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Influence of reactive POSS and DDP on thermal stability and flame retardance of UPR nanocomposites

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Abstract: Unsaturated polyester resins (UPR) were prepared by the melt condensation method based on adipic acid, o-phthalic anhydride, maleic anhydride and ethylene glycol in the presence of PSS-(2,3-propanediol)propoxy-heptaisobutyl substituted (PSS-POSS) or/and 9 wt% [(6-oxide-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl)methyl]butanedioic (DDP). We synthesized UPR containing DDP (DDP-UPR) and UPR containing both DDP and PSS-POSS (DDP-PSS-POSS-UPR series). The chemical structures of the modified polyesters were characterized and confirmed by Fourier transform infrared (FTIR) and ^{31}P nuclear magnetic resonance (^{31}P NMR). The thermal stability and flammability behaviors of UPR were evaluated by thermogravimetric analysis (TGA) and limited oxygen index (LOI) and the vertical burning test. The morphology of residual char of UPR was shown by scanning electron microscopy (SEM). The results indicate that the incorporation of PSS-POSS has little influence on the thermal stability of DDP-UPR, but enhances the flame retardance of DDP-UPR, and when the PSS-POSS content reaches 10 wt%, the DDP-PSS-POSS-UPR has better flame retardance.

Keywords: [(6-oxide-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl)methyl]butanedioic (DDP); (2,3-propanediol)propoxy-heptaisobutyl substituted (POSS); flame retardance; thermal stability; unsaturated polyester resins (UPR).

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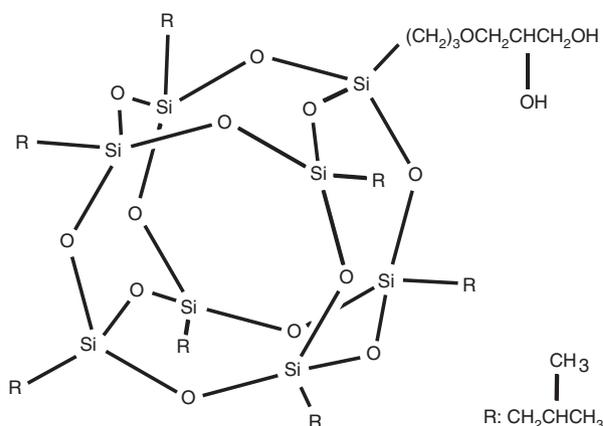
1 Introduction

In recent years, polyhedral oligomeric silsesquioxanes (POSS) have attracted considerable interest in the area of polymer nanocomposites (1–4) because of their special organic-inorganic hybrid structure. POSS consist of a cage-like inorganic Si-O frameworks ($\text{SiO}_{1.5^x}$) and several organic substituents which attached to each Si atom (5). The inorganic framework is ceramic in nature, providing thermal stability and rigidity, while the organic substituents compatibilize the molecule, allowing it to dissolve in polymers, solvents and coatings (6, 7). Further, the organic substituents of POSS vary from reactive groups (alkylene, hydroxy, etc.) to nonreactive groups (hydrogen, alkyl, etc.). The reactive groups in POSS can not only be homopolymerized, but also can copolymerize with other monomers. The nonreactive groups of POSS make them compatible with polymers. Due to different types of organic substituents, nonreactive or reactive, POSS derivatives can be effectively incorporated into polymers by covalent bonds (8), or even simple physical blending (9, 10) to improve their mechanical properties. POSS molecules can bond the polymer backbones inside the chain or end groups (11–13), thus the compatibility between POSS and polymers can have a good improvement and results in a homogeneous distribution of inorganic in the organic phase. For example, Chiu (14) synthesized the sulfone epoxy (SEP)/polyhedral oligomeric silsesquioxane (POSS) nanocomposite which contains bulky POSS side chains by the polyaddition method. The results show that POSS were dispersed uniformly in the epoxy matrix and the thermal properties and flame retardance were both improved.

Unsaturated polyester resin (UPR) is one of the most important thermoset materials due to its outstanding properties, including being easily controllable and its fast cure processes at room temperature (15, 16). However, the disadvantage of high flammability limits the widespread applications of UPR. Therefore, it is necessary to modify UPR to obtain better flame retardance. [(6-Oxide-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl)methyl]butanedioic (DDP) is a kind of phosphorous-containing flame retardant and contains two carboxyls that can chemically link to the molecular chain of UPR with propylene glycol. It had been reported

that conventional UPR were modified with DDP (17, 18). The results show the thermal behavior of DDP-UPR is slightly affected while the flame retardance is significantly improved.

In addition, the POSS derivative PSS-(2,3-propanediol) propoxy-heptaisobutyl (PSS-POSS) is also a good modifier for UPR, and its structure is shown in Scheme 1. There are seven nonreactive and one reactive organic substituent with two hydroxyl groups which can be reacted with carboxyl groups in PSS-POSS. At present, there are no reports about UPR modified with PSS-POSS. In our previous work, UPR containing DDP (DDP-UPR) and UPR containing both DDP and PSS-POSS (DDP-PSS-POSS-UPR) had been synthesized and investigated. We focus on the influence of PSS-POSS on thermal stability and flame retardance of DDP-UPR, changing the content of PSS-POSS in UPR to obtain the DDP-PSS-POSS-UPR series.



Scheme 1: The structural formula of PSS-(2,3-propanediol)propoxy-heptaisobutyl substituted.

2 Experimental

2.1 Materials

Adipic acid, o-phthalic acid (PA) and ditin butyl dilaurate (95%) were all purchased from the Aladdin Industrial Co., Ltd. (Shanghai, China); ethylene glycol (EG) and maleic anhydride (MA) were supplied by the Tianjin Fuyu Fine Chemical Co., Ltd. (Tianjin, China); styrene was supplied by the Sinopharm Chemical Reagent Co., Ltd. (Beijing, China); DDP was purchased from the Zhejiang Province Chemical Industry Research Institute Co., Ltd. (Hangzhou, China); PSS-POSS was purchased from Hybrid Plastics (USA). Cyclohexanone peroxide and cobalt naphthenate were supplied by the Aladdin Industrial Co., Ltd. (Shanghai, China).

2.2 Synthesis of unsaturated polyesters

Unsaturated polyesters (UP) based on the reaction of adipic acid, phthalic acid, maleic anhydride, ethylene glycol, DDP and PSS-POSS were prepared by the melt condensation method. The amounts of reactants are given in Table 1 and the ratio of acid/glycol is designed as 1:1.1 (mol ratio). The reaction mixture was stirred under a continuous nitrogen flow and heated in an oil bath. Ditin butyl dilaurate was added when the system temperature rose to 120°C. The reaction was run for 3 h at 175°C and then the temperature was increased to 190°C until the acid value dropped to 50 mg/KOH. Afterwards, the products were maintained at 165°C in vacuum conditions for 1 h to remove water and the unreacted monomers, and then

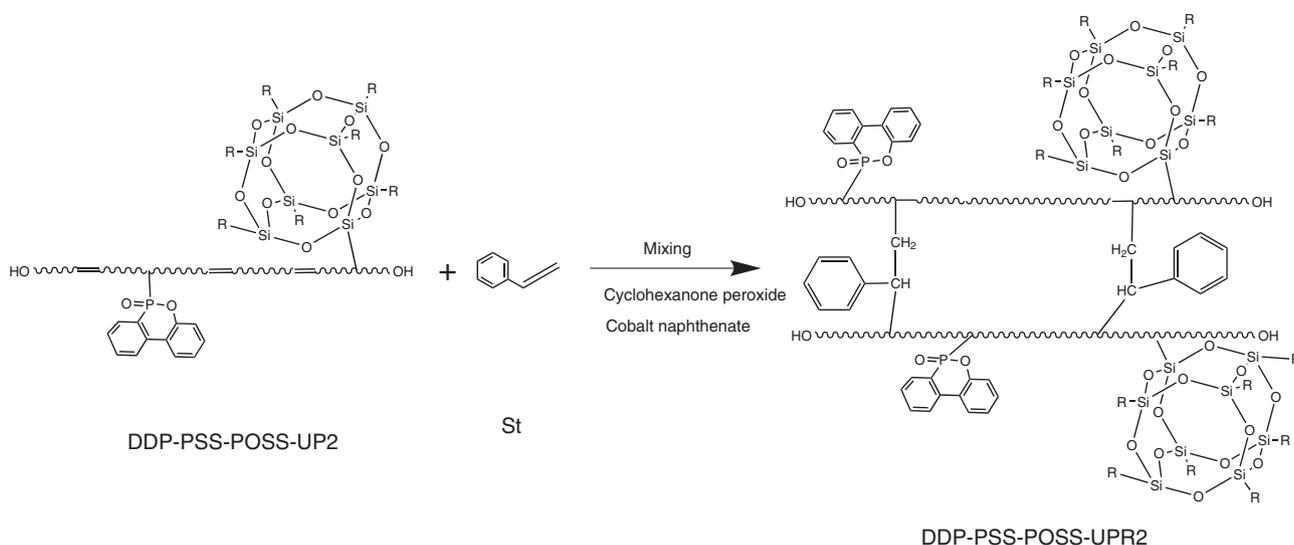
Table 1: Compositions of the prepared unsaturated polyesters.

Materials (g)	UP0	DDP-UP	DDP-PSS-POSS-UP		
			1	2	3
EG	23	21	20	18	17
PA	11.94	11.94	11.94	11.94	11
MA	18.04	18.04	16	15	14
Adipic acid	10.57	6.22	6.22	6.22	6.22
DDP	0	6.35	6.35	6.35	6.35
PSS-POSS	0	0	3.3	6.6	9.9

a small amount of polyesters were taken out for further tests. At the end, the products were cooled to 100°C and diluted using a sufficient quantity of styrene to obtain 65% solution of unsaturated polyesters with hydroquinone. The reaction equation of unsaturated polyesters modified with DDP and PSS-POSS is shown in Scheme 2.

2.3 Curing of the prepared unsaturated polyesters

The polyesters were cross-linked with styrene in the presence of cyclohexanone peroxide as an initiator and cobalt naphthenate as an accelerant. The mixtures which had been stirred evenly were poured into the mould for 24 h and then post cured further at 80°C in a thermostated oven until the unsaturated polyesters and styrene were cured completely. The cured UP0, DDP-UP and DDP-PSS-POSS-UP1, DDP-PSS-POSS-UP2, DDP-PSS-POSS-UP3 were named, respectively, UPR0, DDP-UPR and DDP-PSS-POSS-UPR1, DDP-PSS-POSS-UPR2, DDP-PSS-POSS-UPR3. Scheme 3 shows the curing between unsaturated polyesters and styrene.



Scheme 3: The curing process of DDP-PSS-POSS-UP2 and styrene.

Table 2: Assignment of FTIR spectra of UP0 and DDP-UP.

Wavenumber (cm ⁻¹)	Assignment
UP0	
3500	-OH stretching vibration
3075	=CH- stretching vibration
2957, 1448	-CH ₂ - stretching vibration, bending vibration
1728, 1285	C=O and C-O-C stretching vibration of ester groups, respectively
1645	C=C stretching vibration
1597, 1580	C-C stretching vibration of aromatic ring
DDP-UP	
3500	-OH stretching vibration
2957, 1448	-CH ₂ - stretching vibration, bending vibration
1728, 1285	C=O and C-O-C stretching vibration of ester groups, respectively
1645	C=C stretching vibration
1597, 1580	C-C stretching vibration of aromatic ring
1477, 916	P-C and P-O-C stretching vibration
745	C-H bending vibration of the ortho-disubstituted aromatic ring

at 36–37 ppm. The chemical shift has a little change due to the difference between the chemical environments of ³¹P.

The curing of UPR occurred between the carbon-carbon double bonds. The carbon-carbon double bonds of UP which were provided by maleic anhydride reacted with styrene through free radical polymerization in the presence of an initiator and accelerant.

Figure 4A and B exhibit the uncured and cured IR spectra of UPR0, respectively. Before curing, an obvious characteristic peak at 1645 cm⁻¹ appears, which belongs to the olefinic bonds, but the peak at 1645 cm⁻¹ clearly

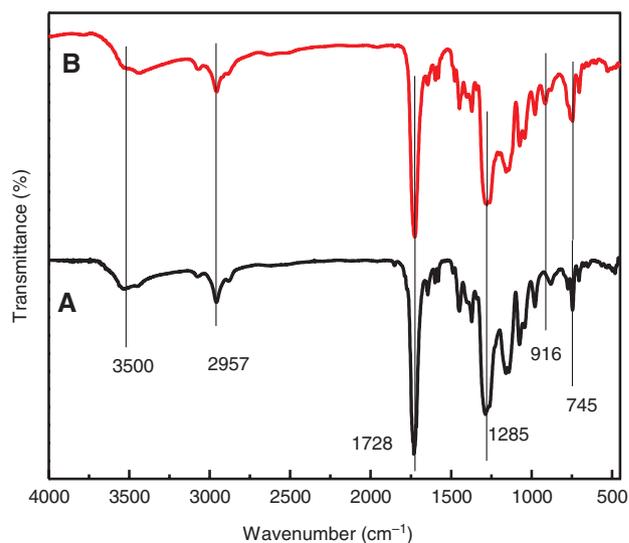


Figure 1: The FTIR spectra of UP0 (A) and DDP-UP (B).

disappeared after curing. It inferred that the UP can form the linkage with styrene to obtain UPR.

3.2 Thermogravimetric analysis

The thermograms of cured UPR are shown in Figure 5. The relevant thermal decomposition data are all given in Table 3. T₅ and T_{max} are defined as the temperature at 5 wt% weight loss and at maximum weight loss rate, respectively.

In Figure 5A, it is noteworthy that there are two steps for the UPR0 curve and only one step for the DDP-UPR and DDP-PSS-POSS-UPR series curves. The step between 200°C and 400°C with the DTG peaks at 380°C–390°C in

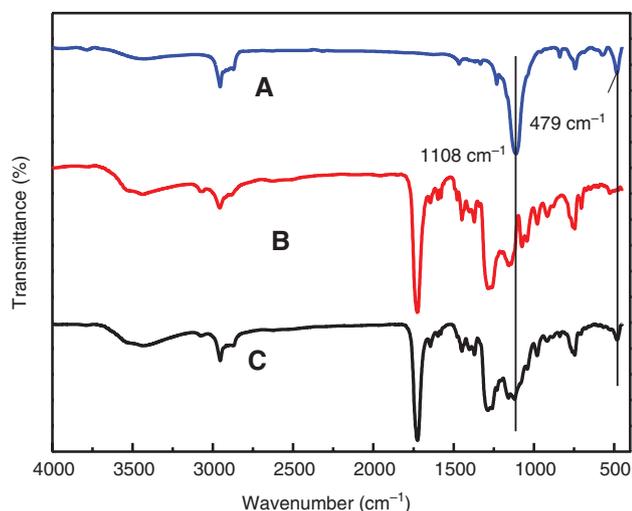


Figure 2: The FTIR spectra of PSS-POSS (A), DDP-UP (B) and DDP-PSS-POSS-UP (C).

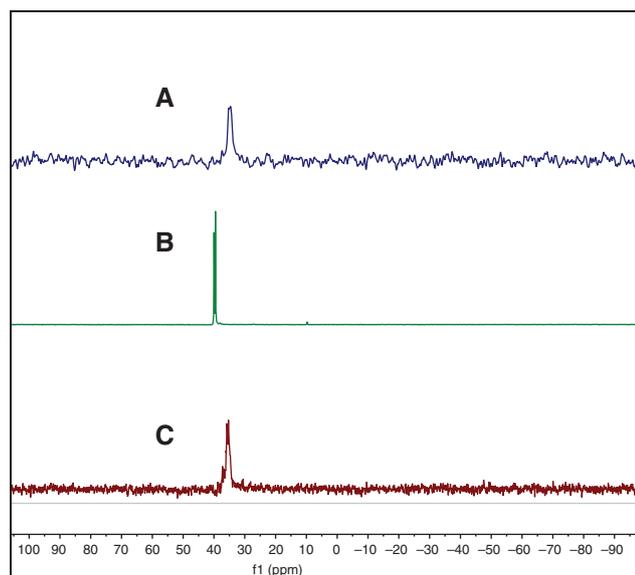


Figure 3: The ^{31}P NMR spectra of DDP-PSS-POSS-UP2 (A), DDP (B) and DDP-UP (C).

all prepared UPR results from the degradation of ester bonds of polyesters (19), and the step in UPR0 between 420°C and 580°C with the DTG peak at 520°C is attributed to the total degradation of the samples (20). As shown in Table 3, the char yield of DDP-PSS-POSS-UPR2 is 9.78%, much higher than that of DDP-UPR (3.53%) and UPR0 (0.22%) at 750°C. It is inferred that DDP and PSS-POSS can promote the formation of char yield. The coverage of high residual char on DDP-UPR and DDP-PSS-POSS-UPR series matrix reduced the conduction of heat and hindered the further decomposition of the polyester resins (21, 22). This can explain why the TGA curves of DDP-UPR

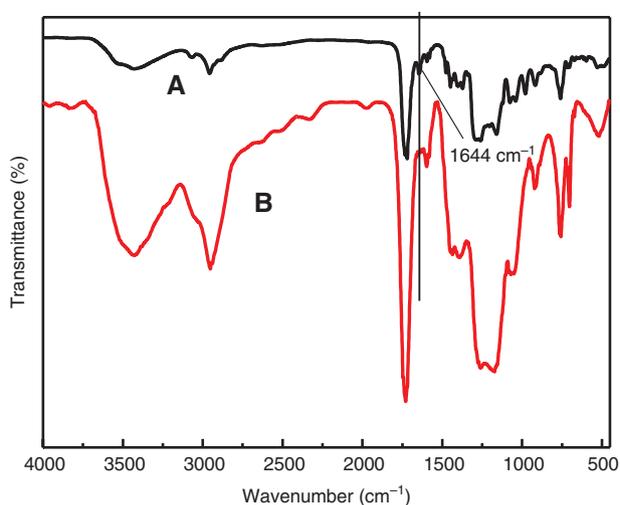


Figure 4: The FTIR of UPR0: before curing (A) and after curing (B).

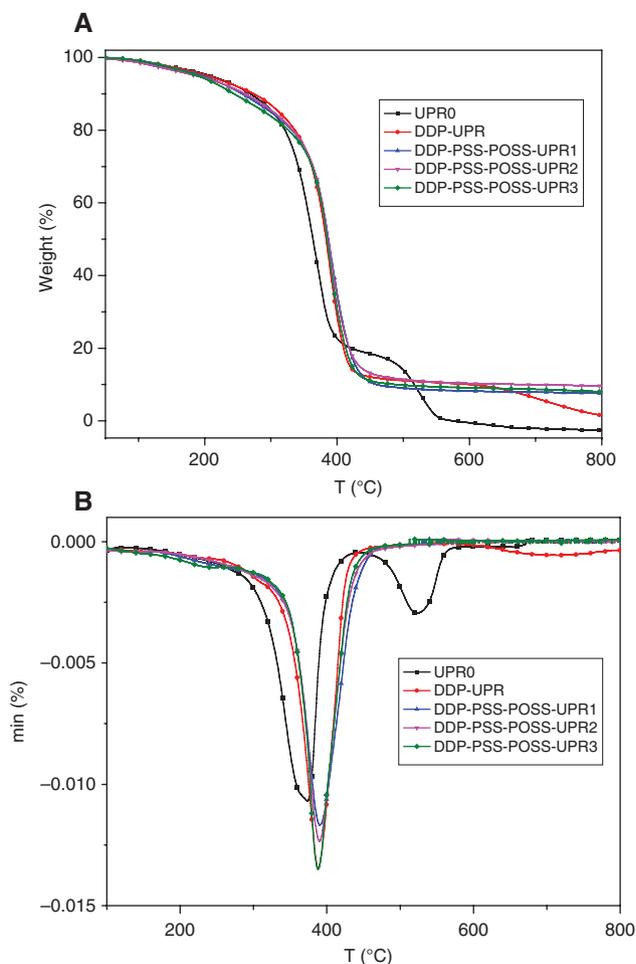


Figure 5: TGA (A) and DTG (B) curves of UPR0, DDP-UPR and DDP-PSS-POSS-UPR series.

and DDP-PSS-POSS-UPR series trend to be flat after the first decomposition. In addition, it can be found that T_5 decreases with the incorporation of PSS-POSS and DDP in

Table 3: TGA and DTG data of UPR0, DDP-UPR and DPP-PSS-POSS-UPR series.

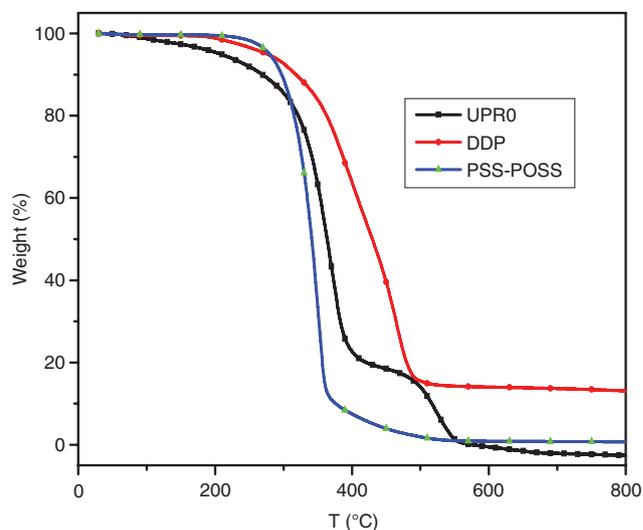
Samples	TG	DTG	Char yield at 750°C/%
	T ₅ (°C)	T _{max} (°C)	
UPR0	207	373	0.22
DDP-UPR	203	388	3.53
DPP-PSS-POSS-UPR1	195	390	7.75
DPP-PSS-POSS-UPR2	186	390	9.78
DPP-PSS-POSS-UPR3	188	388	8.90

Table 3. This is because the bond P-C in the DDP-UPR and DDP-PSS-POSS-UPR series has lower bond energy, which cracked easily during heating (23). Moreover, the inorganic core of PSS-POSS which connected to the side chain of UPR molecular has a bulky volume that easily forms space steric hindrance during chemical reactions with DDP. This resulted in producing many oligomers, which are also prone to decompose at the beginning of heating. In Figure 5A, the TGA curve of DDP-UPR is obviously above the UPR0 curve between 300°C and 400°C, and T_{max} of DDP-UPR is higher than that of UPR0. These consequences illustrate the thermal stability of DDP-UPR is significantly improved compared with UPR0. Figure 6 shows the TGA curves of UPR0, DDP and PSS-POSS, it can be seen that the thermal stability of UPR0 is lower than that of DDP and PSS-POSS before 300°C, and after 300°C, DDP gets higher thermal stability than UPR0 and PSS-POSS. In conjunction of Figures 5 and 6, it can be inferred that DDP makes the major contribution to the improvement of high temperature thermal stability of UPR0. Therefore, due to the relatively poor thermal stability of PSS-POSS itself, the incorporation of PSS-POSS has little effect on the thermal stability of DDP-UPR.

3.3 Flammability analysis

The flammability was investigated by the LOI test and the vertical burning test. The results of LOI test and vertical burning tests are given on Table 4.

As listed in Table 4, the LOI value of DDP-UPR is 24%, which is higher than that of UPR0, indicating DDP has a small influence on the LOI of UPR. Meanwhile, we can figure out that the LOI values of DPP-PSS-POSS-UPR series are higher than that of DDP/UPR and increase slightly with the content of PSS-POSS. When the PSS-POSS content reaches 10 wt%, the LOI value is 26.4%, achieving the best flame retardance in DPP-PSS-POSS-UPR series. In addition, the vertical burning results exhibit that UPR0 and

**Figure 6:** The TGA curves of DDP, PSS-POSS and UPR0.**Table 4:** The flammability data of UPR0, DDP-UPR and DPP-PSS-POSS-UPR series.

Samples	LOI (%)	Vertical burning test		
		t ₁ + t ₂ (s)	Dripping	Rating
UPR0	22	>60	No	Burning
DDP-UPR	24	>60	No	Burning
DPP-PSS-POSS-UPR1	24.6	>60	No	Burning
DPP-PSS-POSS-UPR2	26.4	25.7	No	V-1
DPP-PSS-POSS-UPR3	26	28	No	V-1

t₁ + t₂, The average value of five test samples.

DDP-UPR do not achieve any rating, and DPP-PSS-POSS-UPR2 and DPP-PSS-POSS-UPR3 can achieve a V-1 rating. These mean that the PSS-POSS has flame-retardant efficiency on DDP-UPR. Considering of the flame retardance mechanism of PSS-POSS, it was reported that the decomposition products of DPP-PSS-POSS-UPR series have a silica-like structure (24). The structure has poor thermal conductivity that can act as a heat transfer barrier, restricting the flammability (25). Moreover, DDP and PSS-POSS can promote the formation of the char yield as shown in Table 3. The aggregation of the char yield behaves with good thermal insulation properties and limits the production of combustible gases (26), it also benefits the enhancement of flame retardance.

3.4 Morphology of char layer

Figure 7 shows the SEM images of the char layers of UPR0, DDP-UPR and DPP-PSS-POSS-UPR2 after the vertical

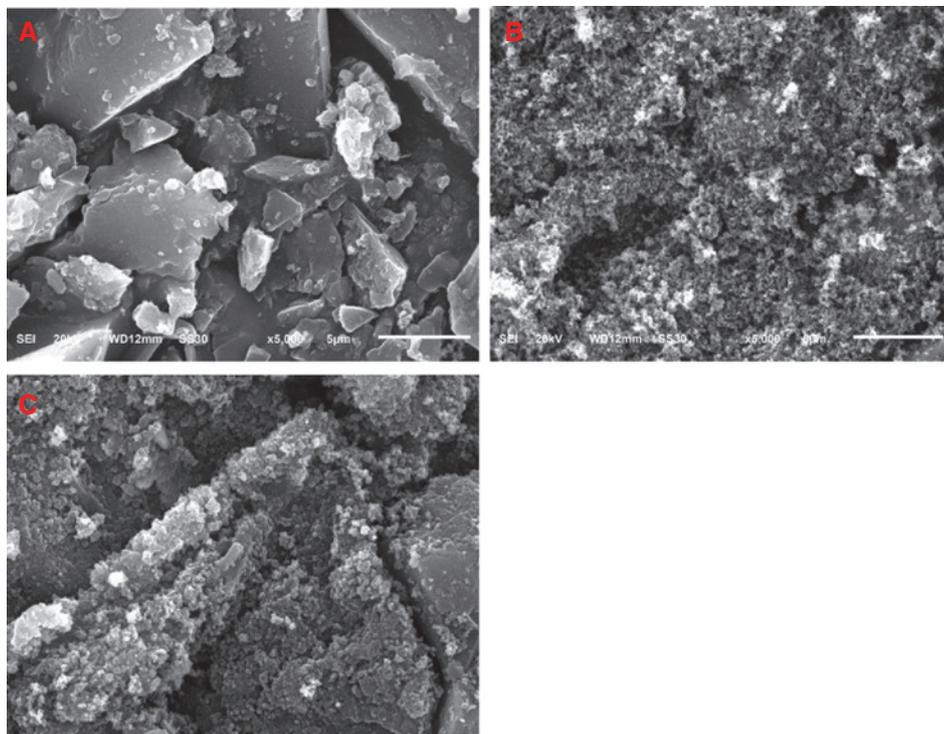


Figure 7: The SEM photos of residual char after the vertical burning test: UPR0 (A); DDP-UPR (B); DDP-PSS-POSS-UPR2 (C) (magnification $\times 5000$; scale bar: $5\ \mu\text{m}$).

burning test. A loose and nubby char layer with lots of large holes distributed on the surface could be observed in the UPR0 (Figure 7A), and the surface of the char layer shows no expansion. On the contrary, the char layer of the Figure 7B and C exhibit much more compact and continuous morphology with a spot of cracks on the surface and both have expansion. This expansion structure hinders the gas diffusion and heat transfer, resulting in the good flame-retardant property of the DDP-UPR and DDP-PSS-POSS-UPR series (27).

4 Conclusion

Unsaturated polyester resins (UPR) modified with DDP and PSS-POSS were successfully synthesized by the method of melt condensation. The incorporation of DDP increases the thermal stability of DDP-UPR in 300°C – 400°C , but the influence of PSS-POSS on the enhancement of thermal stability in the DDP-PSS-POSS-UPR series is not obvious. When the PSS-POSS content reached 10 wt%, the DPP-PSS-POSS-UPR series show excellent flame retardance. Besides, the char yield rises from 3.53% to 9.78% with the increased content of PSS-POSS at 750°C , inferring an improvement of thermo-oxidation retardance. A dense protective char layer was observed in the DDP-PSS-POSS-UPR2 residual

char from SEM, and this is in agreement with good flame-retardant performance in the vertical burning test.

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References

1. Wan C, Zhao F, Bao X, Kandasubramanian B, Duggan M. Effect of POSS on crystalline transitions and physical properties of polyamide 12. *J Polym Sci Part B Polym Phys*. 2009;47:121–9.
2. Balanuca B, Lungu A, Hanganu AM, Stan LR, Vasile E, Iovu H. Hybrid nanocomposites based on POSS and networks of methacrylated camelina oil and various PEG derivatives. *Eur J Lipid Sci Technol*. 2014;116(4):458–69.
3. Spoljaric S, Shanks RA. Novel polyhedral oligomeric silsesquioxane-substituted dendritic polyester tougheners for linear thermoplastic polyurethane. *J Appl Polym Sci*. 2012;126(S2):E440–54.
4. Gnanasekaran D, Ajit WP, Reddy BSR. Influence of moieties on morphology, thermal, and dielectric properties in polyamide-polyhedral oligomeric silsesquioxanes nanocomposites. *Polym Eng Sci*. 2013;53(8):1637–44.
5. Li S, Simon GP, Matison JG. The effect of incorporation of POSS units on polymer blend compatibility. *J Appl Polym Sci*. 2010;115(2):1153–9.
6. Mouritz AP, Mathys Z. Post-fire mechanical properties of marine polymer composites. *Compos Struct*. 1999;47(1):643–53.

7. Lou X, Detrembleur C, Lecomte P, Jérôme R. Novel unsaturated ϵ -caprolactone polymerizable by ring-opening metathesis mechanisms. *e-Polymers* 2002;2(1):1–12.
8. Chiu YC, Tsai HC, Imae T. Thermal degradation analysis of the isocyanate polyhedral oligomeric silsesquioxanes (POSS)/sulfone epoxy nanocomposite. *J Appl Polym Sci.* 2012;124(2):1234–40.
9. Fina A, Tabuani D, Frache A, Camino G. Polypropylene-polyhedral oligomeric silsesquioxanes (POSS) nanocomposites. *Polymer* 2005;46(19):7855–66.
10. Sirin H, Kodal M, Ozkoc G. The influence of POSS type on the properties of PLA. *Polym Compos.* 2016;22(5):107–15.
11. Wu F, Xie T, Yang G. Characterization of PBT/POSS nanocomposites prepared by in situ polymerization of cyclic poly(butylene terephthalate) initiated by functionalized POSS. *Polym Sci Part B Polym Phys.* 2010;48(16):1853–9.
12. Zhang W, Li X, Yang R. Flame retardant mechanisms of phosphorus-containing polyhedral oligomeric silsesquioxane (DOPO-POSS) in polycarbonate composites. *J Appl Polym Sci.* 2012;124(3):1848–57.
13. Zhang Z, Liang G, Wang X. Epoxy-functionalized polyhedral oligomeric silsesquioxane/cyanate ester resin organic-inorganic hybrids with enhanced mechanical and thermal properties. *Polym Int.* 2014;63(3):552–9.
14. Chiu YC, Chou IC, Tsai HC, Riang L, Ma CCM. Morphology, thermal and mechanical properties of the polyhedral oligomeric silsesquioxane side-chain epoxy hybrid material. *J Appl Polym Sci.* 2010;118(6):3723–32.
15. Matynia T, Worzakowska M, Tarnawski W. Synthesis of unsaturated polyesters of increased solubility in styrene. *J Appl Polym Sci.* 2006;101(5):3143–50.
16. Ramis X, Salla JM. Effect of the initiator content and temperature on the curing of an unsaturated polyester resin. *Polym Sci Part B Polym Phys.* 1999;37(8):751–68.
17. Zhang C, Huang JY, Liu SM, Zhao JQ. The synthesis and properties of a reactive flame-retardant unsaturated polyester resin from a phosphorus-containing diacid. *Polym Adv Technol.* 2011;22(12):1768–77.
18. Wang LS, Kang HB, Wang SB, Liu Y, Wang R. Solubilities, thermostabilities and flame retardance behaviour of phosphorus-containing flame retardants and copolymers. *Fluid Phase Equilib.* 2007;258(2):99–107.
19. Asaad JN. Synthesis and characterization of unsaturated polyester/carborundum composites. *J Appl Polym Sci.* 2013;129(4):1812–9.
20. Wazarkar K, Kathalewar M, Sabnis A. Flammability behavior of unsaturated polyesters modified with novel phosphorus-containing flame retardants. *Polym Compos.* 2015. DOI: 10.1002/pc.23716.
21. Gu H, Guo J, He Q, Tadakamalla S, Zhang X, Yan X, et al. Flame-retardant epoxy resin nanocomposites reinforced with polyaniline-stabilized silica nanoparticles. *Ind Eng Chem Res.* 2013;52(23):7718–28.
22. Wurm A, Schick C. Development of thermal stability of polymer crystals during isothermal crystallization [J]. *e-Polymers* 2016;24(1):1–15.
23. Meenakshi KS, Sudhan EPJ, Kumar SA, Umopathy MJ. Development and characterization of novel DOPO based phosphorus tetraglycidyl epoxy nanocomposites for aerospace applications. *Prog Org Coat.* 2011;72(3):402–9.
24. Bai Z, Song L, Hu Y, Gong X, Yuen RKK. Investigation on flame retardance, combustion and pyrolysis behavior of flame retarded unsaturated polyester resin with a star-shaped phosphorus-containing compound. *Anal Appl Pyrolys.* 2013;105(1):317–26.
25. Toldy A, Tóth N, Anna P, Keglevich G, Kiss K, Marosi G. Flame retardance of epoxy resin with phosphorus-containing reactive amine and clay minerals. *Polym Adv Technol.* 2006; 17(9–10):778–81.
26. Schäfer A, Seibold S, Lohstroh W, Walter O, Döring M. Synthesis and properties of flame-retardant epoxy resins based on DOPO and one of its analog DPPO. *J Appl Polym Sci.* 2007;105(2):685–96.
27. Wu K, Kandola BK, Kandare E, Hu Y. Flame retardant effect of polyhedral oligomeric silsesquioxane and triglycidyl isocyanurate on glass fibre-reinforced epoxy composites. *Polym Compos.* 2011;32(3):378–89.