ABSTRACT

The large rack storage fire that occurred in Japan on November 1995 identified the fire risk of plastic pallets. Thereafter, the National Research Institute of Fire and Disaster started research and development of fire-retardant plastic pallets in collaboration with an association of plastic pallet manufacturers and a fire retardant chemical corporation. Flammability and mechanical properties of some synthetic resins were examined to screen useful synthetic resins for making plastic pallets. The flammability of the resin was tested by a cone calorimeter, UL94, and the oxygen index test prescribed in JIS K7201, and comparisons were made between different test results. Finally, a prototype fire-retardant plastic pallet was produced with FR additives combined with Mg(OH)₂ and red Phosphorous. Fire tests of full-scale pallets were conducted with a furniture calorimeter and the effect of the fire retardant was examined with satisfaction. Some of the mechanical properties were examined along with the flammability test.

Keywords: Flammability, fire-retardant, plastic pallet, fire test, cone calorimeter.

INTRODUCTION

A fire occurred in a warehouse in Japan’s Saitama Prefecture in November 1995 and the warehouse was almost completely burnt down. This warehouse had automatic highly palletized rack storage and many plastic pallets were stored for stacking products. Even though automatic sprinklers and a fire alarm system had been installed and activated, the fire spread very rapidly and fire suppression failed. The fire continued for more than 18 hours and three firefighters were killed due to rapid fire growth. The amount of heat released by plastic pallets is about three times as large as that of wooden pallets, and the number of plastic pallets used in warehouses has been increasing every year. Once a fire occurs in such a
warehouse containing many high calorie plastic materials, even if the major products contained are less flammable, it is very difficult to extinguish it. For these reasons, the fire risk in warehouses is now recognized as one of the important fire safety issues and rational countermeasures are expected.

After investigation of the warehouse fire\(^1\), the Fire and Disaster Management Agency addressed some fundamental countermeasures. Major items were (1) stepping up fire safety equipment such as fire alarm systems and sprinklers, (2) mitigation of fire risk caused by flammable plastic pallets, i.e. adoption of non-combustible or fire-retardant (FR) treated plastics.

In July 1998, the Fire Service Law Enforcement was revised to strengthen fire safety countermeasures in warehouses and a new sprinkler installation guideline\(^2\) was proposed that depends on the total amount of heat source in a warehouse. In this guideline, one new class of combustible materials “high calorie melting material” was introduced and pertains to such materials as plastic pallets, of which the amount of heat release is more than 3.4 MJ/kg. In addition to the conventional “designated combustibles” prescribed in Fire Service Law Enforcement, the total stored quantity of such materials should be taken into account when specifying the installation of sprinklers.

There have been many research and development efforts for FR plastic materials\(^3,4,5\), however very few FR pallets have been developed in Japan due to lack of market demand, i.e., weight, mechanical properties and price. Major materials used in plastic pallets are olefin hydrocarbons such as polypropylene (PP). Halogen-containing (mainly bromine, but less often hydrogen chloride compounds) and non-halogen-containing (magnesium hydroxide) chemicals and diantimony trioxide are commonly used as FR chemicals for such plastic applications. The classification of these FR plastics (UL94) and the oxygen index test in JIS K7201\(^7\) are very popular in Japan. However, the Fire Service Law Enforcement has designated plastic materials with an oxygen index of less than 26 as “flammable”, so FR plastic development is finding it somewhat difficult to satisfy both the criteria and mechanical demands. A plastic pallet classification test has already been proposed by UL2335\(^8\), however this is not well known in Japan at the moment, and there will be some limitations to adopt this as a standard test. Because the test uses a combination of pallets and sprinklers to evaluate fire safety, the risk of pallets alone cannot be evaluated.

Under these circumstances, development of fire retardant pallets which can satisfy fire safety as well as practical use needs is one of the key issues for improving warehouse fire safety, and rational test methods to evaluate the flammability of plastic pallets should also be examined. For this purpose, the National Research Institute of Fire and Disaster conducted research and development in collaboration with the Japan Pallet Association and a fire retardant chemical manufacturer. This paper describes the development process, which consists of three stages, and the results of related flammability testing using cone and furniture calorimeters (UL94) and the oxygen index test.

**Block flow of the R&D project**

One of the immediate goals was to develop and introduce less flammable prototype plastic pallets for practical use in the near future. In this R&D collaboration project, polypropylene-based FR plastic pallets were developed in three stages as shown in Figure 1. In each stage, flammability and mechanical properties were examined.

The 1\(^{st}\) stage was prepared for the screening test to find appropriate FR chemicals by using a small test plate of 100 mm x 100 mm x 4 mm thick. Some combinations of FR chemicals, fit for use in plastic
pallets, were investigated from viewpoints of both mechanical and flammability properties. Flammability was examined with a cone calorimeter, UL94, equivalent and oxygen index tests. After obtaining the 1st stage results, the 2nd stage examined the effects that the combination of practically promising non-halogen FR compounds, i.e., red Phosphorous (r-P) and Mg(OH)₂, had on flammability and mechanical properties. Exactly the same tests that applied in the 1st stage were conducted. In the 3rd stage, full-scale plastic pallets were produced using the FR treated resin with the same combination of compounds, and they indicated a highly FR effect and met mechanical properties in the 2nd stage. The flammability of a piece 1/4 the size of a full-scale pallet was examined by using a furniture calorimeter. These test stages are described in Figure 1.

### RESULTS AND DISCUSSION

**The 1st stage development**

There are various kinds of FR chemicals, however it is known empirically that a limited number of FR treatments can be applied to plastic pallets for practical use. At the beginning of this R&D project, relatively popular FR chemicals for basic PP resin were examined in bench scale tests using the cone calorimeter, UL94, and oxygen index tests.
Test resin and flammability test

FR chemicals are classified roughly into two types containing: halogen; and non-halogen additives. Halogen-containing FR chemicals, including bromine and chlorine compounds, are commonly used and their high FR effects are well known. The burning of these FR treated resins, however, tends to generate toxic gases such as hydrogen chloride and dioxin. Recently, the use of those halogen additives is being avoided due to environmental considerations, but Bromine compounds are very popular and well fit for base resin PP. Two specimens of a popular halogen (non-DBDPO type) FR treated resins are examined. Since Mg(OH)₂ is often used as a non-halogen FR additive, this FR chemical was selected as the test resin. Also, r-P is also added to the resin, because it is well-known that r-P additives strengthen FR effects even though r-P is seldom used for plastic pallets. Table 1 shows the test resins examined in the 1st stage consisting of two kinds containing halogen, five kinds of non-halogen-containing (four of them have r-P added) and base resin PP as a reference.

Since Mg(OH)₂ is often used as a non-halogen FR additive, this FR chemical was selected as the test resin. Also, r-P is also added to the resin, because it is well-known that r-P additives strengthen FR effects even though r-P is seldom used for plastic pallets. Table 1 shows the test resins examined in the 1st stage consisting of two kinds containing halogen, five kinds of non-halogen-containing (four of them have r-P added) and base resin PP as a reference.

UL94 flammability tests were conducted for each of the test resins, and “8200R” of the halogen-containing FR chemicals which correspond to the V-0 class, and another halogen, non-halogen compounds without r-P and two with r-P which correspond to V-2 class. Base PP corresponds to HB rating. Also, burning behaviour under radiant heat was examined by the cone calorimeter as follows.

Cone calorimeter test

Each of the test pieces was a plate 100 mm x 100 mm x 4 mm thick, which was set on the plasterboard base in the standard holder so that the surface of the specimen was adjusted at the same level as the top surface of holder frame. The test method followed the normal ISO 5660 flammability test by a cone calorimeter, and the heat release rate was measured by the oxygen consumption method. The ignition
times, combustion products, i.e., smoke density and CO, CO\(_2\) yields were also measured. The external radiant heat flux was set at 15, 20, 30 and 50 kW/m\(^2\) respectively. Figures 2, 3 and 4 show the heat release rate, smoke density and CO concentration under 20 kW/m\(^2\) heat flux conditions. The Figures (a) on the left side show the test results in the case of non r-P FR treated resins and the Figures (b) in the case of r-P FR treated resins.

Figure 2 shows the time-curve of heat release rate for different FR treated resins and non-FR base resin PP. The FR effect of each material can be evaluated by making a comparison with the heat release rate of basic PP. “8200R” of halogen-containing chemical (bromine but not DBDPO) and “EX187” (also containing bromine) show similar heat release rate time curves. The ignition time of such FR treated resin is about 100 seconds delayed and these FR additives have the effect of preventing ignition and burning of volatile vapor at the start of heat exposure. Once the specimen burns, however, the FR effect becomes smaller and the heat release rate is decreased by only 20% less than that of the base PP. This tendency can be explained by the well-known fact that halogen-containing chemicals are effective in retarding combustion in a vapor phase.

![Figure 2: Heat release rate per unit of different FR treated plastics (r-P and Mg(OH)\(_2\): 20 kW/m\(^2\) radiant heat flux).](image)

When the related plastic (“EX-168S”) is added to Mg(OH)\(_2\), where the Mg(OH)\(_2\) itself is non-combustible, then the total amount of heat release is 44% of the base PP. The heat release rate becomes relatively low and the peak heat release rate is about 20% of that of the base PP. Moreover, dehydrated residue of the Mg(OH)\(_2\) remains in layers on the surface and seems to play the role of thermal insulation for radiant and conductive heat transfer, resulting in less burning.

In the case of only r-P being added, the heat release rate becomes lower but the peak heat release rate (PHR) is only reduced by 20% or 30%. However, being combined with melamine-containing FR chemicals increases the FR effect. The test results show that, especially when r-P chemicals are combined with polyphosphate melamine, the PHR is half that of base PP. On the other hand, not much FR effect is observed in the case where the r-P is added with magnesium hydroxide. On the contrary, the combustion period tends to be extended. The qualitative combustion phenomena described here can be observed under other radiant heat flux conditions as well. The effect of the radiant heat flux will be mentioned later.
FR treatment on resins reduces the heat release rate and shortens ignition times, but it generally tends to generate a large amount of hazardous combustion products i.e., smoke and toxic gas such as carbon monoxide (CO). This is the concern from the viewpoint of fire safety. Figures 3 and 4 show the time curve of smoke density and CO yield respectively. These figures indicate that the smoke concentration is almost in proportion to CO yield. Notably, the smoke density and CO yield generated from halogen-containing FR resin doubles or triples in the peak, and the smoke density ranges from four times to ten times that of the base PP.

In contrast, in the case of Mg(OH)$_2$ additives, smoke production is very small and CO yield is hardly measurable. When r-P is added, the amount of smoke escalates to higher than that from the basic PP. Notably in the case of adding only red phosphorus, CO yield is about five times as high as that from the
basic PP. Furthermore, when red phosphorous is added with melamine-containing chemicals, CO is generated nearly in the same amount as that for halogen-containing chemicals. However, smoke density in the case of melamine-containing chemicals decreases and the smoke density is almost half that of halogen-containing chemicals.

The 2\textsuperscript{nd} stage development

Test resin and flammability test

From the flammability screening test results in the 1\textsuperscript{st} stage, it was observed that the FR additive Mg(OH)\textsubscript{2} had a relatively high FR effect. The following tests of FR effects were conducted in the 2\textsuperscript{nd} stage to find effective mixing ratios of Mg(OH)\textsubscript{2} and the combination of Mg(OH)\textsubscript{2} and r-P. Flammability and mechanical properties were also examined in the same manner as conducted in the 1\textsuperscript{st} stage. Table 2 shows the test resin examined in this stage. As for the basic FR chemicals, 50wt\% and 25wt\% of Mg(OH)\textsubscript{2} were prepared and 0wt\%, 5wt\% and 9wt\% of r-P were added.

Cone calorimeter test

Figure 5 shows the heat release rate in the cases where Mg(OH)\textsubscript{2} is 25wt\% in the left side (a) and 50 wt\% in the right side (b). In both figures the test results in the cases of base PP and only r-P FR treated without Mg(OH)\textsubscript{2} are indicated together. The figures indicate that adding only r-P suppresses the heat release rate after ignition, however the PHR is reduced by only 20\%. When only Mg(OH)\textsubscript{2} is added, the PHR rate is highly reduced as a whole and slower combustion continues. When Mg(OH)\textsubscript{2} is at 25wt\%, the FR effect of red phosphorus additives is larger and in proportion to the quantity of r-P additives. However, when Mg(OH)\textsubscript{2} is at 50 wt\%, the fire-retardant effect of Mg(OH)\textsubscript{2} is high enough and r-P additives add no more FR effect.

Figures 6 and 7 show the combustion products of smoke and CO. When only r-P is added, both smoke density and CO yield increase compared with those of base PP. When r-P is added at 9wt\%, the smoke density and CO yield become nine times higher. In the case of Mg(OH)\textsubscript{2} FR treatment, combustion products are suppressed because the heat release rate is small. When Mg(OH)\textsubscript{2} is added at 50wt\%, the smoke density and CO yield are especially well controlled.

PHR by cone calorimeter and other flammability test classifications

The PHR obtained by the cone calorimeter seems to be one of the important indices for fire safety. Figure 8 shows the relationship between the PHR and flammability classifications obtained in other tests (oxygen index and UL94 test) in the 1\textsuperscript{st} and 2\textsuperscript{nd} stages.

As shown in Figure 8, the PHR decreases as the oxygen index increases. This tendency can be clearly observed in the 2\textsuperscript{nd} stage test (Figure 8 (b)), which consists of non-halogen FR treated resin. When the oxygen index is more than 26, the heat release rate is very low and the UL94 classification corresponds to “V-0”. Oxygen index 26 is the criterion value to determine “inflammable synthetic resin” in Japan, as mentioned above. However, in the 1\textsuperscript{st} stage test, bromine-containing FR treated resins give oxygen index values greater than 26 and V-0 or V-1 UL94 classification, the PHR under radiant heat flux becomes higher than that of other flame retardant treated resins.
Table 2: Properties of test plastics for pallets.
(The 2nd stage screening test for finding appropriate combination of FR chemicals, r-P & Mg (OH)₂)

<table>
<thead>
<tr>
<th>Test Plastics</th>
<th>Property</th>
<th>Color</th>
<th>Density (kg/m³)</th>
<th>Burning Heat of Oxygen (kJ/g)</th>
<th>Fluidity (g/10min)</th>
<th>Bending Strength (kg/cm²)</th>
<th>Impact Intensity (J/kgcm/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP base Polypropylene</td>
<td></td>
<td>Natural</td>
<td>0.99</td>
<td>V-2 out</td>
<td>46.6</td>
<td>17.7</td>
<td>8 to 15</td>
</tr>
<tr>
<td>EX745 (r-P[4.8])</td>
<td></td>
<td>Brown</td>
<td>0.92</td>
<td>V-2 out</td>
<td>45.5</td>
<td>19.5</td>
<td>10.0</td>
</tr>
<tr>
<td>EX746 (r-P[9.1]) (EX699)</td>
<td></td>
<td>Brown</td>
<td>0.95</td>
<td>V-2</td>
<td>44.5</td>
<td>20.2</td>
<td>2.7</td>
</tr>
<tr>
<td>EX747 (r-P[4.6]+Mg(OH)₂[25]</td>
<td></td>
<td>Brown</td>
<td>1.09</td>
<td>V-2 out</td>
<td>33.7</td>
<td>22.3</td>
<td>11.0</td>
</tr>
<tr>
<td>EX748 (r-P[4.6]+Mg(OH)₂[50]</td>
<td></td>
<td>Brown</td>
<td>1.31</td>
<td>V-0</td>
<td>22.9</td>
<td>26.5</td>
<td>11.9</td>
</tr>
<tr>
<td>EX749 (r-P[9.1]+Mg(OH)₂[25]</td>
<td></td>
<td>Brown</td>
<td>1.22</td>
<td>V-2 out</td>
<td>33.1</td>
<td>23.4</td>
<td>11.0</td>
</tr>
<tr>
<td>EX750 (r-P[9.1]+Mg(OH)₂[50]</td>
<td></td>
<td>Brown</td>
<td>1.35</td>
<td>V-0</td>
<td>22.0</td>
<td>28.8</td>
<td>10.4</td>
</tr>
<tr>
<td>EX751 (Mg(OH)₂[25])</td>
<td></td>
<td>Gray</td>
<td>1.05</td>
<td>V-2 out</td>
<td>35.0</td>
<td>19.8</td>
<td>11.0</td>
</tr>
<tr>
<td>EX752 (Mg(OH)₂[50])</td>
<td></td>
<td>Gray</td>
<td>1.28</td>
<td>V-2 out</td>
<td>23.7</td>
<td>22.9</td>
<td>12.0</td>
</tr>
<tr>
<td>Mg(OH)₂ base FR</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EX753 (Mg(OH)₂[25])</td>
<td></td>
<td>Gray</td>
<td>1.05</td>
<td>V-2 out</td>
<td>35.0</td>
<td>19.8</td>
<td>11.0</td>
</tr>
<tr>
<td>EX754 (Mg(OH)₂[50])</td>
<td></td>
<td>Gray</td>
<td>1.28</td>
<td>V-2 out</td>
<td>23.7</td>
<td>22.9</td>
<td>12.0</td>
</tr>
</tbody>
</table>

(c) 1) r-P is red-phosphorous flame retardant additive
2) Ratings on this table correspond to the UL 94 test rating however those are not officially certificated by the UL.
3) Oxygen bomb calorimeter.
4) The value derives from the property of popular pallet made of PP.

Figure 5: Heat release rate of different FR treated plastics (mixture of r-P and Mg(OH)₂: 20 kW/m² radiant heat flux).
Figure 6: Smoke yield of different FR treated plastics (mixture of r-P and Mg(OH)$_2$: 20 kW/m$^2$ radiant heat flux).

Figure 7: CO yield of different FR treated plastics (mixture of r-P and Mg(OH)$_2$: 20 kW/m$^2$ radiant heat flux).

Figure 8 indicates that halogen-containing flame retardant materials have effects on ignitability. However, once it burns, the halogen chemical itself becomes an additional heat source. The “V-2” classification resins tested by the UL94 test range between 19 and 24 in oxygen index, however the clear relation between oxygen index and “V-2” and “V-2 out” classifications are not found.
The 3rd stage development

Test resin and flammable test

In the 2nd stage, three flame retardant plastics, Ex-752 (Mg(OH)₂ (50wt%), EX-748 (Mg(OH)₂[50wt%]+r-P[5%]) and EX-750(Mg(OH)₂ [50%]+r-P[10%]) were selected from the viewpoint of both mechanical and combustion properties for plastic pallets. All of them contained 50wt% Mg (OH)₂. The two of them with r-P added correspond to “V-0” classification by the UL94 test. Plastic pallets in full-scale size were produced from these materials and the combustion tests were conducted with the furniture calorimeter as shown in Figure 9 and Table 3.

The size of the plastic pallet was about 1.11 m (w) x 1.11 m (d) x 0.15 m (h). A 1/4 piece of the pallet was used for the burning test. The test piece was located on a stainless steel pan with 70 cm diameter and 10 cm depth. The bottom of the test piece was set 10 cm above the bottom of the pan.

Three sizes of methanol pans were adopted as ignition heat sources, i.e., 5 cm diameter pan with 20 cm³ methanol, 10 cm with 40 cm³ and 20 cm with 80 cm³. These ignition sources were located at the

Figure 9: Experimental setting for 1/4 piece of plastic pallet burning test.
center of the 70 cm diameter pan, which prevented melting plastic from spreading widely. In addition, a 3 cm diameter x 1 cm high solid fuel tablet made of Hexa-methylene tetramine was used and put on the top surface of the plastic pallets. This assumes the situation that a burning firebrand of dripped plastic may cause fire spread downward.

Furniture calorimeter test result

Figure 10 and Table 3 show the heat release rates of the 1/4 piece of full-scale pallet. In the case of the pallet made of base PP without FR treatment, the differences of ignition heat sources did not affect the heat release rate. The heat release rate reached almost 450 kW in the beginning. Afterwards, the heat release rate decreased while the plastic pallet was melting and dripping into the pan, then the heat release rate increased again as a pool fire.

When the solid tablet fuel is used as an ignition heat source, it takes time to ignite due to comparatively large heat capacity of the test pallet against the ignition heat source. However, once it begins to burn, the combustion behaviour appears to be nearly the same as in the cases of other ignition heat sources. The heat release rate of plastic pallets made of only Mg(OH)$_2$ FR treated PP is relatively low, however once it ignites, the burning continues in spite of the size of the ignition heat source. In contrast, when r-P is added the heat release rate becomes lower. It was found that the heat release rate depends on the heat source and combustion continues in the surrounding area of the ignition heat source in this case.

Mechanical properties

In this R&D project, mechanical properties of plastics have been examined by some tests, including the burning test, for practical use. Some of the key properties are listed in Tables 1 and 2. The materials for plastic pallets are selected to satisfy certain levels of mechanical properties. Moreover, mechanical performance tests for plastic pallets were conducted. The results indicate that “the flexural rigidity” of test pallets range from 1.7 times to twice as strong as that of original non-FR treated pallets and satisfy the required standards of the present JIS A-grade. “The sliding friction” property of the test plastic pallet is almost at the same as standard ones. However “the dropping impact test” results indicated that the property of “EX-748” and “Ex-750”, which have r-P added, is lower than that of standard ones. Also, the density of the developed plastic pallets is about 1.4 to 1.6 times larger, and time to plasticize lengthens. These remain as future tasks to be solved.

As mentioned in the beginning of this paper, there are some alternatives for improving fire safety in rack storage having plastic pallets, i.e. stepping up of fire equipment use such as sprinklers or FR treatment for the pallets themselves. Adoption of FR-treated plastic pallets may give more economical selections in certain situations. At the moment, only the oxygen index or classification by UL94 test is
CONCLUSIONS

Development of fire-retardant plastic pallets has been conducted in collaboration between NRIFD and manufacturers of plastic pallets and fire retardant chemicals. Flammability and mechanical properties of some synthetic resins were examined in the two test stages to screen plastic materials from which plastic pallets are made. The flammability of the resins was tested by the cone calorimeter, UL94 and oxygen index test, and those results were discussed. Finally, the combination of Mg(OH)$_2$ and red-Phosphorus
was selected as a FR retardant material. Major results obtained in the tests are as follows:

1. FR resins, with halogen-containing chemicals added, retard the ignition time and suppress burning of the volatile vapor immediately after radiant heat exposure, however once it burns up, the FR effect decreases and more combustion products are generated.

2. In the case of FR resins with magnesium hydroxide added, the heat release rate and the peak heat release rate become relatively low. Also, combustion products are well-suppressed and mechanical properties for practical use is maintained. This FR additive seems to be preferable for plastic pallet materials.

3. Red Phosphorous additive has effects on mitigation of the heat release rate when it is used in combination with other FR chemicals. Use of r-P alone has little FR effect and produces more combustion products of smoke and CO.

4. In general, the peak heat release rate decreases as the oxygen index increases for non-halogen FR treated resin. When the oxygen index is over 26, the heat release rate becomes very low and the UL94 classification corresponds to “V-0”. The “V-2” classification ranges from 19 to 24 in oxygen index and a clear relationship between oxygen index and “V-2” and “V-2 out” classifications were not found.

5. The prototype FR plastic pallets were produced with the combination compounds of Mg(OH)$_2$ and red Phosphorus, and the fire test was conducted with a furniture calorimeter. The FR effects of those plastic pallets were examined in full-scale and a sufficient FR effect was obtained with satisfaction. Along with the flammability tests, some of the mechanical properties were examined and a few mechanical properties needing improvement were identified, such as the dropping impact durability etc.

REFERENCES


6. UL94, ”Testing for flammability of plastic materials for parts in devices and applications”.


8. UL 2335, “Plastic Pallet Classification”.