Fabrication of novel thermal-expandable microcapsules and their applications in intumescent flame-retardant water-based coatings

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Abstract: Thermal-expandable microcapsules (TEMs) for water-based coatings were synthesized with co-polymer of Acrylonitrile (AN) - Methyl methacrylate (MMA) - Ethylhexyl acrylate (EHA) - Divinylbenzene (DVB) as shell and toluene-p-sulfonyl hydrazide as core by suspension polymerization method. It was found that the microcapsules with desirable thermal expansion property and good heat stability could be obtained with a shell monomers composition of 70% AN /20% MMA /9% EHA /1% DVB. When 2% styrene-maleic acid copolymer (SMC) as emulsifier and 3% poly (vinyl pyrrolidone) (PVP) as dispersing agent were used, well defined spherical and more uniform microcapsules could be prepared. It was also found that when the shell/core mass ratio was 3:1, an encapsulation efficiency of ca. 94.5% could be achieved. Beyond this ratio, the increase of encapsulation efficiency reached a plateau. The 100 μm thickness film of water-based coating containing 5% microcapsules could be expanded to the thickness of 450 μm after exposed at 150 °C for 2 minutes. TG analysis revealed the mass loss start temperature of coating increased by more than 30 ℃ when 5% microcapsules were added to water-based coatings, which demonstrated the flame-retardant function of the coatings.

Key words: thermal-expandable, microcapsules, intumescent, waterborne polyurethane, flame-retardant coatings

1 Introduction

The microcapsule which can be used to embed or protect some substances is a semipermeable or sealed mini "container" or "packaging" with a polymer shell. The particle diameter of the microcapsules is small to the micron range or as large as the millimeter range [1-3]. Microencapsulation is a micro-packaging technology which encloses micro-sized materials of solids, liquids or gasses in a shell of natural or synthetic polymer matrix, for the purpose of protecting unstable or susceptible functional materials originating from phenomena in nature, where many capsules with various dimensions exist [4-7]. A cell that envelop active ingredient with a cell wall can be a nano-scale capsule and a bird's egg and a seed are examples of macroscopic capsules. Microencapsulation technology first caught researchers' attention through the patent application of microcapsule for carbonless copying paper by NCR of America in 1953, and then was further explored through encapsulation of active ingredients in pharmaceutical industry. In recent decades, microencapsulation has found wide applications in the fields of pharmaceutical, agricultural, food, cosmetic and textile industries [8-14].

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Today, a lot of development of microcapsule for functional coatings has been reported [15-20]. Microcapsule could combine the properties of different materials (shell and core materials) and have a great potential to meet various performance requirements of functional coatings [21-26]. Thermally expandable microcapsules are available for the formulation of puff inks and phase change materials due to their thermal expansion capacity [27-30]. Intumescent flame retardants (IFRs) have been considered to be a promising method, which is because they are low toxicity, low smoke, halogen free, and also very efficient. Unfortunately, most IFR systems have some disadvantages such as weak water resistance and poor compatibility with polymer matrix. To deal with the above problems, several methods can be employed, such as microencapsulation of IFR with water-insoluble polymers and synthesis of new carbon sources with high water resistivity [31-34]. The core materials of thermally expandable microcapsules are commonly liquid hydrocarbon with low boiling point, which will expand rapidly upon heating [2-5]. Hydrocarbon is combustible, as such, microcapsules having hydrocarbon as core material could not be used as a component for functional flame retardant wood coatings.

Toluene-p-sulfonyl hydrazide (TSH) is a type of solid chemical blowing agent. At around 105 ℃, TSH will begin to decompose into p-toluene sulphonic acid and nitrogen, both of which are non-flammable. In this study, thermally expandable microcapsules having poly (acrylonitrile (AN)-methyl methacrylate (MMA)-Ethylhexyl acrylate (EHA)-divinylbenzene (DVB)) copolymer as shell materials and TSH as core material, was synthesised by suspension polymerisation technique. The effects of various parameters, such as monomers and surfactant compositions on thermal expansion and stability, particle size and size distribution of the microcapsule obtained were also studied. It was found that the water-based wood coatings introduced with microcapsules obtained desirable thermal expansion property and good heat stability.

2 Experimental

2.1 Materials

The following materials were employed in the study reported here. Monomers: Acrylonitrile (AN), Methyl methacrylate (MMA), Divinylbenzene (DVB), Ethylhexyl acrylate (EHA). Core material: Toluene-p-sulfonyl hydrazide (TSH). Emulsifier: styrene-maleic acid copolymer sodium salt (13% solution in water, styrene-maleic acid copolymer (SMC)). Suspension stabilisers: magnesium phosphate [$Mg_3(PO_4)_2$], Poly(vinyl alcohol) (Mw 1000, poly(vinyl alcohol) (PVA)), poly(vinyl pyrrolidone) (Mw 23000, poly(vinyl pyrrolidone) (PVP)). Initiator: azobisisobutyronitrile (AIBN). Chain transfer agent: tert-dodecyl mercaptan (TDM). Other materials: sodium chloride (NaCl), hydrochloride acid (HCl) and so on. All materials supplied by Aldrich-Sigma were analytical reagent grade and used as received.

2.2 Procedure of synthesis of microcapsules by suspension polymerization

Synthesis of microcapsules was preformed according to a process of suspension polymerisation which included five steps described as follows:

(1) Deionised water, magnesium phosphate, PVP or PVA, sodium chloride were charged into a flask successively and stir-mixed to achieve visual uniformity. Then, the pH of the mixture was adjusted to pH = 4 with HCl. After that, 13% solution of styrene-maleic acid copolymer sodium salt as emulsifier was added and dispersed

uniformly in the mixture.

(2) AN, MMA, EHA and DVB were charged into another flask to give a monomer mixture. Core material, TSH was dissolved into the monomer mixture. Then, the initiator AIBN, chain transfer agent TDM was introduced and the mixture stirred to achieve uniformity.

(3) The continuous phase and the dispersed phase were mixed together and agitated at 1,000 rpm for 1 min. Then, the mixture was dispersed by ultrasonication with a JY92-11 ultrasonic generator at a power setting of 200 W for 1 min.

(4) The suspension mixture was then transferred into an air-tight reactor equipped with nitrogen protection, reflux condensation and agitation, and the temperature was raised to 65 ℃ to initiate suspension polymerisation reaction. After 10-15h of reaction, microcapsule slurry was obtained.

(5) The microcapsule slurry obtained was centrifuged at 4000-5000 rpm for 10-15 min in order to remove other residual components and foams. The sedimentation layer was collected and washed three times with deionised water and separated by suction filtration. The solid mass obtained was then dried for 24 h at 40 ℃ under vacuum to obtain microcapsules.

2.3 Characterization of microcapsules

2.3.1 Analysis via SEM

The sample obtained was pre-coated with a 20 nm thick layer of gold, using an ion coater, on the surface as a reflecting layer. Then, a JEOL JSM-820 SEM was used to observe the surface morphology.

2.3.2 Analysis of particle size and size distribution

A MS 2000 type laser particle size analyser with a dynamic light-scattering mechanism was used to determine the particle size and size distribution of the microcapsules. Distilled water was used as dispersing medium.

2.3.3 Thermal gravimetric analysis

A TA instrument TGA 2050 thermo gravimetric analyzer was used to characterize the thermal stability of the sample obtained under nitrogen atmosphere. Analyzes were conducted at a heating rate of 10 ℃ /min in the temperature range of 0 −500 ℃.

2.3.4 Determination of encapsulation efficiency

When syntheticing microcapsules, it is assumed that the mass ratio of the shell/core is n. The quality of the sample microcapsules is M_0, grinded the microcapsules in a mortar, and then washed thoroughly with ethanol many times, weighted the sample in M_1 after dried for 48 hours at 40 ℃ in a vacuum until capsule heart material removed completely, calculated encapsulation efficiency as follows:

$$\mathrm{E}_{\eta}\% = \frac{(M_0 - M_1)}{M_0} \times (1+n) \times 100\%$$

3 Results and discussion

3.1 Effects of monomer composition of shell copolymer on shell properties

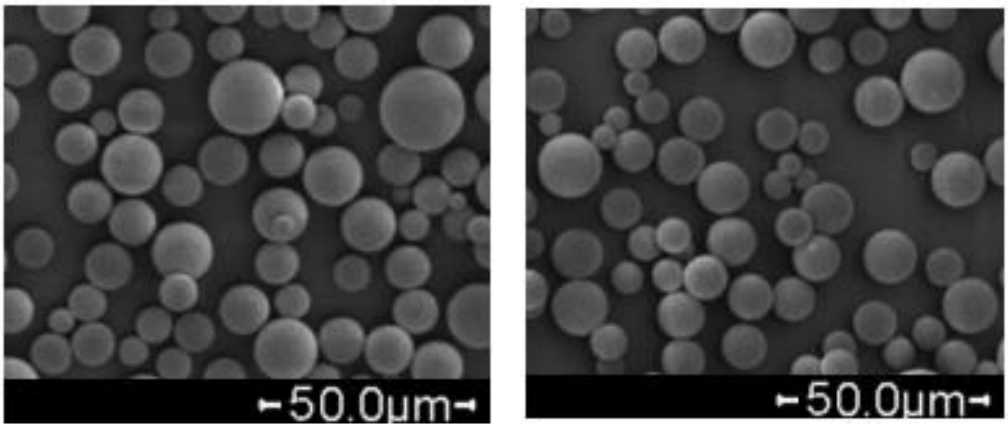
The requirements for polymeric shell of thermally expandable microcapsules are as follows: they should have good ductility and flexibility so that it could expand simultaneously as core material expanded, and they should have good density and gas barrier property so that the vapour of the core material could not permeate and leak out. Polyacrylonitrile has good flexibility and density, and was thus employed as the main polymeric shell composition of thermally expandable microcapsules. In this study, AN was chosen as the main monomer, and the other monomers such as MMA and crosslinking monomer DVB were used to coploymerise with AN to improve the properties of the resulting copolymer shell. The monomer compositions for various samples are shown in Table 1.

Table 1 Monomer composition of copolymeric shell of microcapsule (by mass)

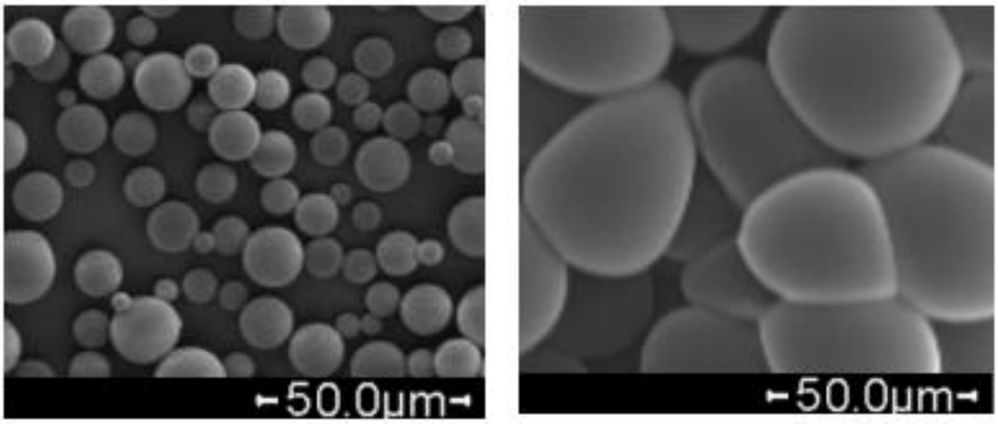
Sample	AN /%	MMA /%	EHA /%	DVB /%
A	70	29	0	1
B	70	20	9	1
C	70	20	10	0

3.1.1 Effects of EHA

Thermally expandable microcapsule samples A and B were heated, and surface morphology of A and B microcapsules observed by SEM before and after heat treatment at 150 ℃ for 2 min, is shown in Figure 1.



Sample A before heating Sample A after heating



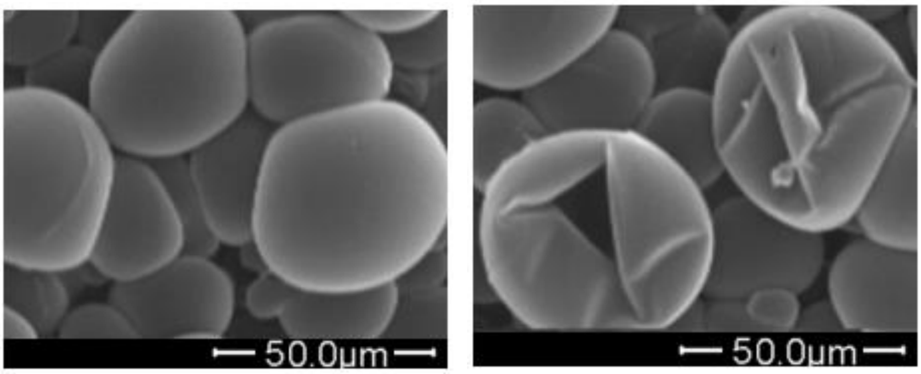
Sample B before heating Sample B after heating

Fig. 1 SEM of microcapsules before and after heating treatment at 150 ℃ for 2 minutes

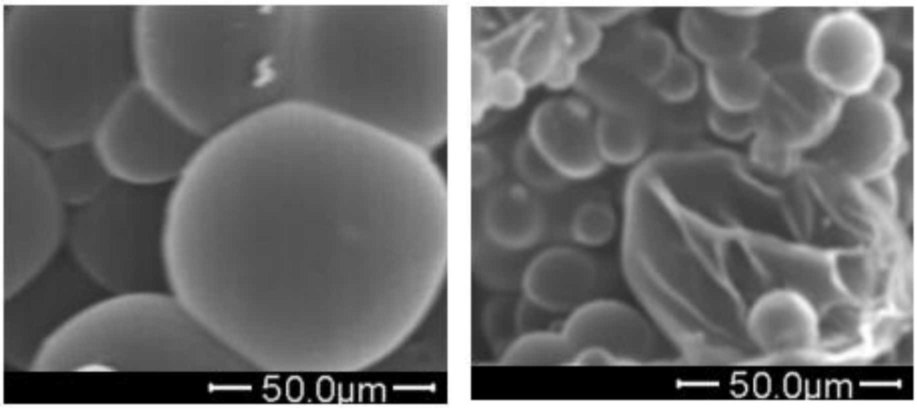
Homopolymer of AN has compact structure, high degree of crystallinity and strong rigid. The glass transition temperature of AN and MMA are 97 ℃ and 105 ℃, respectively, belonging to hard monomer; DVB has two unsaturated double bonds, belonging to crosslinking monomer. Thermally expandable microcapsules with AN/MMA/DVB copolymer shell of which softening point is very high and thermal expansion starting temperature is also high, so the shell did not expand when heated at 150 ℃ for 2 min. When 9% EHA was introduced, B microcapsules expanded when heated at 150 ℃ for 2 min as can be seen from Figure 1 and had large rate of expanded. Introduction of the EHA as soft monomer during the polymerization process, due to its glass transition temperature of -70 ℃, the glass transition temperature of copolymer was decreased, the softening point of the film was also reduced, the tensile performance and thermoplastic were improved.

3.1.2 Effects of DVB

Thermally expandable microcapsule samples B and C were heated at 150 ℃ for 2 min and 10 min respectively to examine the DVB effect in the shell, than observed using SEM, particle morphology is shown in Figure 2.



B after heating at 150 ℃ for 2 min B after heating at 150 ℃ for 10 min



C after heating at 150 ℃ for 2 min C after heating at 150 ℃ for 10 min

Fig. 2 SEM of microcapsules after heating treatment at 150 ℃ for 2 and 10 minutes

B microcapsules expanded when heated at 150 ℃ for 2 min as shown in Figure 2, microcapsule particles are still showing the complete structure. C microcapsules of which thermal stability is poor so that part of the microcapsule particles shell occurred collapse after heated at 150 ℃ for 2 min. When the heating time was extended to 10 min, B microcapsules further expanded and particles maintained a stable single spherical structure, but C microcapsules particles shell stick together after collapse, microcapsule shell were miscible so cannot obtain a single independent microcapsule particles. The introduction of DVB as cross-linking monomer in the comonomer obtained microcapsule shell that maintain flexibility while increasing the thermal stability. The reason is that the introduction of DVB in the copolymer formed a small amount of three-dimensional cross-linked structure, so that the copolymer shell heat softening temperature increased, resulting in the performance of thermal expansion microcapsules.

3.2 Effects of emulsifier on size and size distribution of microcapsules

In the study reported here, a 13% solution of styrene-maleic acid copolymer sodium salt was introduced as emulsifier and its influence on microcapsule size and size distribution was investigated by a combination of electron probe analysis and particle size measurement, with results shown in Figure 3.

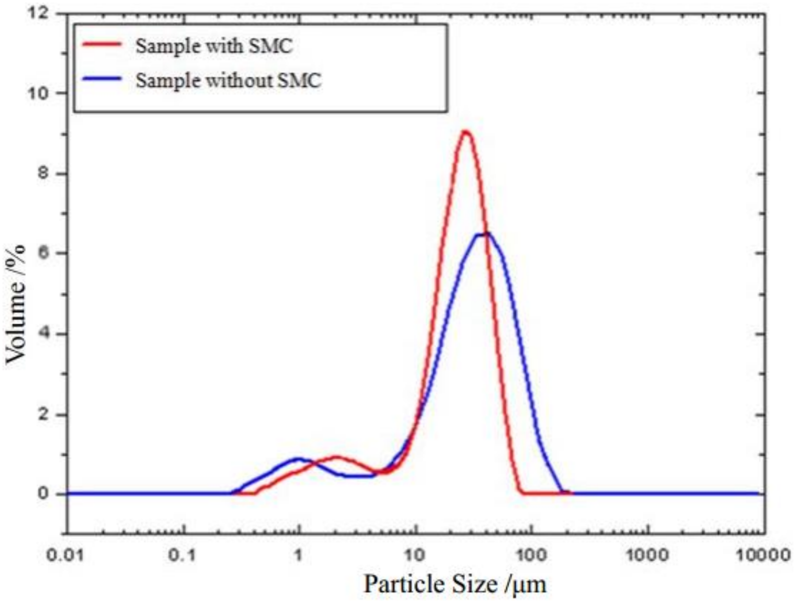


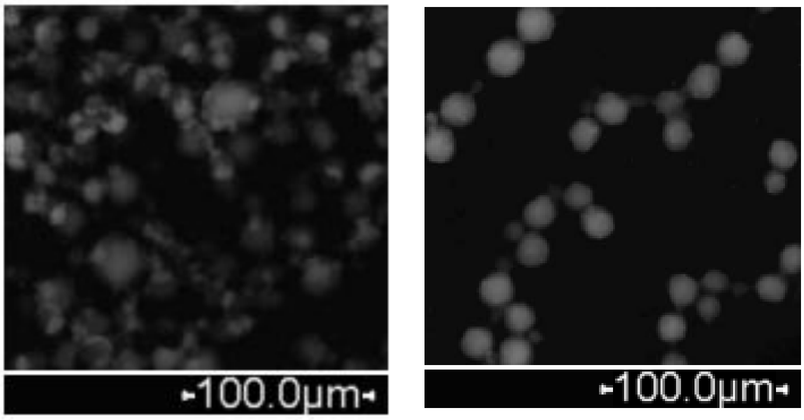
Fig. 3 Size distributions of microcapsules

From Figure 3, it can be seen that microcapsules prepared with SMC as emulsifier had a smaller average size and a narrower size distribution than those prepared without emulsifier. According to the research results of Torza and Mason[6], it was only possible to form a complete microcapsule when the interfacial tension between shell copolymer and water phase was smaller than that between core material and water phase. SMC is a large molecule surfactant which could reduce the interfacial tension between polymer and water phase and improve the dispersion of suspension stabilisers magnesium phosphate and PVP on the oil-water phase interface which resulted in more uniform distribution of capsule size.

3.3 Effects of dispersing agent

A 2% solution of styrene-maleic acid copolymer sodium salt was introduced as emulsifier and a 3% solution of PVA and PVP as dispersing agent synthesized microcapsules by suspension polymerization, respectively, obtaining microcapsules sample D (with 3% PVA) and E (with 3% PVP) after separating, washing and vacuum drying. Analysising microcapsules sample D and E via SEM, the results is shown in Figure 4.

From Figure 4, it can be seen that the samples D which PVA as dispersing agent synthesized microcapsules by suspension polymerization existed severe adhesion phenomena between particles after treatment, the particle surface also distributed a large number of free like dispersant PVA chain segments, microcapsule particles can not be stable and uniformly dispersed. The samples E microcapsules which PVP as dispersing agent synthesized by suspension polymerization show separate particles and the surface is smooth and tidy, and microcapsule particles can be stable and uniformly dispersed, particle size and size distribution is more uniform. This is because the PVA has a high hydrophilic which lead to a higher viscosity of the system in the preparation process, and the PVA has a relatively lower average molecular weight than PVP, in the suspension polymerization process, the dispersant PVA deposite in the interface of copolymer solution drops/water more easily, forming part of the primary particles, resulting in uneven particle size distribution and easier be distributed on the interface of the copolymer to form the bridge between the dispersant. Therefore, in this study, microcapsules synthesized by suspension polymerization using a 3 percent solution of PVP as dispersing agent can obtain better comprehensive performance.



Sample D Sample E

Fig. 4 SEM of microcapsules prepared with different dispersing agent

3.4 The effects of shell/ core mass ratio

To investigate the effect of the shell/ core mass ratio on the encapsulation efficiency (EE), respectively, the shell/ core mass ratio of 1.8:1, 3:1, 7:1 and 10:1 are controlled to prepare microcapsules. Determining the encapsulation efficiency, the relationship between encapsulation efficiency and the shell/ core mass ratio is shown in Table 2.

Table 2 Effects of shell/ core mass ratio on the encapsulation efficiency of microcapsules

Shell/ core mass ratio	1.8:1	3:1	7:1	10:1
Encapsulation efficiency /%	91.6	94.5	95.8	9.65

It can be seen from Table 2 that when the shell/ core mass ratio was 3:1, the encapsulation efficiency of the produce reached 94.5%, then with the shell/ core mass ratio increased, the encapsulation efficiency increased marginally. If the shell/ core mass ratio is too large, although the encapsulation efficiency of core is high, the shell is too thick, a few microcapsules can be preparated and when TSH begin to decompose into nitrogen, too little nitrogen obtianed, so that it’s difficult to achieve the desired expansion of state. Therefore, in this study, microcapsules which prepared at a shell/ core mass ratio of 3:1 can achieve high encapsulation efficiency and higher quality core.

4 Application of microcapsules in the coating

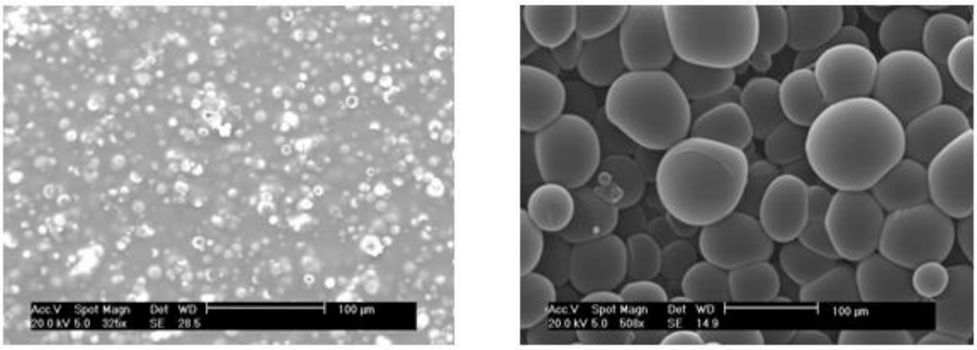
The thermal expansion microcapsules synthesized according to the amount of 5% and supplemented by a small amount of dispersant were added to the waterborne polyurethane wood coating, stirring evenly.

4.1 Coating thermal expansion performance

(a) Before heating (100μm) (b) After heating (450μm)

Fig. 5 Photographs of surface of WPU wood coating containing 5% TEMs

Brushing the coatings on the substrate ensured that the dry film thickness was 100 μm, study the thermal expansion property of the coating after heat treatment at 150 ℃ for 2 min. Figure 5 is the surface photo of the coating before heating and heating at 150 ℃ for 2 min, Figure 6 is the scanning electron micrographs of the coating before heating and heating at 150 ℃ for 2 min.



(a) Before heating (100μm) (b) After heating (450μm)

Fig. 6 SEM images of WPU wood coating containing 5% TEMs

From Figure 6, it can be seen that the water-based polyurethane wood coating which contain thermal expansion microcapsules expanded significantly after heating, the 100 μm thickness film of water-based coating containing 5% microcapsules could be expanded to the thickness of 450 μm after exposed at 150 ℃ for 2 minutes. Coating film expansion is caused by TSH included in the thermal expansion microcapsules core heating and then decomposing into nitrogen, nitrogen occupy most of the space of the coating film after the expansion, the nitrogen is neither combustion nor combustible, so by adding the thermal expansion microcapsules, the coating film thickness of water-based wood coating increased more than four times after thermal expansion, and the expansion coating film contains a relatively large amount of nitrogen. Therefore, the coating is applied to water-based polyurethane wood coating that can obtain flame retardant property, thus can achieve a certain fire-retardant features.

4.2 Thermal stability

Analysising the dry water-based polyurethane wood coating film and dry water-based polyurethane wood coating film which contain 5% thermal expansion microcapsules via TGA, the results is shown in Figure 7.

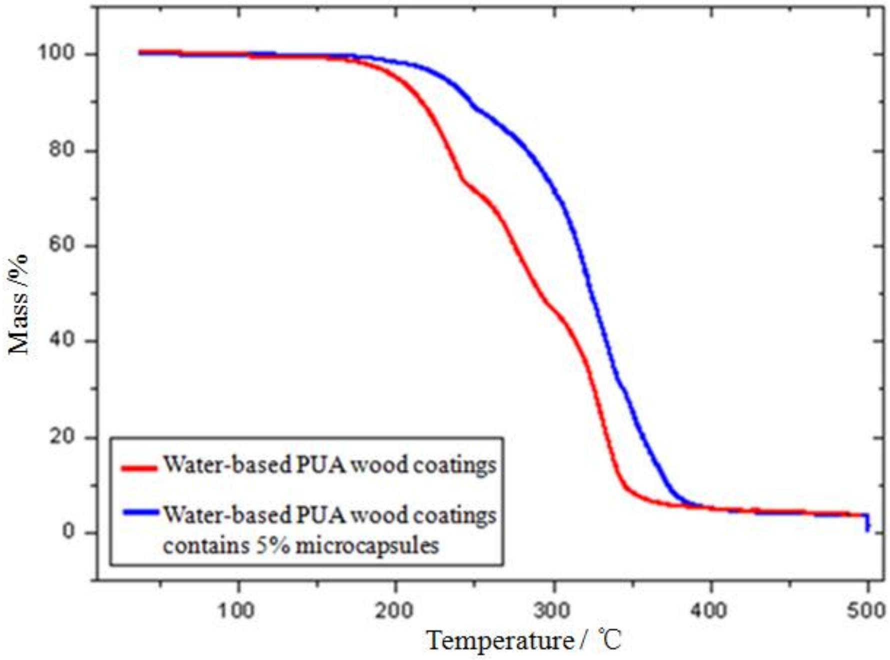


Fig. 7 TGA curves of water-based PUA wood coatings

From Figure 7, it can be seen that the initial thermal decomposition temperature of the water-based wood coatings film which contains 5% thermal expansion microcapsules is above 210 ℃, while the final temperature is about 380 ℃. The initial thermal decomposition temperature of the water-based wood coatings film is about 180 ℃, while the final temperature is about 350 ℃. The starting decomposition temperature of the water-based wood coatings film which contains 5% thermal expansion microcapsules is 30 ℃ higher than that of the water-based wood coatings. In the decomposition process, the mass loss of the water-based wood coatings film which contains 5% thermal expansion microcapsules is higher than that of the water-based wood coatings at the same temperature. If the residual rate is lower than 5% after the water-based wood coatings film ending the decomposition, while the residual rate of the water-based wood coatings film which contains 5% thermal expansion microcapsules is still 25%. The water-based wood coatings film which contain 5% thermal expansion microcapsules show slow mass loss with the increase of temperature between 250-300 ℃, speculating at this temperature range, microcapsules shell have not yet decomposed and still keep the expansion of state, when the temperature was higher than 300 ℃, microcapsules shell had decomposed and internal nitrogen rapidly released, thus losing mass rapidly. Therefore, adding 5% microcapsules can improve the thermal stability of water-based polyurethane wood coatings, so that slow down the thermal decomposition of the coating, therefore, we can achieve a certain fire-retardant features.

5 Conclusions

It was found that the microcapsules with desirable thermal expansion property and good heat stability could be obtained with a shell monomers composition of 70%AN/20%MMA /9%EHA/1%DVB. When 2% SMC as emulsifier and 3% PVP as dispersing agent were used, well defined spherical and more uniform microcapsules could be prepared. It was also found that when the shell/core mass ratio was 3:1, an encapsulation efficiency of ca. 94.5% was achieved. Beyond this ratio, the increase of encapsulation efficiency reached a plateau. The 100 μm thickness film of water-based coating containing 5% microcapsules could be expanded to the thickness of 450 μm after exposed at 150 ℃ for 2 minutes. TG analysis revealed the weight loss start temperature of coating was increased by more than 30 ℃ when 5% microcapsules were added to water-based coatings, which demonstrated the flame-retardant function of the coatings.

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