# Development of the New Halogen-Free Flame Retardant System by Nanoencapsulation

*Jae-Kyung Kim*, Hirofumi Kawanaka**

**ABSTRACT** A large amount of flame retardant is required for high flame retardance of polymer materials, but their physical properties are remarkably lowered. Meanwhile, a demand for the halogen-free flame retardant that does not allow the generation of toxic gases during combustion has been strongly required. But, so far, the halogen-free flame retardant having a performance as high as the halogen flame retardant is not available. Here we propose the nanoencapsulation technology of the halogen-free flame retardant as one promising method to achieve a high flame retardant effect with a small amount of a conventional flame retardant. We succeeded to nanoencapsulate the halogen-free flame retardant in a layered compound by using a co-milling method as a nanoencapsulation technology. We found out that the nanocapsules are co-mixed, with the exfoliated state and the intercalated state in the resin. The results show that the prepared nanocapsule has a good flame retardant effect in spite of a small amount of the flame retardant in the nanocapsule. Also, the synergy effect for the highly flame retardance has been investigated by combining the commercially available flame retardant with the nanocapsule. Then, the cross-linked foam which is highly combustible was applied to confirm the synergy effect, and the material was classified as UL94 V-0.

## 1. INTRODUCTION

Recently, polymer materials are widely used in a variety of applications, such as building materials, vehicles etc. But there was a problem of reduction in physical properties, because a large amount of the flame retardant is required to obtain flame retardance of the polymer materials. Meanwhile, a demand for the halogen-free flame retardant that does not allow the generation of toxic gases during combustion has been strongly required. But, so far, the halogen-free flame retardant having a performance as high as the halogen flame retardant is not supplied in spite of the development and the commercialization of many halogen-free flame retardants by various manufacturers. Then, the development of a halogen-free flame retardant, that makes possible to obtain a high flame retardant effect with a small amount of flame retardant, was desired. Therefore, we proposed the nanoencapsulation of the flame retardant as one promising method.

### 1.1 Development Situation of the Nanocomposite material

As shown in Figure 1, the conventional nanocomposite intercalation reaction occurs in a solution because the ammonium salt used in the reaction can be soluble in water and alcohols. Especially, a bulky and large molecular weight ammonium salt, such as the quaternary ammonium salt, is frequently used. The quaternary ammonium salt can intercalate between the layered compound, and the interlayer distance of the layer compound can be expanded. Due to the expanded layered compound, it is easy to exfoliate in the resin by the mixing process.

Moreover, by inserting the flame retardant between the layers as the second stage of the intercalation process, the nanocomposite can have the flame retardant property.

By mixing the layered compound, which is obtained with this method, into the resin, the layered compound can be exfoliated, and uniformly dispersed (nano-dispersion) in the resin, then the uniform nanocomposite can be produced. Moreover, as described above, the flame retardant intercalated between the layers can be dispersed with the exfoliated layered compound in the resin.

* Research & Development Div.
Polymer Materials R&D Laboratories

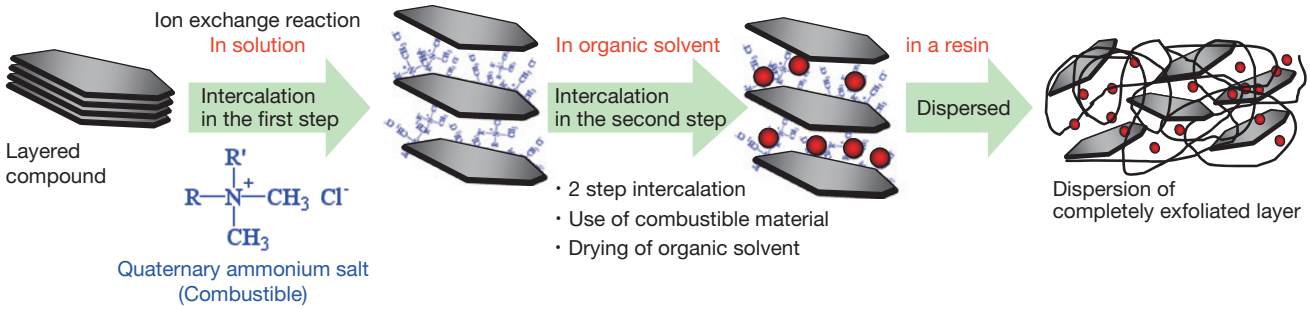


**Figure 1 Conventional nanocomposite technology.**

However, by applying this method to the flame retardant, a problem is created. Most of the final purpose of the conventional nanocomposite material is the complete layer exfoliation in the resin. In other words, full exfoliation of the layered compound in the mixing process results in the exposure of flame retardant, and its degradation is easily caused by the shear stress, the processing temperature and the contact with other agents. Therefore, the flame retardant effect can not be exerted.

### 1.2 Advantages of the Technology

As shown in Figure 2, it is possible to directly insert the flame retardant in the layered compound without using the ammonium salt for expanding the layered compound. And the inserted flame retardant, instead of the quaternary ammonium salt which has no flame retardance, expands into the interlayer distance and the nanocapsule is easily exfoliated in the resin by mixing as well as the flame retardant being nano-dispersed into the resin with the exfoliated layer. Therefore the amount of the flame retardant could be dramatically decreased by the nanoencapsulation. In addition, many flame retardants were hardly soluble to solvents, and the insertion was difficult by the conventional solution methods, but this technology is effective to the intercalation reaction regardless of the hardly soluble compounds. Also, this technology can be applied not only to the flame retardant but also to the many other additives which are hardly soluble into solutions. Furthermore, this technology has the following advantages:

- As the solution method which is needed to a large amount of solvent, the drying process is not necessary, and a great deal of energy is not consumed.
- There is no aggregation problem in drying and in granulation.
- The low cost manufacturing is possible as the process is simple.

In addition, the nanocapsule prepared by the co-milling method can be dispersed with both the exfoliated and intercalated states. So, the intercalated additives can be protected from the shear stress, the thermal history and the influence of other additives in mixing with the resin. Thus, the flame retardant effect can be improved. Accordingly, this technology is called nanoencapsulation technology, distinguishing it from the conventional nanocomposite method, because the nanocapsule is dispersed with both the exfoliated and intercalated states in the resin.

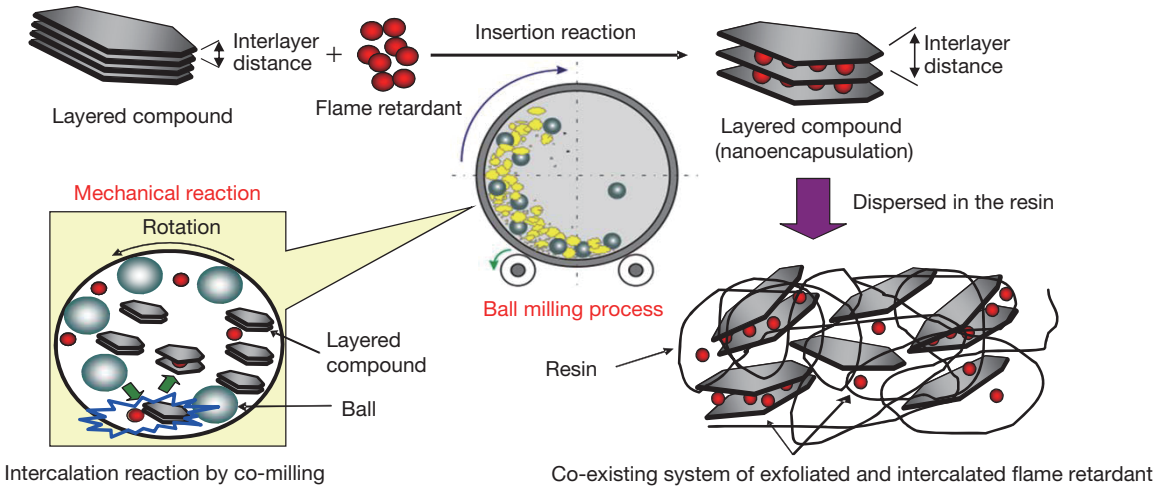


**Figure 2 Nanoencapsulation of flame retardant prepared by the co-milling process.**

## 2 EXPERIMENTS

### 2.1 Preparation of the Nanocapsule

The intercalation reaction to obtain the nanocapsule was carried out in a ball-milling equipment in the desired ratio of the layered compound (swelling mica) and the halogen free flame retardant (polyphosphate ester) under the required reaction conditions.

### 2.2 Dispersion of Nanocapsules in the Resin

The prepared nanocapsule were dry-blended with an engineered plastic resin at each concentration of (5, 20, 30%) and dispersed by a twin-screw extruder under the required condition which has been preliminarily adjusted. Thus a resin in which the nanocapsule was dispersed was prepared. The sample, which had the same composition of the nanocapsule, but was not nanoencapsulated, was prepared to confirm the validity of the nanocapsule on the flame retardance.

### 2.3 Evaluation of the Nanocapsules

Qualitative analysis to investigate the intercalation of the flame retardant in the nanocapsule was measured by the X-ray diffraction. Also, the thermal properties and the quantitative analysis of the flame retardant in the nanocapsule were carried out by Thermogravimetry-Differential Thermal Analysis (TG-DTA) method. Furthermore, the flame retardance of the nanocapsule was confirmed by measuring the self-extinguishing time in vertical combustion and Oxygen Index test.

## 3. QUALITATIVE ANALYSIS AND QUANTITATIVE ANALYSIS OF THE NANOCAPSULES

After the intercalation reaction by the co-milling method, the phenomenon, in which the powder was firmly adhering on the inner wall surface of the ball-mill as shown in Figure 3, was observed. This is the phenomenon where the powder is activated by the intercalation reaction and is easily adhering on the metal surface. It is considered that the reaction is properly progressing.

**Figure 3 In the ball-mill after co-milling.**

The X-ray diffraction analysis results of the layered compound and the obtained nanocapsule are shown in Figure 4.

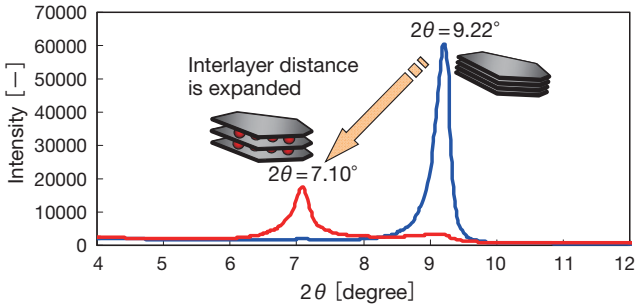


**Figure 4 X-ray diffraction analyses. (blue line: layered compound, red line: nanocapsule)**

The X-ray diffraction intensity curve for the layered compound shown in Figure 4 (blue line) has a peak at around $2\theta = 9°$. According to the reference[1], this peak is derived from the non-insertion portion of the layered compound. The lattice plane spacing d, is approximately 0.92 mm by the Brrag's equation below.

$$n\lambda = 2d \sin\theta$$

$d$ : Lattice plane spacing
$\theta$ : Angle between the lattice plane and X-ray
$\lambda$ : X-ray wave length
$n$ : Integer

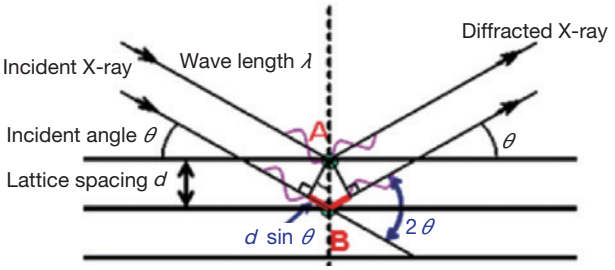


**Figure 5 Bragg's refraction.**

On the other hand, a newly peak appeared at $2\theta = 7°$ for the nanocapsule as shown in Figure 4 (red line). The lattice plane spacing by the peak of $2\theta = 7°$ is calculated as 1.26 nm, and we confirmed that the layer spacing is expanded by the intercalation reaction. In other words, it can be deduced that the polyphosphate ester is intercalated between the layers of the layered compound. And, the amount of the halogen-free flame retardant in the nanocapsule was measured by using the Thermogravimetry analysis (TG analysis). TG analysis results for the layered compound, the halogen free retardant and the obtained nanocapsule are shown in Figure 6. In the case of the layered compound in Figure 6 (①), no weight reduction is observed in the range from room temperature to 600℃. And, in the case of the polyphosphate ester in Figure 6 (②), the weight is sharply decreased at 300℃ and the decomposition occurs. In addition, the Thermogravimetry curve

(TG curve) of the nanocapsule is shown in Figure 6 (③). As shown in Figure 6, the decomposition temperature of the nanocapsule is 300℃ to 600℃ or higher, and shifted to the higher temperature more than 150℃ compared to the decomposition temperature 300 to 420℃ of the polyphosphate ester. In addition, the weight is gradually reduced. It means that the heat resistance was enhanced and the sustainable release was possible by trapping the polyphosphate ester in the nanocapsule. From the above results, we concluded that the nanocapsule was successfully obtained. From the TG-DTA curve, the amount of the flame retardant (meq/100 g) in the layered compound per 100 g of the layered compound is calculated as approximately 8 meq/100 g from the following equation.

$$M\,(\mathrm{meq/100\ g}) = \frac{10^5 \times \{A\,(\mathrm{mg}) - B\,(\mathrm{mg})\} / C}{B\,(\mathrm{mg})}$$

$M$ : Intercalation amount (meq/100 g)
$A$ : TG at decomposition starting point (mg)
$B$ : TG at decomposition finishing point (mg)
$C$ : Molecular weight of the flame retardant

In the above equation, “meq” means milliequivalent. 1 equivalent weight is a unit indicated as a number of charges, 1 gram equivalent is equivalent to a quotient (g) obtained by dividing the molecular weight by the valence of the molecule.

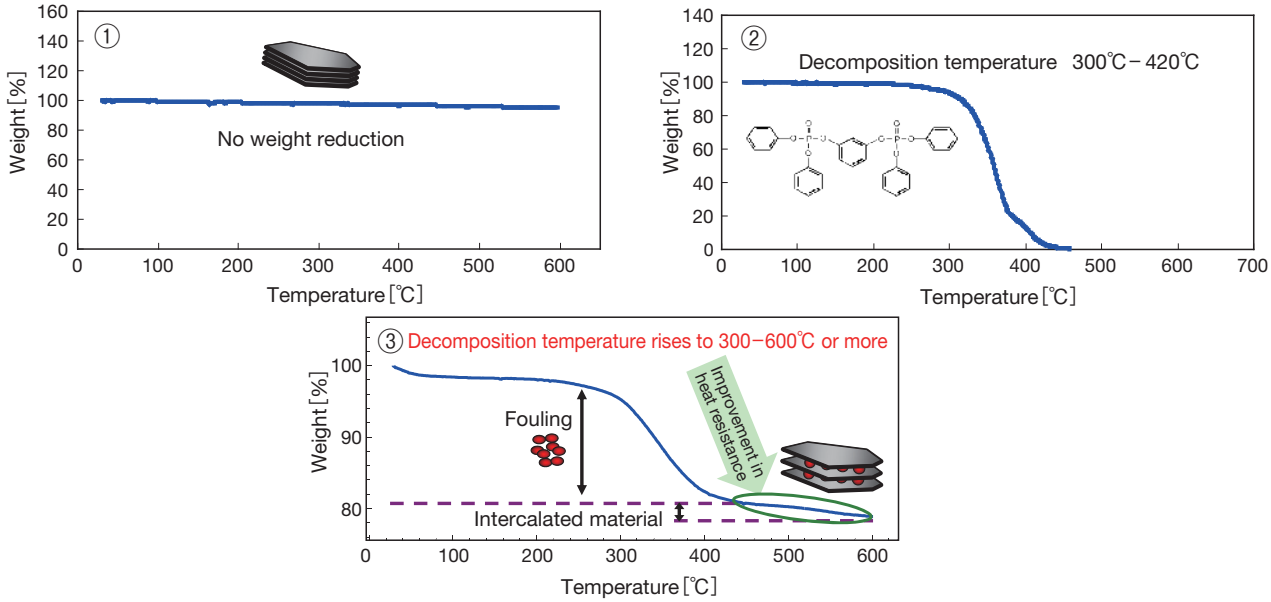


**Figure 6 Thermogravimetry curves (TG curves)(① Layered compound, ② Polyphosphate ester, ③ Nanocapsule).**

## 4. DISPERSION OF THE NANOCAPSULES IN THE RESIN

The degree of the exfoliation dispersion in the mixing process of the nanocapsule material and of the non-nanocapsule material, described in 2.2, was evaluated by the X-Ray diffraction method. The evaluation result is shown in Figure 7. In comparison with the X-Ray diffraction intensity curve shown in Figure 4 (red line), the peak position of the nanocapsule in the resin is located at $2\theta = 4.6°$, lower than that ($2\theta = 7°$) of the nanocapsule. Also, the intensity of the peak is lower and broader. It is clarified that the nanocapsules are partially exfoliated in the resin by shear stress of the extruder and some parts of the nanocapsules are dispersed while maintaining the intercalated state. On the other hand, in the case of the non-nanocapsule material, the peak of the $2\theta = 9°$ does not shift to the lower angle side, and this implies that the dispersion into the resin occurs without exfoliation.

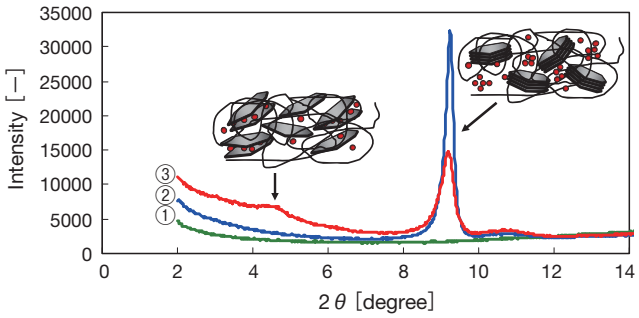


**Figure 7 X-ray diffraction intensity (① neat resin, ② non-nanocapsule material, ③ nanocapsule material).**

## 5. THE FLAME RETARDANCE OF THE NANOCAPSULE

The flame retardance of the nanocapsule and the non-nanocapsule was evaluated with the self-extinguishing time after 10 s of ignition vertically as well as the oxygen index. The concentration of the nanocapsule and the non-nanocapsule in the resin is 5 wt%. Also, neat resin is evaluated with above tests as the standard data. At first, the results of self-extinguishing time are shown in Table 1.

**Table 1 The results of the self extinguishing time with neat resin, non-nanocapsule material, and nanocapsule material.**

| | | | | | |
|---|---|---|---|---|---|
| ①Neat resin | N＝1 | N＝2 | N＝3 | N＝4 | N＝5 |
| Self-extinguishing time(s) | *NG | *NG | *NG | *NG | *NG |
| ②Non-nanoencapsulated material | N＝1 | N＝2 | N＝3 | N＝4 | N＝5 |
| Self-extinguishing time(s) | 42 | *NG | 72 | *NG | 51 |
| ③Nanoencapsulated material | N＝1 | N＝2 | N＝3 | N＝4 | N＝5 |
| Self-extinguishing time(s) | 22 | 22 | 22 | 40 | 36 |

*NG：Complete combustion

As shown in Table1, the neat resin was completely combusted after ignition vertically during 10 s. But, the nanocapsule and the non-nanocapsule material immediately generated a char (a char layer formed by the combustion) after the ignition and it was observed that the combustion of the material was delayed. However, the self-extinguishing time for the non-nanocapsule material was dispersed and 30 s longer than for the nanocapsule material. Next, the oxygen index of the neat resin, non-nanocapsule material, nanocapsule material was carried out. The results are shown in Figure 8.

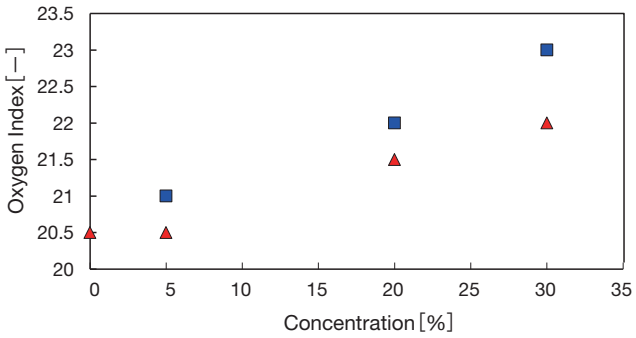


**Figure 8 The effect of the concentration of the non-nanocapsule material and the nanocapsule material with respect to the oxygen index. (▲: the non-nanocapsule material, ■: the nanocapsule material).**

As shown in Figure 8, the oxygen index is increased with the increase of the concentration of the nanocapsule and the non-nanocapsule in the resin. Compared, the oxygen index of the nanocapsule material is higher than that of the non-nanocapsule material. To understand why the nanocapsule material shows the higher oxygen index than the non-nanocapsule material, the char layer after the combustion and the combustion behavior were observed.

Figure 9 shows the deformation of the char layer with combustion time.

These samples were taken from the oxygen index test of the materials with the same concentration of the non-nanocapsule in the resin.

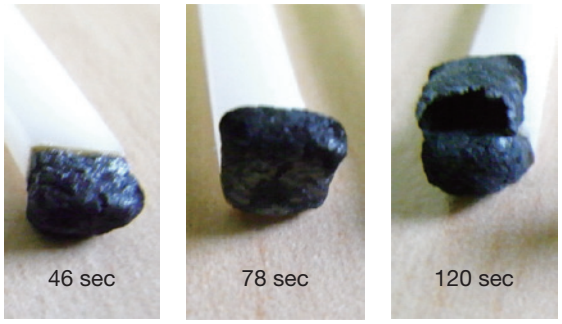


**Figure 9 Deformation of the char layer by combustion time.**

Figure 9 shows that the char layer is deformed according to the progress of the combustion. It means that the char layer of the non-nanocapsule material was deformed and collapsed by the combustion, and the resin exposed by the collapsed char layer was re-ignited. It is speculated that it is difficult for the char layer formed by the non-nanocapsule to suppress the diffusion of the flammable gas and the oxygen which cause the combustion. Moreover, due to the low strength of the char layer, it is easier to collapse. And then the mixing of the flammable and the oxygen in the resin exposed by the collapsed char layer occurs and the combustion was continuing.

Based on this speculation, the char layers of the nanocapsule material and of the non-nanocapsule material after the combustion were compared to confirm the flame retardant effect of the nanocapsule material. Figure 10 shows the surfaces of the char layers after the combustion, and Figure 11 shows the cross sections of the char layers.

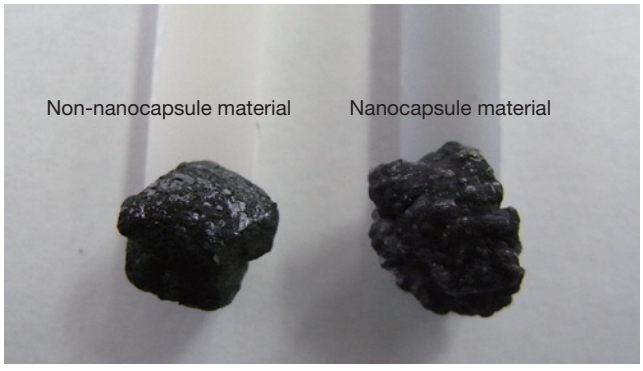


**Figure 10 The surface of the char layers after combustion.**

As shown in Figure 10, the surface of the nanocapsule material has a roughness structure more than that of the non-nanocapsule material. As shown in the TG curve of the nanocapsule in Figure 6, the weight reduction is slowly and the curve shifts to the high temperature side. From this fact, it is speculated that the flame retardant, which was well-dispersed with the exfoliation of the nanocapsule in the resin, forms the uniform char layer at the initial stage of the combustion. After that, the secondary char layer is formed by the decomposition of the flame retardant intercalated in the nanocapsule existing on the surface and in the inside of the material. As the result, the dense char layer with the roughness structure on the surface of the material is formed.

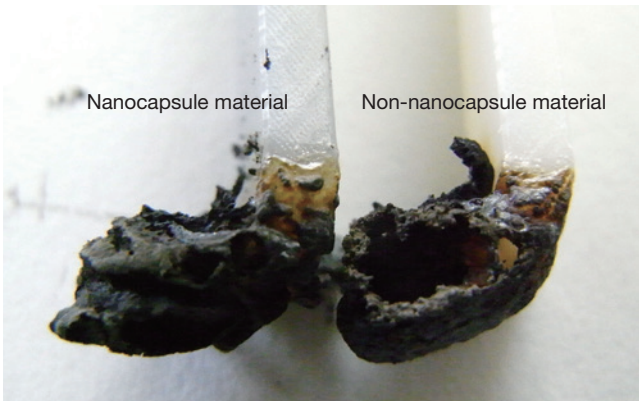


**Figure 11 The cross section of the char layer after combustion.**

As shown in Figure 11, in the case of the non-nanocapsule material, a large cavity was formed in the char layer. On the other hand, the nanocapsule material does not have a large cavity but has the homogeneous char layer.

Although the char layer is formed by the combustion of the non-nanocapsule material, it is difficult to form the homogeneous char layer due to the poor dispersion of the flame retardant in the resin. And then, the dense of the char layer could be lowered and the combustion in the char layer by mixing the flammable gas and the oxygen occurs from the parts in which the char layer is not formed. So, the large cavity in the char layer could be formed.

Due to the large cavity in the char layer, the char layer collapses easily as shown in Figure 9, and then the combustion from the exposed resin continues.

On the other hand, as described in 1.2 section, the nanocapsule material could have the uniform char layer because the flame retardant had been nano-dispersed in the resin. Then the large cavity shown in the non-nanocapsule material was not formed.

From the above description, we conclude that the following speculation can be carried out. The non-nanocapsule material can not form the dense char layer because of the poor dispersion of the flame retardant in the resin, but the nanocapsule material can form the dense char layer by the nano-dispersed flame retardant and the large cavity in the char layer is not created. Moreover, some flame retardants nano-dispersed in the resin still maintain the intercalated state, and the secondary char layer is also formed by their decomposition. The results can improve the strength of the char layer. Therefore, the diffusion of the flammable gas and the oxygen can be suppressed by the dense and strong char layer, and then the combustion can be prevented. This is why the oxygen index of the nanocapsule material is increased.

## 6. FLAME RETARDANT MECHANISM OF THE NANOCAPSULE

The flame retardant system by nanoencapsulation and its effectiveness has been described above. By the way, due to the higher demand for the products which correspond to high standard of the flame retardance like UL94 V-0, the further improvement of the flame retardance could be necessary. Accordingly, a possible method to improve the flame retardance with the basic concept of the flame retardant mechanism is investigated.

Figure 12 shows the basic concept of the flame retardance. The combustion is as follows. The melting and the thermal decomposition of the organic material are caused by the heat radiation and the thermal diffusion in the material by the heat source. The thermal decomposed materials (mainly flammable gas) diffused from the inside and outside of the materials mix with the ambient oxygen and the combustion occurs. In short, the combustion is caused by the following chain reaction: heating → decomposition→ diffusion → ignition.

A flame retardant mechanism at each step (the following ① to ⑥) shown in Figure 12 is effective to inhibit the combustion chain. As shown in Table 2, in general, the flame retardant mechanism is categorized into the gas phase reaction and the solid phase reaction.

①Cooling by an endothermic dehydration reaction with heating.
②Increasing an amount of the solid residue and reducing an amount of a flammable gas.
③Inhibition of the flammable gas diffusion.
④Dilution of the oxygen and the flammable gas concentration by generating a nonflammable gas in the thermal decomposition.
⑤Blocking the diffusion of the oxygen by forming the inflammable protective layer.
⑥Suppressing the radical chain reaction by interrupting free radicals generated in the combustion process.

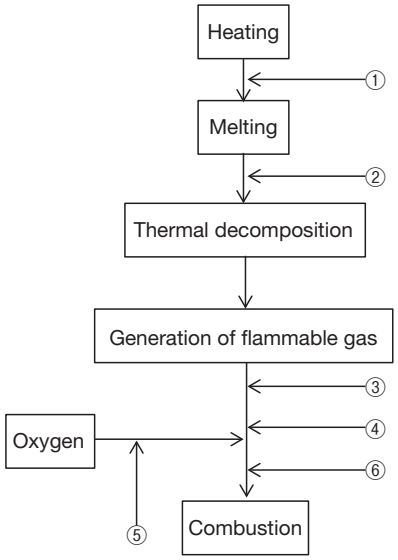


**Figure 12 The basic concept of the flame retardance.[2)]**

**Table 2 The flame retardant mechanism of the flame retardant system.[3)]**

| Flame retardant mechanism | Representative example |
|---|---|
| Gas phase | 1) A radical trapping effect by the Halogen compounds and the Phosphorus compounds. |
| | 2) A synergy effect by Halogen compounds + Antimony trioxide (Zinc borate, ZnS etc.). |
| | 3) An endothermic dehydration reaction by the Hydrate metal compounds. |
| | 4) The inflammable gas generation and the oxygen dilution by Nitrogen compounds. |
| Solid phase | 1) A char formation by the Phosphorus compounds. |
| | 2) A thermal insulating inorganic layer formation by the Hydrate metal compounds + the Silicon compounds. |
| | 3) A thermal insulating inorganic layer formation by the Hydrate metal compounds +the Zinc borate. |
| | 4) A foamed char formation by Intumescing system (Ammonium polyphosphate (APP) + Nitrogen compounds). |
| | 5) Nanocomposite + Silicon oxide by conventional flame retardant system + Char formation |

Based on the basic concept shown in Figure 12, the flame retardance by the nanocapsule corresponds to ③ and ⑤. That is, the flame retardance of the nanocapsule mostly corresponds to the solid phase reaction because the homogeneous formation of the char layer by well-dispersed nanocapsule improves the gas barrier, and then the diffusion of the oxygen and the flammable gas can be suppressed. In the case of the gas phase in the combustion process, the combustion generally occurs with mixing the flammable gas and the oxygen. So, we consider that the flame retardance of the nanocapsule could be improved by adding the flame retardant which plays a role in the gas phase reaction. Then, the flame retardant system (generation of an inflammable gas in the thermal decomposition) shown in Figure 12-④, which dilutes the concentration of the flammable gas and the oxygen, was applied. For the above purpose, the flame retardance of the nanocapsule is investigated by adding the nitrogen compound corresponding to the gas phase flame retardant system as shown in Table 2-(4).

## 7. THE COMPOSITIONS OF CROSS-LINKED FOAM AND EVALUATION OF FLAME RETARDANCE

For the issue described in the previous section, the combination of the nanocapsule and a nitrogen compound (a commercial flame retardant) was applied to the polyolefin foam which is highly combustible. And, the flame retardance for the compound was evaluated by the oxygen index and the UL94 vertical flame retardant test. The results show in Table 3 and Figure 13.

**Table 3 The comparison of the flame retardance between specimens mixed with the commercially available flame retardants.**

| Item | Non-nanocapsule | Nanocapsule |
|---|---|---|
| Oxygen index | 30.6 | 31.8 |
| UL94 Vertical flame retardant test | Not applicable | V-0 |

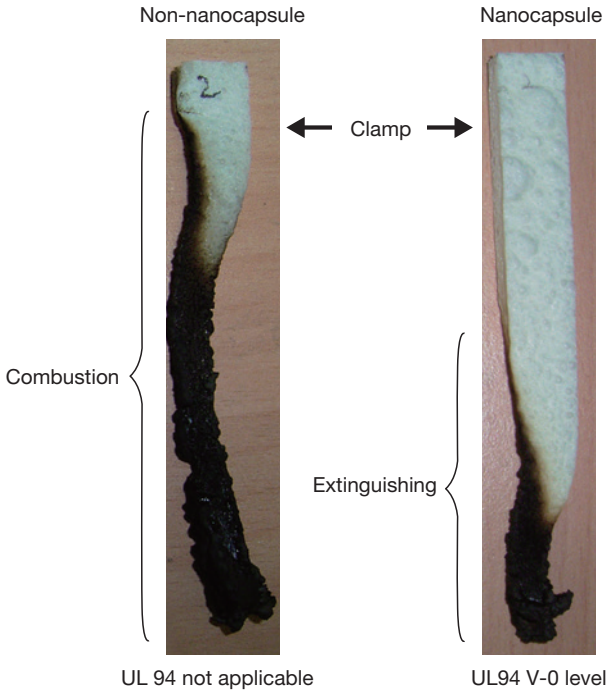


**Figure 13 The comparison between the UL94 combustion test results.**

As shown in Table 3, the specimens prepared by the compositions of the non-nanocapsule were not applicable in the UL94 vertical flame retardant test because the specimens were nearly burned down to the clamp after the ignition. On the other hand, the specimens prepared by the compositions of the nanocapsule were extinguished immediately in the first ignition, and were extinguished in the second ignition as well, thus it was assigned to class UL94 V-0. From the results of the flame retardant test, the nanocapsule has a good performance for its flame retardance in comparison to the non-nanocapsule. And, as shown in Table 2, the combination of the two types of flame retardant system (the solid phase reaction induced by the nanocapsule and the gas phase reaction induced by the commercial flame retardant) indicated the synergy effect. So, the flame retardance of the foam could be improved up to the high flame retardant level.

## 8. CONCLUSION

The nanoencapsulation of the halogen-free flame retardant was successfully obtained by the co-milling method. And from the results of the X-ray diffraction, the nanocapsule was well-dispersed with both exfoliated and intercalated states in the resin. The prepared nanocapsule has a good flame retardant effect in spite of a small amount of the flame retardant in the nanocapsule, and it is obvious that the flame retardance can be improved by the increase of the amount of the flame retardant in the nanocapsule. Furthermore, the flame retardant cross-linked foam which was assigned to class UL94 V-0 could be obtained by using the nanocapsule and the commercial flame retardant. It is because of the combination of the flame retardants induced the synergy effect on the flame retardance.

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