



Flame retardancy of linear polyurethane with Diels–Alder adducts

Mingxin Cai¹ · Zeying Tian¹ · Liang Cui² · Tianxiang Fan¹ · Pengfei Du^{1,3} 

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Abstract

Flame retardant polyurethane was synthesized via introducing thermally reversible covalent Diels–Alder (DA) adducts into the polyurethane main chain. Firstly, furan-terminated polyurethane prepolymer (PU-Furan) was synthesized from the reaction between isocyanate-terminated prepolymer with or without DOPO-based polyester polyols and furfuryl amine. Secondly, polyurethane with DA adducts (PU-DA) was obtained via Diels–Alder reaction between PU-Furan and commercial 1,1'-(methylenedi-1,4-phenylene) bismaleimide. PU-Furan and PU-DA were characterized by DSC, TGA and ¹H NMR, confirming the introduction of the DA adducts into the polyurethane chain. The results of the limiting oxygen index test, Underwriter Laboratory 94 vertical burning (UL-94) test and cone calorimeter test demonstrated that the introduction of the DA adducts improved the flame retardancy of the polyurethane significantly, especially when the polyurethane with flame-retardant element P, due to the synergism flame-resistant effect between flame-retardant element P and thermally reversible DA adducts.

Keywords Diels–Alder adducts · Flame retardancy · Polyurethane · DOPO-polyester polyols

Introduction

Polyurethanes are characterized by the presence of the urethane groups (–NHCOO–) or urea groups (NH–CONH) from three basic components: polyisocyanates, polyols and low molecular weight bifunctional chain extender.

✉ Pengfei Du
24080430@qq.com

¹ Quangang Petrochemical Research Institute, Fujian Normal University, Quanzhou 362807, China

² PetroChina KunLun Lubricant Qualification Test Center, Lanzhou 730060, China

³ Fujian Key Laboratory of Pollution Control and Resource Reuse, Fuzhou 350007, China

Polyurethanes are widely applied in a variety of industries, due to their excellent mechanical properties, abrasion resistance, adhesion, chemical resistance and low temperature resistance [1].

However, the major disadvantage of polyurethane is poor fire performance due to high content of C, H and O. Much effort has been devoted to assessing and reducing their fire hazard. Extraordinary diverse methods were used to enhance the flame retardancy of the polyurethane. (1) Flame retardant additive blended into the polyurethanes [2, 3] or heat-resistant materials coated onto polyurethane surfaces [4, 5]; additive flame retardant was intimately blended into the polyurethane during processing, but did not chemically react with polyurethane; (2) retardant segment or heat-intumescence became integrated into the polyurethane network structure via chemical modification during the synthesizing process [6, 7]. Among the flame-retardant elements used in polyurethane, phosphorus is ideal flame-quenching ingredients and desirable radical scavengers during the combustion [8, 9]. Phosphorus-containing flame retardants can act either in the vapor phase by a radical mechanism to interrupt the exothermic processes and suppress combustion or in the condensed phase to change the degradation path in which more char is produced and less volatiles are released [9]. The nitrogen-containing flame retardant can convert into an inert gaseous by-product and help form dense char. Based on this, many research was focused on P–N synergistic flame retardant and the final polymer exhibited excellent flame-retardant efficiency [10–12].

Diels–Alder (DA) reaction is a [4+2] cycloaddition between diene and dienophile. DA reaction between furan and maleimide is much more popular in synthesizing thermally reversible polymers due to the more electron-insufficient C=C bond [13, 14]. Based on the thermally reversibility of the furan/maleimide DA reaction, many precursor studies expanded its application to the field of polymer materials, such as self-healing materials [15–17], recyclable materials [18], 3D printing materials [19], hot-melt adhesive [20]. Du zongliang et al. [8, 21] designed a self-healing, mechanically enhanced, recyclable, and flame-retardant polyurethane system based on reversible DA/retro-DA reactions and cyclotriphosphazene derivatives. The LOI increased from 18.3 to 26.3% due to the introduction of the DA adducts and cyclotriphosphazene derivatives, indicating that the reversible DA adducts benefit the flame retardancy.

To further enhance the flame retardancy of the polyurethane with DA adducts, linear polyurethane was synthesized via introducing thermally reversible covalent Diels–Alder adducts into the polyurethane main chain with(PU-DA) or without DOPO polyester polyols(DOPO-PU-DA). Upon heating, the DA adducts returned back to furan-terminated polyurethane prepolymer and 1,1'-(methylenedi-1,4-phenylene) bismaleimide and this took away partial heat generating in the combustion. Meanwhile, the linear polyurethane drips easily during the combustion and will take away another partial heat generated in combustion. Finally, the introduction of the DOPO polyester polyols enhanced the flame retardancy of the soft segment, which will exhibit synergism flame-resistant effect on the hard segment (DA adducts) during the combustion process. This paper will provide a new way to prepare flame-retardant polyurethane via introducing thermally reversible bonds into the polyurethane.

Experimental

Materials

Furfuryl amine (99%,AR.) and 1,1'-(methylenedi-1,4-phenylene) bismaleimide (BMI,95%,AR.) were purchased from Adamas and used as received; Toluene-2,4-diisocyanate (TDI, CP.) was purchased from Bayer and used as received; DOPO-polyester polyols (Mn=770) were synthesized in our laboratory [7].

Polyether polyol (DL-2000D, Mn=2000,CP.) and 1,4-butanediol (BDO, 98%,CP.) were supplied by Shandong Bluestar Dongda Chemical Co., Ltd., and were used after 2 h drying under vacuum at 100 °C; *N,N*-Dimethylformamide (DMF,AR.) was purchased from China National Medicines and was used after dried with CaH₂ and purified by vacuum distillation.

Synthesis of PU-DA

TDI (17.4 g, 100 mmol) reacted with DL-2000D (100.0 g, 50.0 mmol) using 120 ml DMF as solvent at 60 °C under nitrogen atmosphere in a 500 ml three-necked round bottom flask, equipped with mechanical stirrer. Three hours later, furfuryl amine (8.0 g 80 mmol) dissolved in 8 ml DMF was added dropwise into the solution at room temperature. Three hours later, the solution was heated to 60 °C and kept for 30 min to make sure that all the isocyanate be consumed by furfuryl amine. Then, BMI (14.4 g, 40 mmol) dissolved in 20 ml DMF was added into the solution. One hour later, the whole solution was poured onto a PTFE plate and was put in a 60 °C oven for about 24 h to remove DMF. Finally, a polymer film (132 g) was obtained as final product (PU-DA). Yield: 94.3%.

Synthesis of DOPO-PU-DA

TDI (17.4 g, 100 mmol) reacted with DL-2000D (75 g, 37.5 mmol) and DOPO-polyester polyol (10.00 g, 13.0 mmol) using 105 ml DMF as solvent at 60 °C under nitrogen atmosphere in a 500 ml three-necked round bottom flask, equipped with mechanical stirrer. Three hours later, furfuryl amine (8.0 g 80 mmol) dissolved in 8 ml DMF was added dropwise into the solution at room temperature. Three hours later, the solution was heated to 60 °C for about 30 min to make sure that all the isocyanate be consumed by furfuryl amine. Then, BMI (14.4 g, 40 mmol) dissolved in 20 ml DMF was added into the solution. One hour later, the whole solution was poured onto a PTFE plate and was put in a 60 °C oven for about 24 h to remove DMF. Finally, a polymer film (116 g) was obtained as final product (DOPO-PU-DA). Yield: 93.0%.

Characterization

¹H NMR spectroscopy was performed on an Avance-400 spectrometer (Bruker, Switzerland) with deuterated DMSO d-6 as solvent at 25 °C. ATI-FTIR was

performed on a Paragon 1000 spectrometer (PerkinElmer). FTIR spectra were recorded in the range of 4000–400 cm^{-1} .

DSC data were obtained from -60 to 160 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under nitrogen flow (TA Instruments Q2000). Thermogravimetric analysis (TGA) of polyurethane with DA adducts was performed on a TGA instrument Q5000IR (TA) at a heating rate of 20 $^{\circ}\text{C}/\text{min}$ in N_2 atmosphere from room temperature to 800 $^{\circ}\text{C}$. The tensile properties of polyurethane with DA adducts were measured on Instron 4465 testing machine (Instron Corp., the USA). The elongation rate was set to be 50 mm/min . The specimens were dumbbell-like with the size of $20 \times 4 \times 0.4 - 1$ mm .

LOI tests of polyurethane with DA adducts were performed on limit oxygen index meter (JF-3, Nanjing Jiangning Analytical Instrument Co., Ltd.). Underwriter Laboratory 94 vertical burning test (UL-94 V) was performed on horizontal and vertical combustion meter (CZF-3, Nanjing Jiangning Analytical Instrument Co., Ltd.). The two specimens ($125 \times 13 \times 0.9 - 1.0$ mm) for tests were both prepared from cutting the polymer films via surgical blade. Cone calorimeter test (FTT Limited, the UK) was employed to investigate the fire performance of polyurethane with DA adducts according to the standard of ASTM E1354-17. Every specimen ($100 \times 100 \times 1.0$ mm) was exposed horizontally under a heat flux of 35 kW/m^2 . The residual char after the cone calorimeter test was observed under magellan 400 scanning electron microscope (FEI, the USA). FTIR was performed on a Paragon 1000 spectrometer (PerkinElmer). FTIR spectra were recorded in the range of 4000–400 cm^{-1} .

Results and discussion

Polyurethanes with Diels–Alder (DA) adducts (with or without DOPO-polyester polyols) were synthesized via the procedure in Fig. 1. Comparing with MDI or polymeric MDI as reactants [22], TDI can react with furfuryl amine at room temperature to synthesize isocyanate terminated polyurethane prepolymer due to the less reactivity of the second isocyanate. The polyurethane with DOPO-polyester polyols (DOPO-PU-DA) exhibited similar phenomenon as the polyurethane PU-DA.

The structure of PU-Furan was firstly investigated via ^1H NMR, as shown in Fig. 2. The peaks of the 8.4 and 6.8 ppm attributed to the H in urea confirmed the reaction between isocyanate and furfuryl amine (f, e). The peaks of the 6.3, 6.4, 7.5 and 4.3 ppm also confirmed the presence of furan groups (b, c, a, d) in PU-Furan. The peak at 9.5 ppm (g) was ascribed to urethane hydrogen. The broad peaks at 7.4, 7.0 ppm were ascribed to the hard segment (TDI), while the peaks at 2.1 and 3.5, 1.0 ppm were ascribed to soft segments (polyepoxypropane segment), respectively. The peaks at 2.5 and 3.3 ppm were ascribed to the DMSO- d_6 , while the peaks at 7.9, 2.7 and 2.9 ppm were ascribed to the solvent DMF.

All of these peaks confirmed the structure of the furan terminated polyurethane prepolymer. Comparing with PU-Furan, PU-DA exhibited the characterized peaks of the DA bonds as shown in Fig. 1a'–c', h', i'. Meanwhile, the DA reaction between PU-Furan and BMI was also confirmed by the decreasing of the characterized peak (7.5 ppm) attributed to furan ring (a).

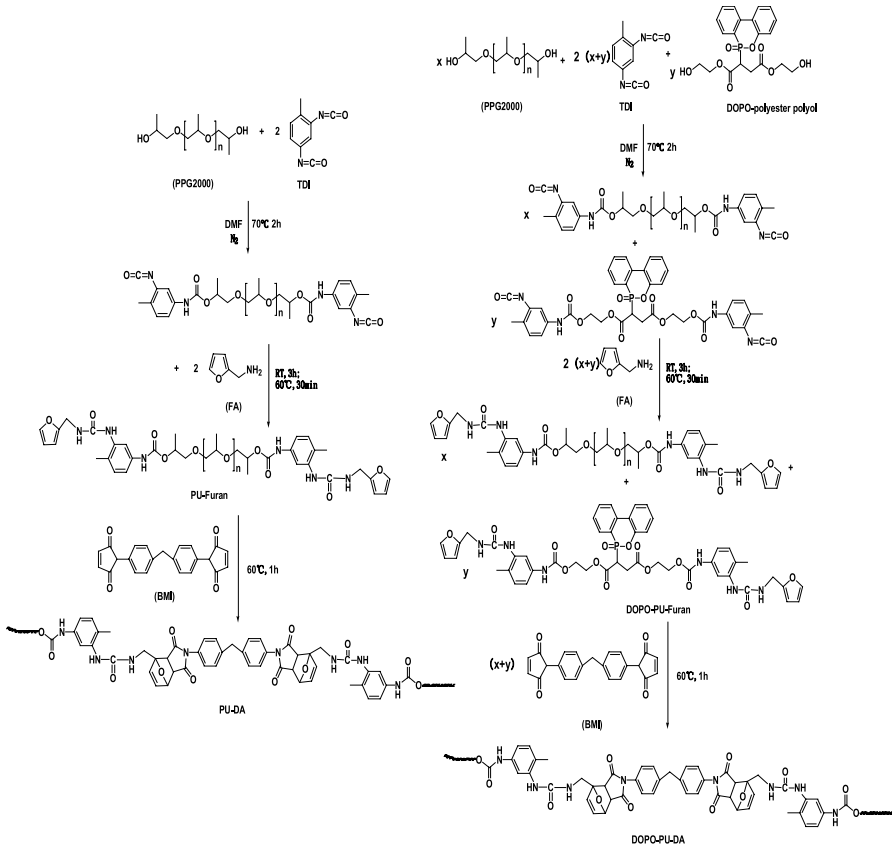


Fig. 1 Synthesis scheme of linear flame retardant polyurethane with and without DOPO-polyester polyols

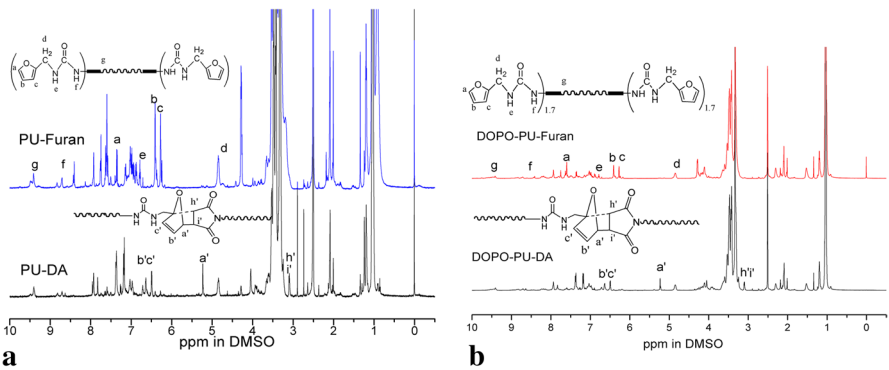


Fig. 2 **a** ¹H NMR of PU-Furan and PU-DA; **b** ¹H NMR of DOPO-PU-Furan and DOPO-PU-DA

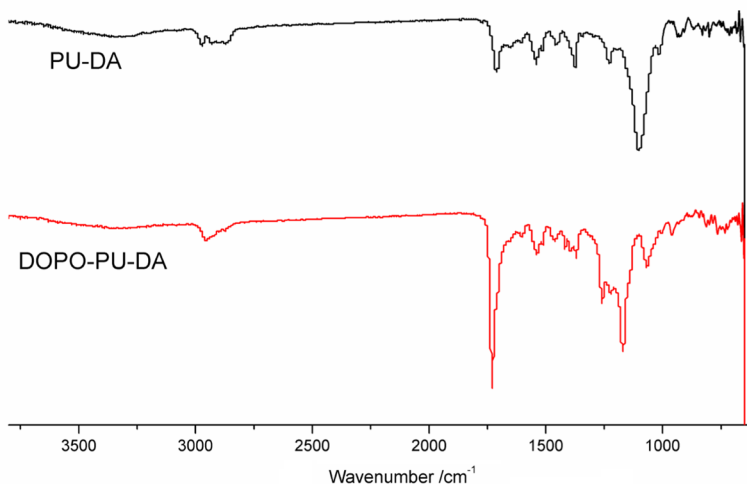


Fig. 3 ATI-FTIR spectra of PU-DA and DOPO-PU-DA

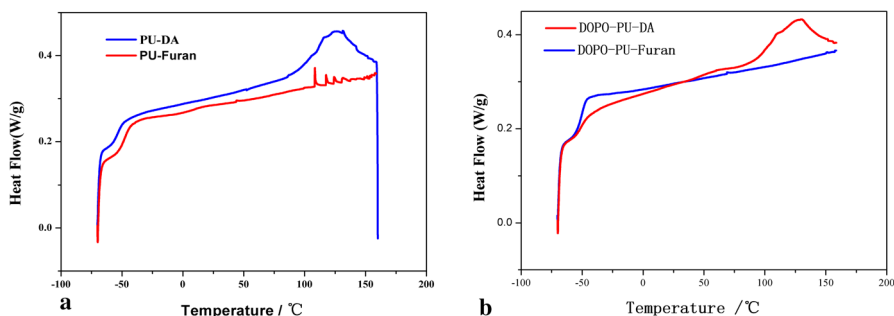


Fig. 4 **a** DSC curves of PU-Furan and PU-DA; **b** DSC curves of DOPO-PU-Furan and DOPO-PU-DA

The DOPO-PU-Furan and DOPO-PU-DA also exhibited similar characterized peaks, as well as the characterized peaks of DOPO segment at 8.2 ppm, as shown in Fig. 2b. This confirmed the introduction of the DOPO polyester polyols segment in DOPO-PU-Furan and DOPO-PU-DA.

ATI-FTIR spectra of PU-DA and DOPO-PU-DA (Fig. 3) confirmed the ^1H NMR results. The absence of 2270 cm^{-1} confirmed that the isocyanate groups were all consumed by the furfuryl amine.

Compared with PU-DA, DOPO-PU-DA exhibits much more strong C=O extensional vibration peak of ester groups at 1730 cm^{-1} and much more strong C–O extensional vibration peak of ester groups at 1258 cm^{-1} . Meanwhile, the P–O–C extensional vibration peak at 1067 cm^{-1} also confirmed the successful introduction of DOPO polyester polyols in the DOPO-PU-DA.

The thermal properties of PU-DA and DOPO-PU-DA were investigated via DSC and TGA. As shown in DSC curves (Fig. 4), they both exhibited significant

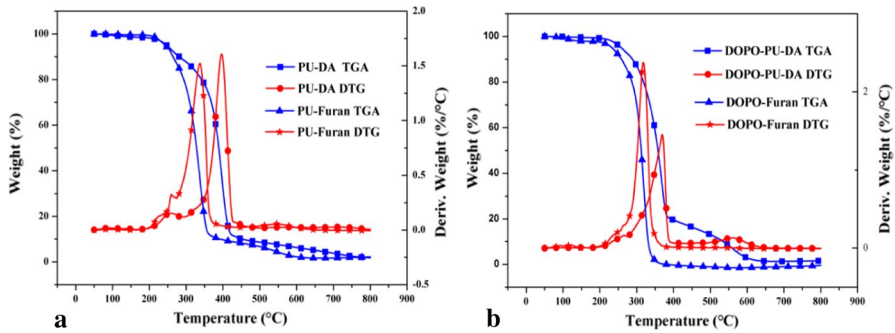


Fig. 5 a TGA of PU-Furan and PU-DA; b TGA of DOPO-PU-Furan and DOPO-PU-DA

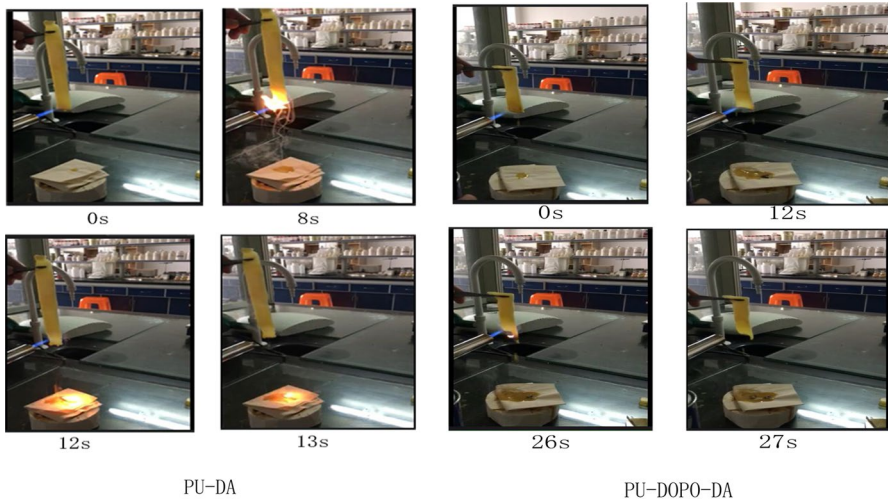


Fig. 6 Pictures taken during the combustion process of PU-DA and DOPO-PU-DA

endothermic peak at around 120 °C, while their intermediates did not. The significant endothermic peaks at around 120 °C of the two polyurethane with DA adducts can be explained by the retro DA reaction, confirming the presence of the DA bonds.

From the TGA curves in Fig. 5, PU-DA and DOPO-PU-DA both exhibited a significant higher amount of char residue than their intermediates, indicating the successful introduction of cross-linker BMI. Meanwhile, they also exhibited slower weight loss after 250 °C than their intermediates as shown in Fig. 4, indicating higher thermal stability after cross-linking with BMI.

Flame retardancy of linear polyurethane with DA adducts

Flame retardancy of linear polyurethanes with DA adducts was firstly investigated by burning the polyurethane samples with butane lance. As shown in Fig. 6(left),

the flame of PU-DA spread up very slowly after being ignited by the butane lance and droplet generated immediately due to the retro-DA reaction and the lower melting point of the intermediate. The retro-DA reaction and melting of the polyurethane took away partial heat of the combustion process and consequently improved the flame retardancy of PU-DA. However, the droplet of the PU-DA ignited the inflammable paper towel in 12 s, indicating that the introduction of the DA adducts could not meet the flame retardancy standard during the real life. As for the polyurethane with both DA adducts and DOPO-polyester polyols, DOPO-PU-DA exhibited similar phenomenon except of igniting the inflammable paper towel (even after 27 s combustion) as shown in Fig. 5 (right). Conclusions can be made that the DA adducts and flame-retardant element P both played important role in improving the flame retardancy of the linear polyurethane.

Flame retardancy of linear polyurethane with DA adducts was secondly investigated by LOI test and UL-94 test. The results of the LOI test and UL-94 test as well as the mechanical properties are listed in Table 1. The LOI value of PU-DA (28.5%) was much higher than the traditional polyurethane without DA adducts(20.0) [7]. After being ignited during the LOI tests and UL-94 tests, the DA adducts in PU-DA returned back to PU-Furan and BMI. Droplets generated immediately due to that the lower molecular of the PU-Furan. These were the main reasons that PU-DA exhibited much higher LOI values than the traditional polyurethanes. However, PU-DA was classified as “V-1” during the UL-94 test, because the droplet of PU-DA can ignite the inflammable cotton during the UL-94 test, same as Fig. 5. As for the polyurethane with both DA adducts and DOPO-polyester polyols, DOPO-PU-DA was classified as “V-0” during the UL-94 test. (The detailed combustion time is listed in Table S1.) DOPO-PU-DA also exhibited higher LOI value (30.0%) than PU-DA. Conclusions can be made that the introduction of retardant element P prevented the droplet from igniting the inflammable cotton during the UL-94 tests. Conclusions can be also made that the DA adducts and the retardant element P played synergism flame-resistant effect on DOPO-PU-DA.

Consequently, the flame retardancy of polyurethanes with DA adducts was evaluated by cone calorimeter test which reflects real combustion situation. The testing details of the samples and the results of the cone calorimeter test are listed in Table 2.

As shown in Fig. 7a, b, the peak heat release rate (HRR) and total heat release (THR) of DOPO-PU-DA decreased 28.4% and 16.3% comparing with the PU-DA without retardant element P. This confirmed that retro DA reaction and droplet generation took away partial heat from the polyurethane during the combustion. This result indicated that DA adducts and the retardant element P played synergism

Table 1 The flame retardancy and mechanical property of polyurethane with DA adducts

Samples	UL94 rating	LOI (%)	Tensile strength (MPa)	Elongation at break (%)
PU-DA	V-1	28.5	3.3	1066
DOPO-PU-DA	V-0	30.0	4.7	767.4

Table 2 The testing details of the sample and the results of the cone calorimeter test

Samples	Thickness (cm)	Mass loss (%)	SEA (m^2/kg)	PHRR (Kw/m^2)	THR (MJ/m^2)	TTI (s)	TSP (m^2)	av-EHC MJ/kg
PU-DA	1.0	91.5	1280.7	470.2	41.7	26	2.45	13.9
DOPO-PU-DA	1.0	92.5	600.4	336.5	34.9	23	3.10	11.7

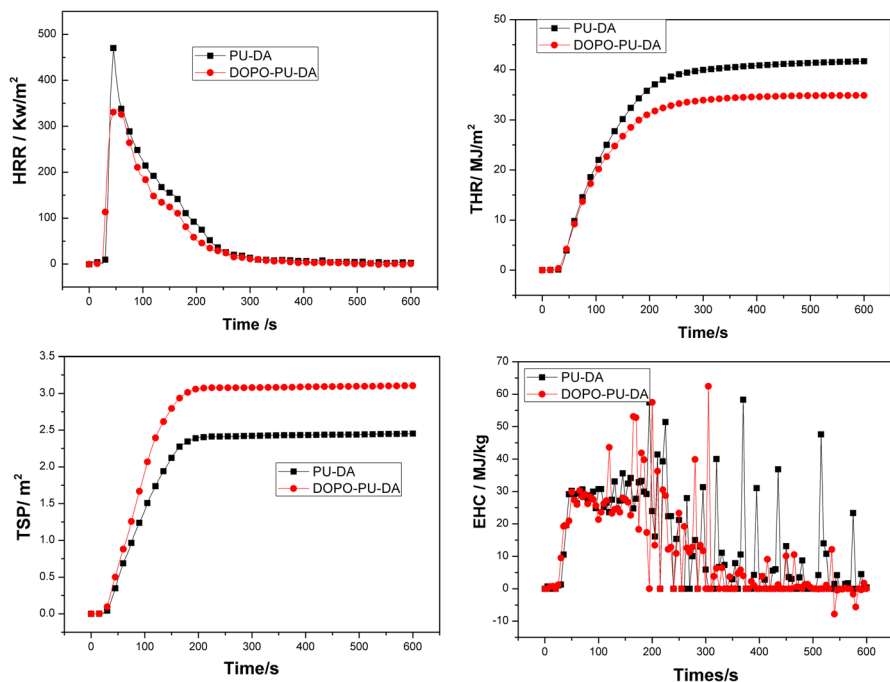


Fig. 7 HRR, THR and TSP curves of PU-DA and DOPO-PU-DA

flame-resistant effect on DOPO-PU-DA. The total smoke production TSP values of DOPO-PU-DA were 26.5% higher than PU-DA without DOPO polyester polyols, as shown in Fig. 7c. This could be explained by that the benzene ring in DOPO polyester polyols changed into graphitized carbon particles during the combustion via polycondensation reaction. Meanwhile, the introduction of the DOPO polyester polyols was beneficial to form dense carbon layer during combustion. DOPO-PU-DA exhibited similar effective heat of combustion (EHC) curves as PU-DA in Fig. 7d, indicating condensed phase flame retardancy during the combustion.

The morphology of the polyurethane samples after the cone calorimeter test was observed via digital pictures and SEM as shown in Fig. 8. From the pictures obtained from the SEM (at 100 μm or 20 μm) or the digital picture, DOPO-PU-DA exhibited dense residual char without any obvious micro-holes except several cracks. While PU-DA exhibited much looser residual char full of continuous micro-holes. The DOPO segment fractured into viscous phosphoric acid, metaphosphoric acid and polyphosphoric acid, which did good to form dense residual char and increase the residual char amount during the combustion process. Conclusions can be made that the introduction of the retardant element P improved the flame retardancy via generating dense char layers during the combustion process.

The residual char after cone calorimeter test was also investigated via FTIR, as shown in Fig. 9. The disappearance of the peaks at 2915 cm^{-1} and 1718 cm^{-1} indicated that the CH_2 groups and $\text{C}=\text{O}$ groups disappeared during the cone calorimeter

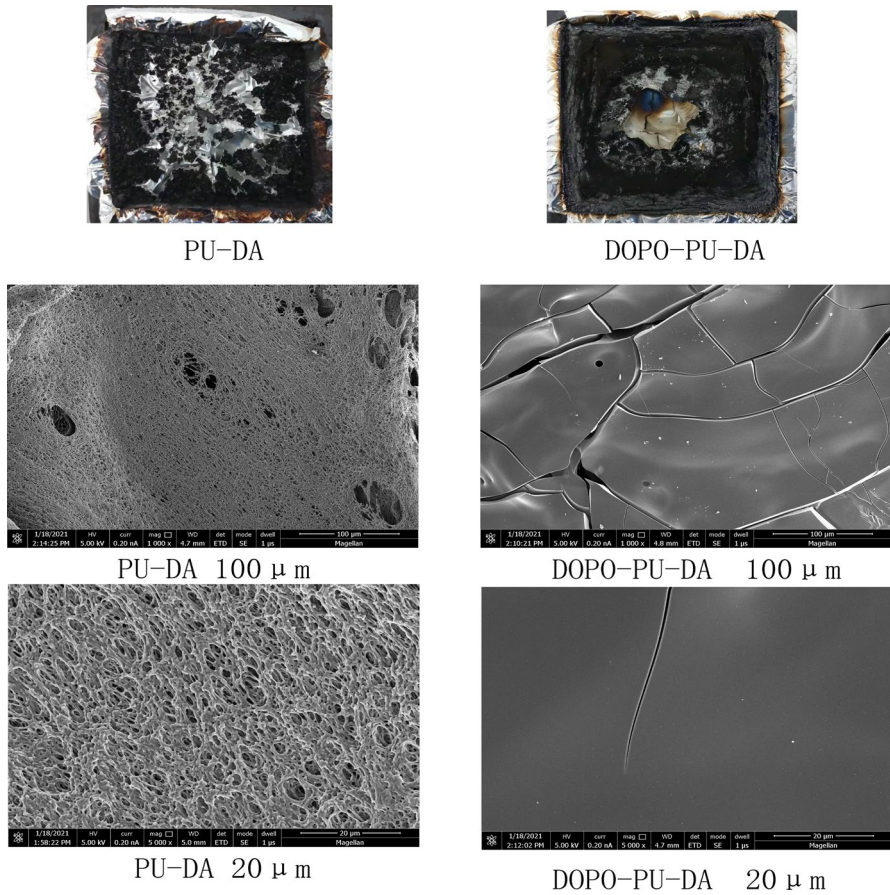


Fig. 8 Digital pictures and SEM images of PU-DA and DOPO-PU-DA after cone calorimeter test

test. As for DOPO-PU-DA, the characterized peak at 1085 confirmed the presence of P–O–C groups in the residual char [23].

All the above results confirmed that the two linear polyurethane with DA adducts (PU-DA and DOPO-PU-DA) exhibited good flame retardancy.

Conclusions

Flame-retardant polyurethane was synthesized via introducing thermally reversible covalent Diels–Alder adducts into the polyurethane main chain with (DOPO-PU-DA) or without DOPO polyester polyols (PU-DA), confirmed by the DSC, TGA and ¹H NMR. The LOI value of PU-DA was 28.5%, much higher than the traditional polyurethanes due to that the retro DA reaction and droplet generation took away partial heat during the LOI tests. However, PU-DA was classified as “V-1” due

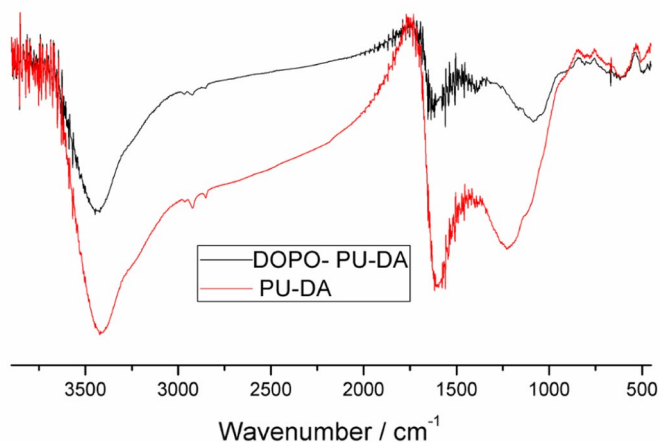


Fig. 9 FTIR spectra of residual char after cone calorimeter test

to the droplet of PU-DA can ignite the inflammable cotton during the UL-94 test. DOPO-PU-DA with both DA adducts and flame-retardant element P was classified as “V-0” during the UL-94 test and exhibited higher LOI value (30.0%) than PU-DA due to that the DOPO segment improved the flame retardancy via generating dense char layers during the combustion process. Conclusions can be made that the DA adducts and the DOPO segment played synergism flame-resistant effect on DOPO-PU-DA during the combustion process.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00289-022-04229-8>.

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