

Influence of cross-linking agent on the hydrophobicity of microencapsulated ammonium polyphosphate with tung oil phenolic resin

Weiying Gao^{1,2,3,a}, Shujun Wang^{1,2,b}, Fanbin Meng^{1,2}, Huanqing Ma^{1,2}
and Yuanhao Wang⁴,

¹State key laboratory of heavy oil processing, China University of Petroleum (Beijing), Beijing 102249, China;

²College of Science, China University of Petroleum (Beijing), Beijing 102249, China;

³Department of Science and Technology, Chinese People's Armed Police Force Academy, Langfang 065000, China;

⁴Faculty of Science and Technology, Technological and Higher Education Institute of Hong Kong, New Territories, Hong Kong.

^agaowei12@sohu.com, ^bbjwsbj@sina.com

Keywords: Ammonium polyphosphate; microencapsulation; tung oil phenolic resin; cross-linking agent; hydrophobicity.

Abstract. Ammonium polyphosphate (APP) was encapsulated with different cross-linked structure tung oil phenolic resin (TPF) by in situ polymerization and it was performed that a study on the influence of the cross-linking agent type on the hydrophobicity of the APP microcapsules. The chemical and physical features of APP microcapsules were characterized by Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS). The hydrophobicity was assessed by the water contact angle (WCA). The results showed that the APP microcapsules with different cross-linked structure TPF shell had been achieved successfully and the cross-linking agent type had important influence on the hydrophobicity of APP microcapsules.

1. Introduction

Because of its low smoke, low-toxicity and less corrosive substances during its combustion, ammonium polyphosphate $[(\text{NH}_4)_{n+2}\text{P}_n\text{O}_{3n+1}]$ is widely used as flame retardant in the fields of coating industry, plastics, wood, rubber or as extinguisher in the fields of forest fire, coal field fire. When exposed to an external heat flux, APP would play a role as acid source to react with carbon source and gas source to give off inert gas, e.g. N_2 , NH_3 , CO_2 and form a intumescent carbonaceous char layer as a kind of physical barrier to inhibit the transfer of heat and diffusion of inflammable gases^[1-4]. Unfortunately, The fire retardancy of APP is not permanent due to its weak water resistance and poor compatibility in polymers. Microencapsulation technique is a good choice to overcome above problems. In previous study by Wu et al., microcapsules containing APP with various shells, such as melamine-formaldehyde, nylon-6, ureaformaldehyde, epoxy resin and gel-silica, were reported^[5-10]. To the best of our knowledge, microcapsules containing APP with tung oil-modified phenolic resin shell has not yet been reported.

The main content of tung oil is α -Eleostearate. The tung oil phenolic resin (TPF) is a modified phenolic resin by introducing α -Eleostearate into the main chain of a phenolic resin (PF). The flexibility of PF has been improved and it is more hydrophobic and easily compatible with polymer due to the existence of α -Eleostearate^[11]. Based on above mentioned advantages, a novel type of APP microencapsulated with TPF (TPFAPP) was prepared and a study on the influence of the cross-linking agent type on the hydrophobicity of APP microcapsules was performed in this paper.

2. Experimental

2.1 Materials

APP(an average degree of polymerization $200 < n < 400$)was supplied by Wuhan Hongxinkang Fine Chemical Corp.,Ltd, China. TPF was purchased from Anhui Tianyu High Temperature Resin Material Corp.,Ltd. Hexamethylene Tetramine(HMTA) ,ethylene diamine(EDTA), ethanol and chloroform used were reagent grade.

2.2 Preparation of microcapsules

A 250 ml three-necked round bottom flask was equipped with a mechanical stirrer. Then, 8.6g 41.5% TPF ethanol solution and 63.4g ethanol were poured into the flask and the mixture was stirred for 5 min at room temperature. Then, 10g APP, 1g OP-10, and 0.5g dimethylsilicon oil were added and stirred for 15 min. After that 16g 4.54% cross-linking agent ethanol solution was added dropwise to the mixture, keeping at the same temperature for 1 h. Finally the mixture were filtered, washed with ethanol, and dried at 60 °C to achieve the final microcapsulated APP powders. In order to further investigate the influence of different cross-linking agent on the hydrophobicity of microcapsules, some samples were cured at 160 °C for 3 h.

APP microcapsules with HTMA cross-linking TPF shell was represented by HTPFAPP, APP microcapsules with EDTA cross-linking TPF shell was represented by ETPFAPP. The weight ratio of TPF to cross-linking agent was 1:0.2.

2.3 Measurements

2.3.1 Fourier transforms infrared analysis

FTIR spectra were obtained on a JASCO480 spectrometer (German Bruker) with thin KBr as the sample holder. Transition mode was used and the wave number range from 4000 to 500 cm^{-1} .

2.3.2 X-ray photoelectron spectroscopy

The XPS spectra were obtained on a K-Aepna spectrometer (Thermo Fisher Scientific,USA) with Al $K\alpha$ excitation radiation ($h\nu = 1253.6\text{eV}$) in ultrahigh vacuum conditions.

2.3.3 hydrophobicity analysis

The hydrophobicity of samples was characterized by contact angle of the powders with deionized water. The powder samples were first pressed into wafers at 15 MPa and then measured using JC2000D contact angle analyzer (Shanghai Zhongchen Digital Technology Equipment Co., Ltd. China).

3. Results and discussion

3.1 Chemical characterization

The FTIR spectra of APP,HTPFAPP and ETPFAPP are presented in Fig.1. As seen in Fig.1(a), the important characteristic absorption bands of APP were as follows: 3200 cm^{-1} (N-H symmetric stretching vibration), 1692 cm^{-1} (N-H bending vibration), 1239 cm^{-1} (P=O), 1065 cm^{-1} (P-O symmetric stretching vibration), 871 cm^{-1} (P-O asymmetric stretching vibration), 1020 cm^{-1} (PO₂ and PO₃) and 800 cm^{-1} (P-O-P). After being coated by TPF, the spectra changed, as seen in Fig.1(b) and Fig.1(c). The intensities of absorption peak at 3400 cm^{-1} and 1636 cm^{-1} increased due to introducing TPF groups: O-H and C=C, indicating the existence of TPF in the structure of TPFAPP. In addition, the absorption peak of ETPFAPP were more stronger than that of HTPFAPP, which showed that the amount of precipitated TPF due to EDTA cross-linking (ETPF) was more than that of precipitated TPF due to HTMA cross-linking (HTPF).

It can be seen from Fig.2(a) that the peak at 134.24eV, 400.26eV, 285.04eV and 532.06eV are assigned to P_{2p}, N_{1s}, C_{1s}, O_{1s} of APP. After microencapsulation, the intensities of P_{2p}, N_{1s} and O_{1s} peaks greatly decreased and the intensities of the C_{1s} peaks, centered at 290.08eV, increased sharply, as seen in Fig.2(b) and Fig.2(c). The above changes indicated that APP was well coated by TPF. Meanwhile the intensities of P_{2p} and N_{1s} peaks of ETPFAPP were weaker than that of HTPFAPP, indicating that APP was better coated by ETPF, which was in accordance with the data of FTIR.

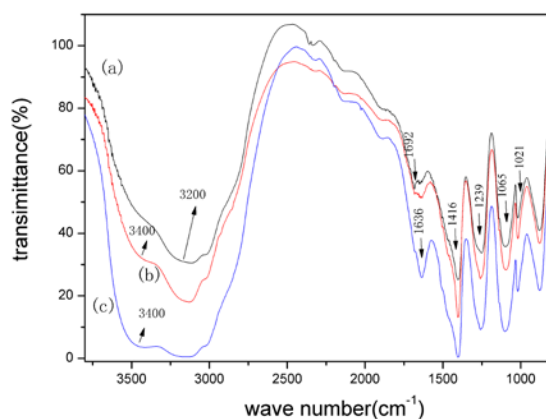


Fig.1 FTIR spectra of (a) APP,(b) HTPFAPP,(c) ETPFAPP

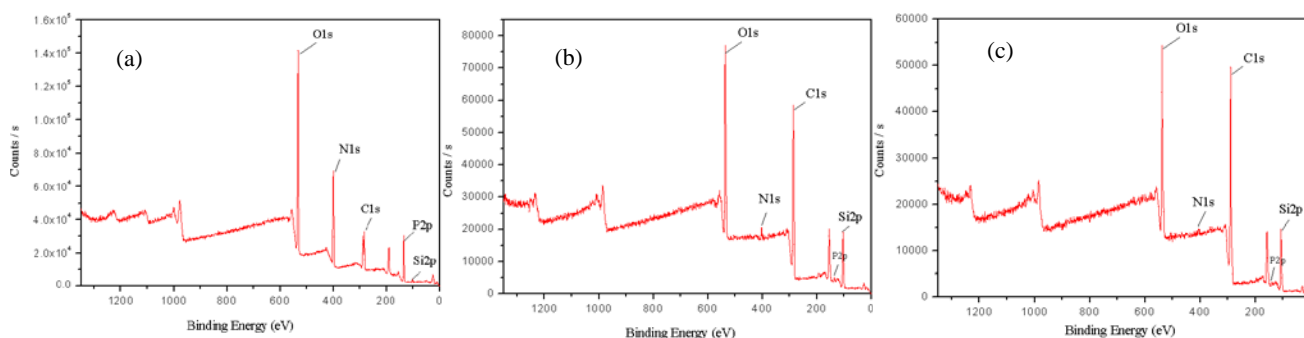


Fig.2. XPS spectra of (a) APP, (b) HTPFAPP,(c) ETPFAPP

3.2 Hydrophobicity of APP microencapsules

The hydrophobicity was assessed by the water contact angle(WCA).The larger the WCA is, the better the hydrophobicity is.The WCA photographs of APP and its microencapsules are shown in Fig.3.It can be seen from Fig.3(a) that the WCA of original APP was 23°, showing that APP was very hydrophilic. After microencapsulation, the WCAs of HTPFAPP and ETPFAPP all sharply increased, improving the hydrophobicity of APP. However, the WCA of HTPFAPP was 80°, lower than that of ETPFAPP(86°),as seen in Fig.3(b) and Fig.3(c). It is mainly because the amount of precipitated ETPF was more than that of precipitated HTPF and APP was better coated by ETPF,which can be confirmed by the data of FTIR and XPS. But after heat curing, the WCAs of HTPFAPP and ETPFAPP increased to 104° and 93° respectively due to the removal of some hydroxyl and the formation of lipophilic groups,as seen in Fig.3(d) and Fig.3(e).The WCA of HTPFAPP increased by 24°, higher than 8° by which the WCA of ETPFAPP increased, indicating that the structure of HTPF was different from that of ETPF and APP was better coated by HTPF or HTPF itself being more hydrophobic owing to thermo-crosslinking.The above results showed that the type of cross-linking agent had important influence on the hydrophobicity of APP microcapsules. The main reasons are as follows: Although the film-forming materials are all TPF, the mechanisms of TPF cross-linking are different due to different cross-linking agent,so different structure TPF will form, leading to different physical and chemical properties, which can be also confirmed by the powders color.From the visual perspective, HTPFAPP was a white powder, slightly red. ETPFAPP was a lighter yellow powder. After heat curing, HTPFAPP turned to orange and ETPFAPP turned to brown.

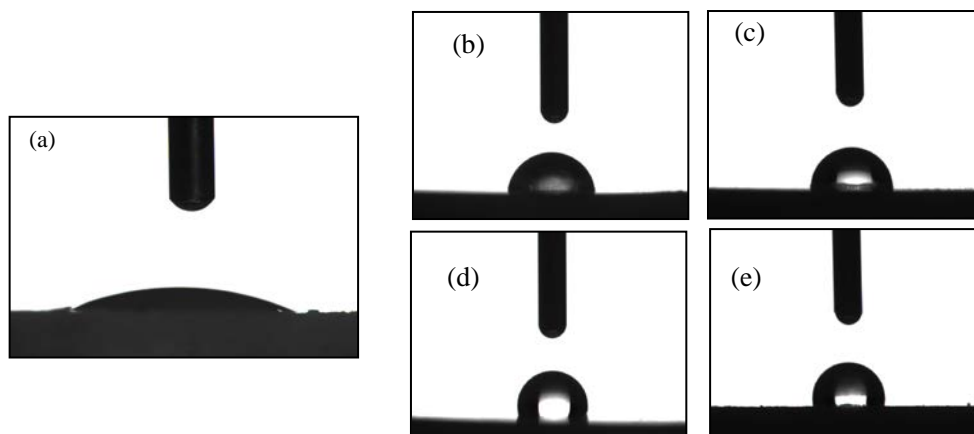


Fig.3 WCA photographs:(a) APP, (b) HTPFAPP, (c) ETPFAPP , (d) Heat cured HTPFAPP, (e) Heat cured ETPFAPP

4. Conclusion

In this paper, APP was encapsulated with different cross-linked structure tung oil phenolic resin by in situ polymerization and it was performed that a study on the influence of the cross-linking agent type on the hydrophobicity of APP microcapsules. The FTIR and XPS analysis showed that APP microcapsules with different cross-linked structure TPF shell had been achieved successfully and APP was better coated by ETPF before heat curing. The WCA data indicated that the type of cross-linking agent had important influence on the hydrophobicity of APP microcapsules. The hydrophobicity of ETPFAPP was better than that of HTPFAPP. However, HTPFAPP was more hydrophobic after heat curing. The main reason is that the mechanisms of TPF cross-linking are different due to different cross-linking agent, so different structure TPF will form, which lead to different physical and chemical properties.

References

- [1]. Wu Q, Qu B. Synergistic effects of silicotungstic acid on intumescent flame-retardant polypropylene. *Polym Degrad Stab.* Vol.74(2001), p. 255–261.
- [2]. Chen Y H, Liu Y, Wang Q et al. Performance of intumescent flame retardant master batch synthesized through twin-screw reactively extruding technology: effect of component ratio. *Polym Degrad Stab.* Vol.81(2003), p. 215–224.
- [3]. Ni JX, Chen LJ, Zhao KM et al. Preparation of gel-silica/ammonium polyphosphate core-shell flame retardant and properties of polyurethane composites. *Polym Adv Technol.* Vol. 22(2011), p.1824–1831.
- [4]. D. Saihi, I. Vroman, S. Giraud et al. Microencapsulation of ammonium phosphate with a polyurethane shell, Part II. Interfacial polymerization technique. *Reac Func Polym.* Vol.66(2006), p. 1118–1125.
- [5]. Wu K, Zhang YK, Hu WG et al. Influence of ammonium polyphosphate microencapsulation on flame retardancy, thermal degradation and crystal structure of polypropylene composite. *Composites Science and Technology.* Vol. 81(2013), p.17-23.
- [6]. Liu MF, Liu Y, Wang Q. Flame-retarded poly(propylene) with melamine phosphate and pentaerythritol/polyurethane composite charring agent. *Macromol Mater Eng.* Vol.292(2007), No.2, p. 206–13.
- [7]. Wu K, Song L, Wang ZZ et al. Preparation and characterization of double shell microencapsulated ammonium polyphosphate and its flame retardance in polypropylene. *J Polym Res.* Vol.16, No.3 (2009), p.283–294.
- [8]. Wu K, Song L, Wang ZZ, Hu Y. Microencapsulation of ammonium polyphosphate with

urea–melamine–formaldehyde resin and its flame retardance in polypropylene. *Polym Adv Technol*. Vol.19(2008),No.12, p.1914–1921.

[9].Giraud S., Salaüna F., Bedek G. et al. Influence of chemical shell structure on the thermal properties of microcapsules containing a flame retardant agent. *Polym Degrad Stab* Vol.95(2010), p.315-319.

[10]. Chen XL, Jiao CM, Zhang J. Microencapsulation of ammonium polyphosphate with hydroxyl silicone oil and its flame retardance in thermoplastic polyurethane. *J Therm Anal Calorim*. Vol.104(2011), p.1037–1043.

[11]. Yu G, LuPS, Wang Y, et al. Study on phenol-formaldehyde resins modified with tung oil(桐油) —Synthesis, Mechanism and Characterization. *Chemistry and Industry of Forest an Products*, Vol.14(1993), p. 23-31.