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ORIGINAL ARTICLE

The fire-retardant properties of the melamine-modified urea–formaldehyde resins mixed with ammonium polyphosphate

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Abstract Fire retardancy of melamine-modified urea–formaldehyde resin (MUF) containing intumescent fire-retardant ammonium polyphosphate (APP) (MUF/APP) was conducted by cone calorimeter with surface treatment of medium density fiberboard (MDF). The results showed that the six MUF resins synthesized with different F/(M + U) and M/U molar ratios containing APP significantly improved the fire retardancy of the MDF by prolonging ignition time, reducing heat release rate and total heat release, and decreasing mass loss rate. The fire-retardant properties of the six synthesized MUF/APP acted differently even though each MUF resin containing the same mass ratio of APP. The melamine content in the MUF should not be too high, otherwise it would decrease the fire-retardant properties of MUF/APP. Based on this study, the higher the APP amounts, the better the fire-retardant performance of the resin was. The fire retardancy of MUF/APP increased with the increase in the amount of glue that spread on the material surface. However, only the amount of glue spread exceeded 250 g/m^2, whereas the ability of MUF/APP in inhibiting heat release did not increase significantly any longer.

Keywords Intumescent fire retardant (IFR) · Melamine-modified urea–formaldehyde resin (MUF) · Ammonium polyphosphate (APP) · Fire retardancy · Surface treatment

Introduction

Fire-retardant treatments of wood products are designed to reduce their flammability. The common method of introducing fire retardants in wood or plywood is through soaking or pressure impregnation [1, 2]. The surface coating of resins with fire retardants was found to be an effective and economical method of improving fire endurance [3, 4]. Such a surface treatment method can remove infusion and re-drying process, reduce the cost of the process and is applicable to any species because of no permeability limit. Based on their fire preventive effect, bond strength and formaldehyde emission, Kawarasaki et al. [3] selected some fire retardants mixed with melamine formaldehyde resin (MF) or urea–formaldehyde resin (UF) to examine their influence on fire preventive of plywood. The results showed that intumescent fire retardant (IFR) using ammonium polyphosphate (APP) as the catalyst, pentaerythritol as the carbonific material, and dicyanodiamide or azodicarbonamids as the blowing agent mixed with MF adhesive was a suitable surface treatment.

Compared with MF and UF resin, melamine-modified urea–formaldehyde resin (MUF) also has good water resistance, low formaldehyde emission, lower cost and a longer storage period. Varying F/(M + U) and M/U molar ratios could produce a series of MUF resins [5–7]. No report is available about MUF resins mixed with IFR. This paper would evaluate the fire retardancy of MUF resins containing APP using CONE, and discuss about the effects of formulations of MUF, mass ratios of MUF/APP and the amount of glue spread on the fire retardancy.

Materials and methods

MUF resin preparation and bond performance test

Six types of MUF resins were prepared according to the method of Tohmura et al. [5] (Table 1). The bond

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Table 1 Composition of MUF resins [5]

Parameter	MUF1	MUF2	MUF3	MUF4	MUF5	MUF6
Final F/(M + U) molar ratio	1.5	1.5	1.5	1.125	1.125	1.125
Final M/U molar ratio	0.5	0.7	1.0	0.3	0.6	1.0
Melamine content (wt% to MUF resin)	34	40	46	29	40	50

MUF melamine (M)–urea (U)–formaldehyde (F)

performance test of all MUF resins was conducted according to the Chinese standard GB/T 17657 (1999) [8]: 4 h of boiling, drying at 63 ± 3 °C for 20 h, then 4 h of boiling and drying at room temperature for 10 min. Then testing and calculating the bonding strength of 3-layered poplar veneer plywood samples. Plywood hot process conditions: hot press 1.0 Mpa at 120 °C with a pressing time of 5 min.

Samples preparation

Samples of medium density fiberboard (MDF) with thickness of 15 mm were cut into a size of 100 mm × 100 mm. The MDF containing 14 % solid UF resin per unit dried fiber was purchased from Beijing Wood Processing Factory. The average density and moisture content of the MDF before the treatment were 0.703 g/cm^3 and 8 %, respectively. Three replicates were prepared for MUF/APP surface treatment and the fire retardancy test.

MUF/APP preparation and treatment of samples

For test of the effects of different MUF on the fire-retardant performance, six types of MUF resins containing APP with the mass ratio of 100:50, respectively, were used. The MDF samples were brush coated on one surface with MUF/APP at the glue spread amount of 400 g/m^2 (about 4 g MUF/APP resins were evenly brush coated to one of 100 mm × 100 mm surface).

For test of the effects of different MUF/APP mass ratio on the fire-retardant performance, selected MUF3 resin based on fire retardancy and bonding strength was used. Then, the MUF3 was mixed with APP with the mass ratio of 100:0, 100:40, 100:50 and 100:60, respectively. The MDF samples were brush coated on one of the 100 mm × 100 mm surface with 4 g MUF3/APP at the glue spread amount of 400 g/m^2.

For test of the effects of glue spread amount on the fire-retardant performance, the MDF samples were brush coated using MUF3 containing APP with the mass ration of 100:60 on one of 100 mm × 100 mm surface with 2, 2.5, and 4 g. The glue spread amount of sample was 200, 250, and 400 g/m^2, respectively.

After coated with a layer of resin, all MDF samples were placed at room temperature so that the resin slowly solidified and then conditioned at 23 ± 2 °C and 50 ± 5 % RH for about 24 h to eliminate the water of resin. The range of moisture content of the specimen before test was about 10–12 %.

Fire retardancy test

The fire retardancy test was conducted according to the standard of International Organization for Standardization IS05660-1 using CONE [9]. In the CONE, a 100-mm square specimen was exposed to a constant external heating flux. All the tests were conducted at an irradiance level of 50 kW/m^2. All specimens were tested in the horizontal orientation. To prevent the side effects, side and back surfaces of specimen were covered with aluminum foil paper. After wrapping, the wrapped specimen shall be placed in the specimen holder and covered by a retainer frame (The size of the heating surface was 94 mm × 94 mm). The distance between the bottom surface of the cone heater and the top of all specimens is 25 mm. The heating surface of the treated samples was coated with resin surface. The primary result from the CONE was a heat release rate (HRR, in kW/m^2) curve over the duration of the test. The time to sustained flaming was measured as well. The duration time of all test samples from the start of heating to the end of the experiment was 600 s. The total heat release (THR, in MJ/m^2) was the cumulative heat release (area under the heat release curve) through the duration of the test. In addition, the mass of individual specimen was weighed and recorded before and after burning. The mass loss rate (%) was calculated using the following equation:

The mass loss rate (%) = $(M_b - M_a)/M_b \times 100$ (M_b: the mass of the specimen before burning, M_a: the mass of the specimen after burning for 600 s).

From the heat release and mass loss, the effective heat of combustion (EHOC) (heat release per unit mass loss) was calculated. The average effective heat of combustion (AEHOC) was computed from the THR divided by the total mass loss. Ignitability is determined by observing the time for sustained ignition of the specimen.

The values determined above were recorded for each individual test and averaged for the three replicates. The most typical curve of HRR and THR of the three specimens was showed in Figs. 1, 2 and 3.

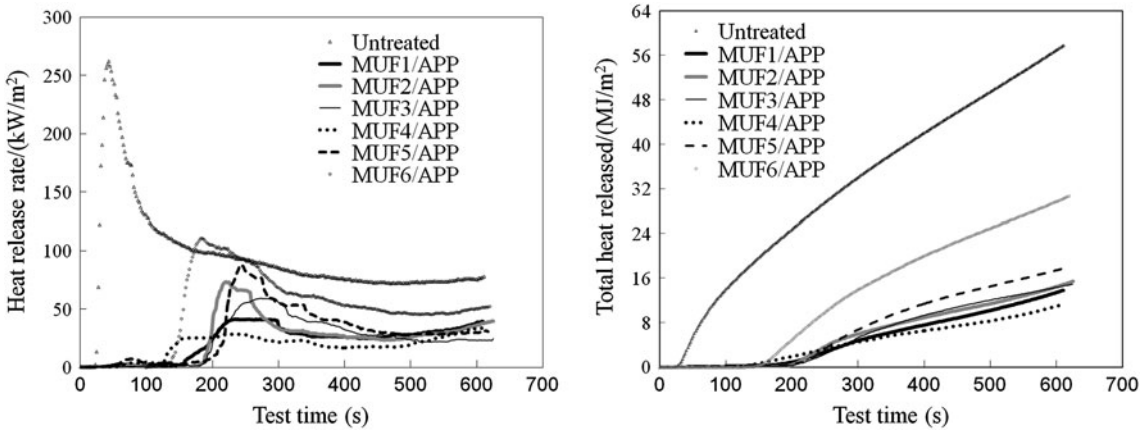

Fig. 1 Heat release rate and total heat release of the MDF surface treated with the six types of melamine-modified urea–formaldehyde resins (MUF) containing the same amount of ammonium polyphosphate (APP)

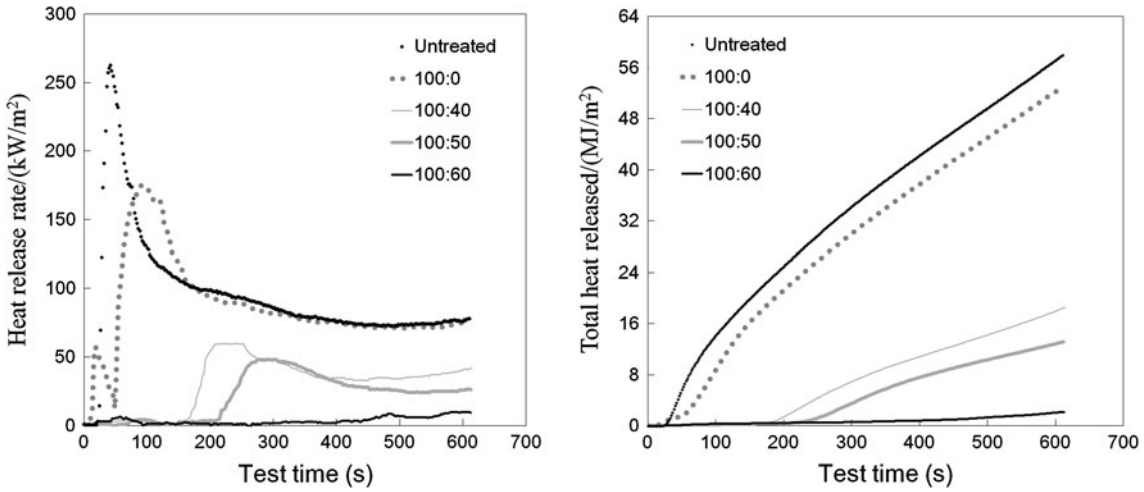

Fig. 2 Heat release rate and total heat release of the MDF surface-treated MUF3 containing ammonium polyphosphate (APP)

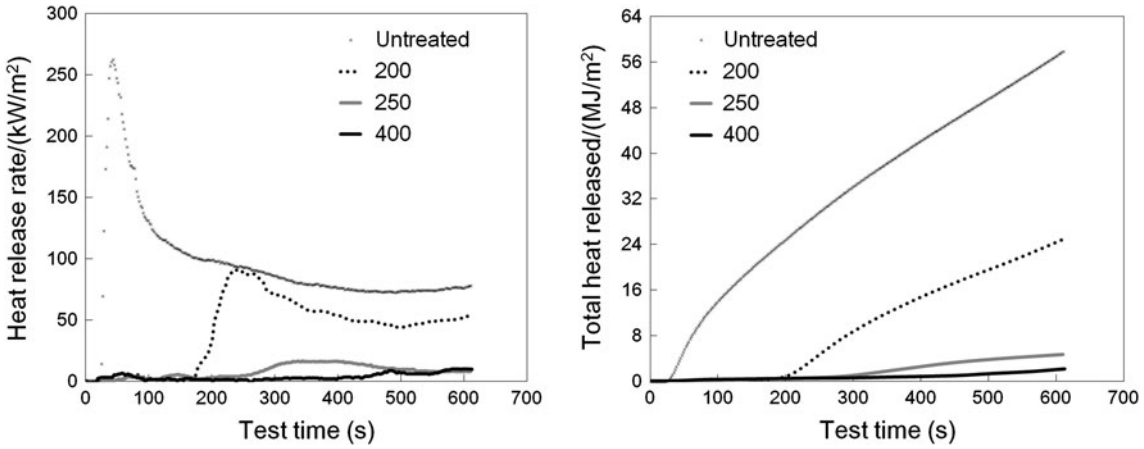

Fig. 3 Heat release rate and total heat release of the MDF surface treated with MUF3 containing the same amount of ammonium polyphosphate (APP) but different glue spread amount on the MDF surface (g/m^2)

Results and discussion

Effects of MUFs on fire retardancy

Table 2 and Fig. 1 showed the results of effect on fire retardancy of the six types of MUF resins containing APP. The ignition times of the untreated samples were 32.2 s, however, the ignition times prolonged significantly and varied from 121.2–190.5 s in the samples surface treated with the MUFs containing APP. The longer ignition time means the material is more difficult to ignite. So prolonging the ignition time has benefit to reduce the flammability of treated samples and of fireproofing and fire hazard reduction.

The surfaces of the MUFs/APP-treated samples were observed for thermal decomposition, charring and foaming, then formation of a black fluffy intumescent layer at the beginning of heating (Fig. 4). The layer was gradually inflated, thickened, and assumed to form a protective layer on the sample as barrier protecting the inner material from fire and combustion and cut off the heat and oxygen transfer into inner. Meanwhile, the treated samples produced large amounts of non-flammable gas along with thermal decomposition to dilute the concentration of the combustible gas, thereby extending the ignition times. With the extension of the heating time, the bubble contracted, and the thickness of the intumescent layer reduced. Then dispersed cracks were formed on the charred layer, and the protective layer damaged, resulting in weakening and loss of the protection ability, end of the material ignition. The observation was consist with the test on the fire retardancy of strandboard by surface treatment with melamine and phosphoric acid [4].

HRR is another critical factor in the spread of flames over a surface and in the overall growth of a compartment fire. It is an option for evaluating the degree of

Table 2 The burning behavior of the medium density fiberboard surface treated with MUFs/APP (MUF resins containing APP with the mass ratio of 100:50, the glue spread amount is 400 g/m^2)

Parameter	Untreated	MUF1/APP	MUF2/APP	MUF3/APP	MUF4/APP	MUF5/APP	MUF6/APP
Ignition times (s)	32.2	140.4	176.0	190.5	121.2	186.4	132.4
1st peak heat release rate (kW/m^2)	262.6	41.4	73.2	59.1	28.7	88.2	111.5
Times to 1st peek heat release rate (s)	42	238	221	275	235	243	182
$q_{A,180}$ (kW/m^2)	138.8	28.8	42.2	43.8	23.9	52.6	82.1
$q_{A,300}$ (kW/m^2)	119.2	27.9	38.4	35.8	22.3	45.4	72.4
$Q_{A,tot}$ (MJ/m^2)	34.3	5.1	7.8	5.0	4.8	8.0	20.0
Ave. effective heat of combustion (MJ/kg)	10.3	5.7	6.5	5.7	4.4	6.6	9.6
Mass loss rate (%)	45.3	22.8	23.1	25.4	22.4	27.5	30.3
Bonding strength after the delamination test (MPa)	/	0.71	0.86	1.04	0.39	0.65	0.75

All values are averages of three replicated experiments. $q_{A,180}$: the average heat release rate per unit area over the period starting at ignition time and ending 180 s later, $q_{A,300}$: the average heat release rate per unit area over the period starting at ignition time and ending 300 s later, $Q_{A,tot}$: total heat released per unit area over the period starting at ignition time and ending 300 s later

MUF melamine-modified urea–formaldehyde resin, *APP* ammonium polyphosphate

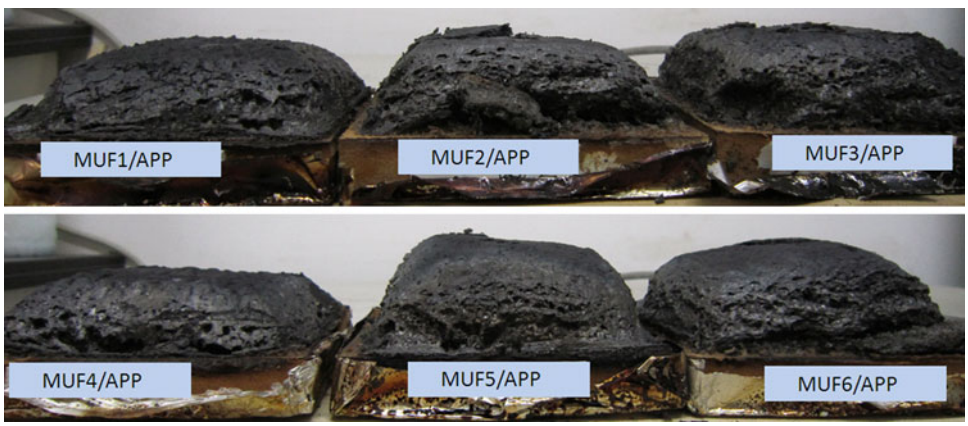

Fig. 4 Black fluffy intumescent layer on the surfaces of the MUFs/APP-treated samples

combustibility of different materials. Figure 1 illustrates the curves of the HRR and THR of the MDF surface treated with MUFs/APP. Compared with the untreated samples, the value of first peak HRR was reduced and the time of the first peak HRR was delayed in the surface-treated samples, and the THR of the treated samples was decreased significantly. Based on the first peak value of HRR, the MUFs/APP were ranked as: MUF4/APP < MUF1/APP < MUF3/APP < MUF2/APP < MUF5/APP < MUF6/APP; based on THR over the period starting at ignition time and ending 300 s later, the MUFs/APP were ranked as: MUF4/APP < MUF3/APP < MUF1/APP < MUF5/APP < MUF2/APP < MUF6/APP; and based on AEHOC: MUF4/APP < MUF3/APP = MUF1/APP < MUF2/APP < MUF5/APP < MUF6/APP. Except MUF6/APP, the average HRR of MUFs/APP at the first 300 s was all below 50 kW/m^2, and the THR of the first 300 s below 8 MJ/m^2, but in the control about 120 kW/m^2 and 35 MJ/m^2, respectively. The results suggested that violent exothermic process and the heat release of the materials were suppressed by each mixture of MUF resin containing APP.

The mass loss rate of the treated specimen was reduced significantly, and the MUFs/APP was ranked as: MUF4/APP < MUF1/APP < MUF2/APP < MUF3/APP < MUF5/APP < MUF6/APP (Table 2).

HRR, THR, AEHOC and the average mass loss rate all decreased significantly when the MDF was surface treated with MUFs/APP, which showed that the MUFs/APP be more effective in retarding fire for the MDF. Each MUF resin containing APP at the same mass ratio, but the fire retardancy of each MUF/APP was different. The MDF surface treated with MUF4/APP had the best performance of fire retardancy, followed by MUF1/APP and MUF3/APP, last MUF6/APP. Kawarasaki et al. [3]. reported that with the same kind and the same mass ratio of the flame retardant, the flame retardant properties of the UF resin-retardant composite were better than that of MF resin retardant. UF composite resin system of the ignition times (214 s) was longer than MF resin's (131 s). It suggested the mass ratio of M in melamine-IFR composite had a negative impact on the fire retardancy. Guo [10] believed that a higher char yield of intumescent fire-retardant foam layer of carbon foam was more homogeneous and foam walls were thick, and the fire-retardant effect was good. But the increase of the contents of melamine in the resin's fire-retardant composite could decrease the char yield, and increase the viscosity [10–12]. It proposed that the resin-intumescent flame retardant composite must have an appropriate proportion of M. In this research, melamine content (wt to MUF resin) of the six types of MUF was 34, 40, 46, 29, 40 and 50 %, respectively. The ascending order of the count of M is listed as: MUF4/APP, MUF1/APP, MUF3/APP, and MUF6/APP. The order is consistent with the order of fire-retardant performance. It suggested the melamine content in the MUF should not be too high; otherwise the fire-retardant properties of MUF/APP would decrease.

Bond performance of the MUFs

The bond strength of MUFs/APP after delamination test is showed in Table 2. MUF3/APP performed the best. MUF3/APP has a longer shelf storage time of storage in room temperature for 2 months. As MUF3/APP showed good fire retardancy among treatments, it would be used in the following tests.

Effect of MUF3/APP mass ratio on the fire retardancy

Figure 3 and Table 3 showed the results of effect of MUF3/APP mass ratio on the fire retardancy. The fluffy protective layer did not occur in the only MUF3-treated samples. MUF3 resin on the surface of MDF was ignited quickly and form a small exothermic peak, followed by the ignition and the formation of a strong exothermic peak (Fig. 3). The ignition time of the untreated and treated with only MUF3 resin specimen was 32.2 s and 17.2 s, respectively. The THR for 180, 300 and 600 s of the MUF3-treated sample was decreased only by 16, 12 and 9 % compared with the control. The mass loss rate for combustion 600 s was lower than the control only by about 9 %. It suggested that MUF resin alone would be difficult to prevent the ignition and heat release of the material. When adding APP in MUF3 resin with mass ratio at 40:100, 50:100 and 60:100, the ignition times of the treated samples were delayed by 129, 158.3 and 339.6 s, respectively, in comparison with the untreated samples (Table 3). The THR for 600 s of the MUF3/APP-treated samples with mass ratio at 100:40, 100:50 and 100:60 was decreased at

Table 3 Effect of MUF3/APP mass ratio on the fire-retardant performance (the glue spread amount is 400 g/m^2)

Parameter	Untreated	Mass ratio of MUF3:APP			
		100:0	100:40	100:50	100:60
Time to ignition (s)	32.2	17.2	161.2	190.5	371.8
Delay of the ignition time (s)	/	15	129	158.3	339.6
Total heat released/(MJ/m^2)					
180 s	23.0	19.4	0.6	0.3	0.3
300 s	34.3	30.1	6.9	5.0	0.8
600 s	57.2	52.3	18.0	12.8	4.3
Mass loss rate (%)	45.3	41.1	25.8	25.4	20.8

All values are averages of three replicated experiments

MUF melamine-modified urea–formaldehyde resin, *APP* ammonium polyphosphate

rate of 69, 78 and 93 %. The mass loss rate for combustion 600 s was lower than the untreated by about 43, 44 and 54 %. It suggested that adding APP to MUF resin could significantly improve the fire retardancy of the material; the higher the APP amount was, the better fire-retardant performance was.

Table 3 shows that there is no significant difference on THR for combustion to 180 s below 1 MJ/m^2 despite the mass ratio of APP. Combusted for a longer time to 300 s, the THR of MUF3/APP with addition of APP amount from 100:40 to 100:60 was 6.9, 5.0 and 0.8 MJ/m^2, respectively. When to 600 s, the THR difference with raising APP amount was more significant. With the MUF3/APP mass ratios from 100:40 to 100:60, the increased amount of THR from 180 s to 600 s was declined by 17.4, 12.5 and 4.0 MJ/m^2, respectively. It suggested that with the increase of the APP amount in the composite, not only the capacity of anti-release heat was enhanced, but also the persistence of fire retardancy increased.

The first peak HRR of MUF3/APP gradually declined and the time to the first peak HRR delayed with APP amount increasing. The first peak HRR of MUF3/APP with mass ratio 100:60 did not occur and combustion heat release of treated sample slowed (Fig. 3).

Effects of glue spread amount on the fire retardancy

Fire test results are shown in Table 4 and Fig. 4. The ignition time was prolonged as 173.2, 264.5 and 371.8 s, with the delay of 141.0, 232.3 and 339.6 s, respectively, in comparison to the untreated. At the same time, the THR at 180 and 300 s decreased significantly with the increase of glue spread amount from 200 to 400 g/m^2 (Table 4). The mass loss rate of treated samples at 200, 250 and 400 g/m^2 decreased at the rate of 39, 46 and 54 %, respectively. It showed that the property of fire retardancy increased with the increase of glue spread amount.

Table 4 Effects of glue spread amount on the fire-retardant performance (MUF3 containing APP with the mass ratio of 100:60)

Parameter	Untreated	Glue spread amount (g/m^2)		
		200	250	400
Time to ignition (s)	32.2	173.2	264.5	371.8
Total heat released/(MJ/m^2)				
180 s	23.0	1.5	1.0	0.3
300 s	34.3	13.6	2.0	0.8
600 s	57.2	20.5	3.9	4.3
Mass loss rate (%)	45.3	27.6	24.4	20.8

All values are averages of three replicated experiments

MUF melamine-modified urea–formaldehyde resin, *APP* ammonium polyphosphate

It can be learned from Table 4 that THR for combustion to 180 s did not vary from the amount of glue spread with the value below 1.5 MJ/m^2. Combusted for a longer time to 300 s, the THR of MUF3/APP increased by 13.6, 2.0 and 0.8 MJ/m^2, respectively, with additional amount of glue spread from 200 to 400 g/m^2. When to 600 s, the THR difference with raising glue spread amount was more significant. With the glue spread amount from 200 to 400 g/m^2, the increased amount of THR from 180 to 600 s declined to 19.0, 2.9 and 4.0 MJ/m^2, respectively. It suggested that MUF3/APP not only suppressed the release of heat, but also gradually enhanced the persistence of the fire retardancy with the increasing glue spread amount on the surface of MDF.

The first peak HRR of MUF3/APP gradually decreased and the time to the first peak HRR delayed with the increase of glue spread amount. The first peak HRR of MUF3/APP with 400 g/m^2 glue spread did not occur and the combustion heat release of treated sample slowed down (Fig. 4).

The THR for 180, 300 and 600 s did not decrease significantly from the glue spread amount of 250 to 400 g/m^2 (Table 4; Fig. 4). Only 50 g/m^2 differences from 250 to 200 g/m^2, the THR for 300 and 600 s increased significantly: from 2.0 to 13.6 MJ/m^2, from 3.9 to 20.5 MJ/m^2. This showed that the capability of inhibiting heat release of MUF3/APP increased significantly until the amount of glue spread exceeded 250 g/m^2.

Conclusions

The six formulated MUFs containing APP significantly improved the fire retardancy of the MDF by prolonging the ignition time, reducing the HRR and THR, and reducing the mass loss rate.

The fire-retardant properties of the six formulated MUF/APP acted differently even though each MUF resin containing the same mass ratio of APP. The MDF surface treated with MUF4/APP had the best fire retardancy, followed by MUF1/APP, MUF3/APP, MUF2/APP, and then MUF5/APP and MUF6/APP. The melamine content in the MUF should not be too high, otherwise it would decrease the fire-retardant property of MUF/APP.

Adding APP in MUF resin could significantly improve the fire retardancy of the material, the higher the APP amount, the better fire-retardant performance. The suitable mass ratio of MUF/APP could be determined according to the fire retardancy requirements on the material, resin curing performance and storage stability.

The fire-retardant capability of MUF/APP increased with the increasing amount of glue spread on the material surface. However, the inhibiting heat release capability of

MUF/APP would not increase significantly only when the amount of glue spread exceeded 250 g/m^2.

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