content of flame retarder as 5-25 %.

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2. Materials

Binder

UP resin containing 38 % styrene monomer was used as the binder, 8 mineral turpentine solution of cobalt octoate as an accelerator and methyl ethyl peroxide (MEKPO) as an initiator. Constitutional formula and properties of ortho type UP resin, are shown in Figure 1 and Table 1, and of initiator used in this experiment in Figure 2 and Table 2, respectively.

Flame Retarder

Compounds of chemicals such as halogen, phosphorous, antimonic nitrogen, bromine and so on are generally used as flame retarder for UP resin. It is an effective method to select the flame retarder based on the TGA (thermogravimetric analysis) curves of the UP resin and one flame retarder.

Two kinds of incombustibles were used jointly at the definite ratio: One is Decabromodiphenyl Oxide made by A company in the U.S.A., which is an aromatic bromine organic compound, and another one is Antomony Trioxide made by domestic B company, which was used to get an reciprocal action of flame retarder. The constitutional formula of Decabromodiphenyl Oxide is shown in Figure 3, and the TGA curves of Decabromodiphenyl Oxide and UP resin in Figure 4. The chemical properties of

Decabromodiphenyl Oxide and Antimony Trioxide are listed in Table 3 and 4, respectively.

Fine Aggregate and Filler

The maximum size of fine aggregate was 0.2 mm, and the moisture content in silica sand was below 0.1 %. Calcium carbonate was used as filler, whose particle size was 1-30 _, fineness was 2500-3000 _/g, and moisture content was below 0.1 %. Physical properties and chemical composition of the calcium carbonate are listed in Table 5 and 6.

Test Specimen

UP resin Specimen

As a result of persistent effort in studying the incombustibility of UP resin, theories on the selectivity of flame retarder and the additive ratio have already been established. The effect of reciprocal action caused by a combined use of the antimony trioxide (Sb2O3) and the halogen compound with the UP resin is the most typical example.

In order to compare the incombustible capacity of UP resin itself according to the addition of the flame retarder, four specimens to each of five mixing ratio were produced: The relative ratio of two halogen organic compounds, Decabromodiphenyl Oxide and Antimony Trioxide, were tuned from 1:1 to 4:1 with a constant total content of 20 % suggested by the makers of compounds.

Polymer Mortar Specimen

In order to verify quantitatively the incombustible effect, according to various contents of resin of the polymer mortar used with UP resin, four specimens for five mixing ratio were made by varying the ratio were made of resin to calcium carbonate plus silica from 12:88 to 24:76. Also, flame retarders such as antimony trioxide (Sb2O3) and Decabromodiphenyl Oxide with the weight-mixing ratio of 1:4 to the above mentioned mortar were added in order to analyze the effect of reciprocal action of flame retarder in each case of adding flame retarder to mortar. Total contents of these flame retarders were 5 %, 7.5 %, 10 %, 12.5 %, and 15 % to the contents of resin as listed in Table 7.

The sizes of these specimens were 10×10×120 mm (width×height×length) as regulated in KS M 3015 (Testing Methods for Thermosetting Plastics).

Test Method

Even if there exist the methods and standards for evaluating the capacity of incombustibility of plastic in standards such as IEC, UL, JIS, ASTM, KS and so on, the standard method of experiment evaluating incombustible capacity and the decision condition for the grade of incombustibility for polymer concrete and polymer mortar have not been established.

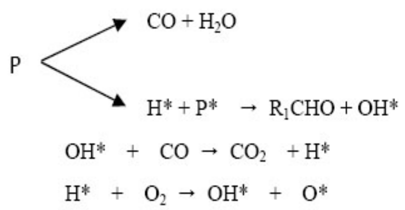
In this experiment, the incombustible capacity of specimen was analyzed and compared based upon the flame lingering time and the combustion length regulated in KSM 3015. The flame lingering time mentioned in the KS M 3015 means the self extinguishing time in specimen, when the specimen is detached from being attached for 30 s to the blue ignition flame end of which makes an angle of 30° with vertical direction.

If the extinguishing time exceeds 180 s, then the fire was blown out and the specimen was evaluated as being combustible. And the combustion length means the burned length, during self-extinguishing, measured from the end attached to flame. It is called the noncombustibility if the combustion length is less than 25 mm and the self-extinguishment if the length is in the range between 25 mm and 100 mm. The KS M 3015 method is shown in Figure 5.

Theories of Combustibility and Incombustibility of UP resin

Combustion of UP resin

Generally, combustion of UP resin is the process that C-C and/or C-H binding among the polymer chain obtain the activation energy, which is necessary to be broken, and that an external heat destroys the binding. The combustible monomer gas generated at the previous stage interacts with oxygen in the air and then is ignited and burned. The process takes stages of combustion such as heating, melting, decomposition, vaporization, diffusion, ignition, combustion and so on. The process can be expressed as a simplified model as follow (Lee, 1996):



Theory of Incombustibilization

Several methods of incombustibilization of UP resin are generally used. For example, the content of combustible materials decreases by adding the inorganic filler, or flame retarder, or surfaces of hardened UP resin are coated with incombustible fireproof materials.

The incombustibilization by adding flame retarder can be reached to the purpose of incombustible effect, in which the amount of H* radical or OH* are reduced. The halogenated hydrogen generated when the organohalogens (symbolized as XBr) is being burned dilutes the combustible gas decomposed from UP resin and interacts with OH* radical to control the chain reaction of combustion (Takiyama, 1994).

Also if two kinds of flame retarder are used jointly, the reciprocal action of flame retarder can be obtained. Reciprocal action of halogen group and antimony are typical examples. If the halogen and the antimony are coexisted, the catalytic reaction can be obtained from the interaction inside flame between the oxidized substance of both elements and OH* radical as well as so-called the wall effect that blocks the air by noncombustible gas of antimony+halogen compound generated by burning is occurred (Hanabusa, 1978).

$Sb2O3 + HBr \rightarrow 2SbOBr + H2O$

$5Sb4Obr (S) \rightarrow Sb4O5Br2 (S) + SbBr3 (g) \uparrow$

$4Sb4O2Br2(S) \rightarrow 5Sb3O4Br(S) + SbBr3(g) \uparrow$

$3Sb3O4Br(S) \rightarrow 4Sb2O3(S) + SbBr3(g) \uparrow$

$Sb2O3(S) \rightarrow Sb2O3(I)$

It has been reported that the incombustible operation of antimony-halogen is most efficient when the antimony: chlorine mole ratio is 3:1, and the total contents of these is 25 % to the resin in case that the halogen group element is chlorine. The reduction of properties of polymer products can, however, be decreased by adding a large quantity of incombustible material, since the same effect can be achieved by using less content than 25 % in case when the bromine group, newly developed recently, among halogen incombustible materials was used with the antimony.

3. Results and Discussion

Incombustible Characteristics of hardened UP Resin

The incombustibility for two sets of five different specimens was tested as shown in Table 7. One set did not contain a flame retarder and another had added two different flame retarders, where the relative ratio of two flame retarder were varied from 1:1 to 1:4.

The first one was evaluated as combustible based upon KS M 3015 since the duration of combustion was over 180 s after removing the flame, and later four specimens were evaluated as non-combustible since the combustion had ceased as soon as the flame was removed.

Incombustible Characteristics of Polymer Mortar

Flame Lingering Time

The flame lingering time for the polymer mortar in which the contents of used UP resin were varied in the range of 12-24 % and flame retarder contents of 0 % and 5-12.5 % were measured. For the polymer mortar without flame retarder, the time increased to 56-175 s when the contents of UP resin was increased to 12-24 %, which was shorter than 180 s of the standard time for being combustible.

When the contents of flame retarder were increased to 5-12.5 %, the flame lingering times were conspicuously reduced as 2-0 s for 12 % of UP resin, 10-0 s for 15 %, 23-0 s for 18 %, 46-0 s for 21 % and 96-0 s for 24 %. Relationship between the contents of UP resin and the flame lingering time according to the contents of flame retarder are shown in Figure 6. And relationship between flame retarder contents and flame lingering time according to the contents of UP resin in Figure 7. Also relationship among the UP resin contents, flame retarder contents and flame lingering time, are shown in Figure 8.

Combustion Length

The combustion length of polymer mortar was also surveyed by varying the contents of UP resin to 12-24 % and the contents of flame retarder to 0 % and 5-12.5 %. The polymer mortar without flame retarder was evaluated as non-combustible since when the contents of UP resin was increased to 12-24 % the combustion length was increased to 6-15 mm. The combustion length when the contents of flame retarder were increased to 5-12.5 % was conspicuously reduced as 1-0 mm for 12 % of UP resin, 2-0 mm for 15 %, 4-0 mm for 18 %, and 7-0 mm for 21 % and 11-0 mm for 24 %. Relationship between the UP resin contents and combustion length according to flame retarder contents are shown in Figure 9. And the relationship between flame retarder contents and the combustion length according to UP resin contents in Figure 10. Also relationship among the flame retarder contents, the UP resin contents and the combustion length, are shown in Figure 11.

From these results by considering the flame lingering time and the combustion length based upon KS M 3015, the relationship between the contents of UP resin and the contents of flame retarder, whose all measured values were near zero, are as follows: The polymer mortar was perfectly non-combustible when the used contents of UP resin (ratio in the mortar)-the contents of flame retarder(ratio at the UP resin) are 12 %-about 5 %, 15 %-about 7.5 %, 18 %-about 10 %, 21 %-about 12.5 %, 24 %-about 12.5 %, respectively.

4. Conclusions

This study was conducted to investigate the incombustible characteristics of various formulations of polymer mortars based upon the method regulated in KS M 3015. Results from this study are as follows:

The flame lingering time and the combustion length for the hardened UP resin for the case that the contents of flame retarder is 20 % are all zero regardless of the composition ratio of Decabromodiphenyl Oxide and Antimony Trioxide: It should be noted that the contents of flame retarder was added more than normal quantity.

When the used contents of UP resin was increased to 12-24 %, the flame lingering time for polymer mortar were 56-175 s and the combustion length were 6-15 mm, which were tested by the method regulated in KS M 3015: The polymer mortar was evaluated as non-combustible.

The polymer mortar is rated as non-combustible when the contents of UP resin (ratio at the mortar)-the contents of flame retarder (ratio at the UP resin) are 12 %-about 5 %, 15 %-about 7.5 %, 18 %-about 10 %, 21 %-about 12.5 %, 24 %-about 12.5 %, respectively.

If the industrial retarder is used, the total cost increment for producing an actual good is estimated as 10 % below. Further researches should be conducted relative to the strength characteristics and the quality deterioration due to the addition of flame retarder in polymer mortar or concrete used in a structure according to the variables such as the used contents of UP resin, the contents of flame retarder and the kinds of flame retarders.

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Table 1. Properties of Unsaturated Polyester Resin

Specific gravity	Viscosity (25 ℃, poise)	Acid value	Styrene content (wt. %)
1.13	3.6	20.0	40.0

Table 2. Properties of Initiator

Component	Specific gravity	Active oxygen
MEKPO 55 %, DMP 45 %	1.12	10.0

Table 3. Typical Properties of Decabromoddiphenyl Oxide

Formula weight	Assay, Decabromoddiphenyl oxide GC area	Organic bromine content (Theoretical)	Specific gravity	Inorganic bromine
959.2	97 %	83.3 %	3.3	< 29 ppm

Solubility at 25 ℃ (g/100g solvent)

Water, Methanal, Pentane, Styrene	Acetone, Benzene	Toluene
< 0.1	0.1	0.2

Table 4. Typical Properties of Antimony Trioxide

Chemical formula	Molecular weight	Melting point (℃)	Boiling point (℃)	Specific gravity
Sb_2O_3	291.5	656	1425	5.3

Table 5. Properties of Heavy Calcium Carbonate

Specific gravity (gr/cc)	Absorption (cc/gr)	Water content (%)	pH	Mean grain size (□)	Retained percentage of 325 mesh sieve
0.75	0.20	<0.3	8.8	13	0.03

Table 6. Chemical Component of Heavy Calcium Carbonate

(Unit : %)

CaO	Al_2O_3	Fe_2O_3	SiO_2	MgO	Ignition loss
53.7	0.25	0.09	2.23	0.66	42.4

Table 7. Mix Proportion of UP Resin and Polymer Mortar using UP Resin

Resin specimens	UP resin (wt.%)	Flame retarder(wt.ratio)	
		A (SB_2O_3)	B (Decabromoddiphenyl Oxide)
UP-0-0	100	0	0
UP-1-1		1	1
UP-1-2		1	2
UP-1-3		1	3
UP-1-4		1	4

Mortar specimens	UP resin (wt.%)	Filler	Sillica sand	Flame retarder (A/B=4, wt.ratio)
PM0-12	12	1	4	0
PM0-15	15			
PM0-18	18			
PM0-21	21			
PM0-24	24			
PM5-12	12			
PM5-15	15			
PM5-18	15	1	4	5
PM5-21	21			
PM5-24	24			
PM7.5-12	12			
PM7.5-15	15			
PM7.5-18	18	1	4	10
PM7.5-21	21			
PM7.5-24	24			
PM12.5-12	12			
PM12.5-15	15			
PM12.5-18	18	1	4	12.5
PM12.5-21	21			
PM12.5-24	24			

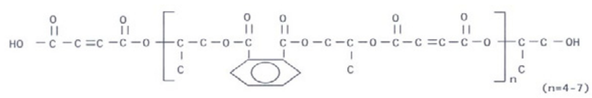

Figure 1. Constitutional Formula of Ortho Type Unsaturated Polyester Resin

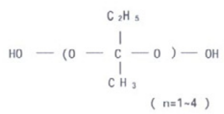

Figure 2. Constitutional Formula of Initiator

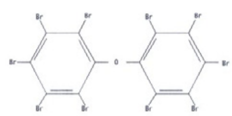

Figure 3. Constitutional Formula of Decabromoddiphenyl Oxide

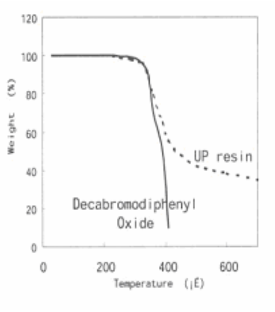

Figure 4. Relationship between temperature and weight

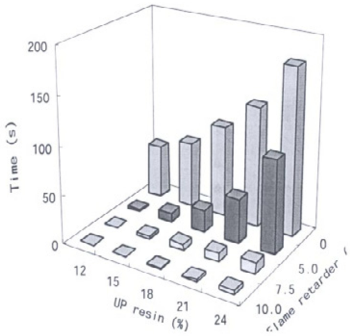

Figure 8. Relationship among the UP Resin contents, Flame Retarder contents and Flame Lingering Time

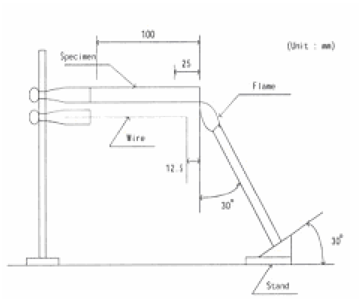

Figure 5. Device for Incombustibility Test

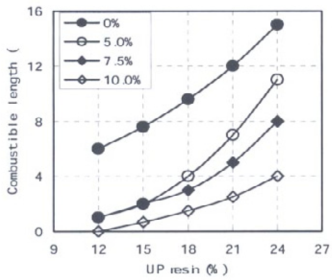

Figure 9. Relationship between UP Resin contents and Combustion Length according to Flame Retarder

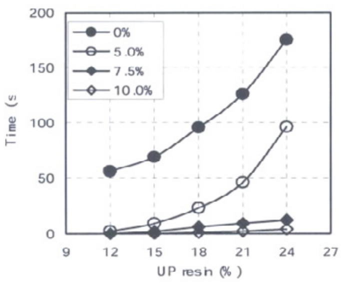

Figure 6. Relationship between UP Resin contents and Flame Lingering Time according to Flame Retarder contents

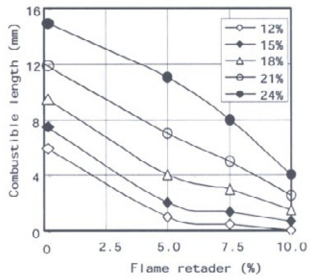

Figure 10. Relationship between Flames Retarder contents and combustion length according to UP Resin Contents

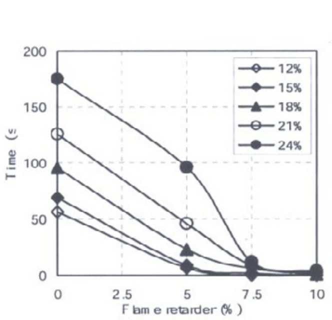

Figure 7. Relationship between Flames Retarder contents and Flame lingering Time according to UP Resin contents

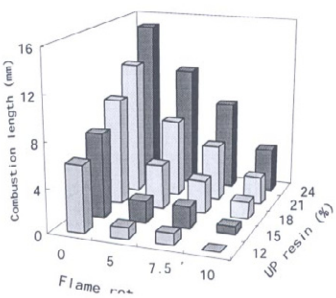

Figure 11. Relationship among the UP Resin Contents Retarder contents and Combustion Length