

# Synthesis and Characterization of Phosphorus-Containing Waterborne Polyurethanes: Effects of the Organophosphonate Content on the Flame Retardancy, Morphology, and Film Properties

He Chen, Yunjun Luo, Chunpeng Chai, Jiong Wang, Jie Li, Min Xia

School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China

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**ABSTRACT:** A series of waterborne polyurethanes (WPU) with different contents of reactive organophosphonate were well prepared. Their structures were characterized by Fourier transform infrared and  $^1\text{H-NMR}$  spectroscopy. Thermogravimetry and derivative thermogravimetry revealed that the WPU films containing phosphorus possessed lower onset and maximum degradation temperatures but higher char yields. Differential scanning calorimetry analysis suggested phase mixing of the hard and soft domains. The mechanical properties decreased with increasing amount of organophosphonate, whereas the limiting oxygen index results of the WPU films indi-

cate that the flame retardancy was improved significantly by the incorporation of organophosphonate. The water uptake values of the organophosphonate-containing WPU films were higher than those of the phosphorus-free ones, whereas the static contact angles of the films indicated that the surface hydrophilic properties were not affected by segmenting in this phosphorus-containing oligomer. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3107–3115, 2008

**Key words:** flame retardance; morphology; polyurethanes; thermal properties

## INTRODUCTION

The development of waterborne polyurethanes (WPU) is becoming more and more important for the continuous reduction in cost and the control of volatile organic compound emissions.<sup>1–3</sup> Compared with the conventional solvent polyurethane (SPU), WPU presents many advantages, such as environment friendliness, low viscosity at high molecular weight, and good applicability.<sup>2,4</sup> These outstanding properties of WPU and its controllable chemical compositions have led to increasing application areas for this kind of fascinating polymer.<sup>5</sup> The wide applications of WPU have consequently resulted in a desire for higher flame retardancy. Two approaches have been used to confer flame retardancy on the polymer system: the blending of flame-retardant compounds with the polymeric materials and the incorporation of reactive flame-retardant compounds into the polymers. The latter method has recently drawn much attention because of several drawbacks of the former,<sup>6–8</sup> such as the requirement of large amounts of flame-retardant compound, which may migrate toward the surface of the film after applica-

tion and lead to a deterioration in the film properties of the polymer.<sup>9–11</sup> Phosphorous compounds have been widely used as flame-retardant materials because of their high flame-retardant efficiency, lower production of corrosive and toxic gases in flames, and lower destruction to the earth's environment.<sup>12–17</sup> Huang et al.<sup>18</sup> introduced aziridinyl phosphazene into WPU as a flame retardant and a postcuring agent. The flame retardancy of the WPU films were enhanced, whereas their mechanical properties decreased significantly; the tensile strength and elongation at break dropped from 8.1 kg/cm<sup>2</sup> and 713% to 5.6 kg/cm<sup>2</sup> and 41.6%, respectively. Celebi et al.<sup>19</sup> synthesized flame-retardant WPU by incorporating bis(4-amino phenyl) phenyl phosphine oxide into the WPU structure in the chain-extension step. The limiting oxygen index (LOI) improved from 24 to 27%, and the content of this phosphorous compound was rather constrained because it behaved as hard segments and because of the existence of a rigid phenyl moiety, which consequently stiffened the PU films at high content ratios.

We previously prepared a dibromoneopentyl glycol modified WPU by a chain-extension step. The LOI was improved significantly when the content of dibromoneopentyl glycol reached 15%. However, the films became stiff, and the elongation at break dropped.<sup>20,21</sup> In this research, the phosphorus-

Correspondence to: Y. Luo (yjluo@bit.edu.cn).

containing polyol Exolit OP550 was chosen to segment into the WPU macromolecule because Exolit OP550 is a highly effective flame-retardant oligomer with a phosphorus content of 17%. In addition, Exolit OP550 can act as a soft segment in the WPU morphology, which means that the incorporation of Exolit OP550 would affect the flexibility of the films little. Furthermore, the content of Exolit OP550 in WPU macromolecules could be adjusted to a high ratio as a polyol component because its ratio of polyol is highest among all of the components of WPU. The aim of this study was to improve the flame retardancy of WPU and to investigate the effects of this kind of organophosphonate on the properties and morphology of modified WPU.

## EXPERIMENTAL

### Materials

Toluene diisocyanate was purchased from Shanghai Reagent Factory (Shanghai, China) and was used as received. Poly (propylene glycol) (PPG) with a molecular weight of 1000 was obtained from Tianjin Petrochemical Factory (Tianjin, China) and was dried *in vacuo* at 90°C for 2 h before use. Dimethylolpropionic acid (DMPA) was obtained from Ling Chemical Co. (Beijing, China) and was dried *in vacuo* at 85°C for 4 h before use. Triethylamine and methyl ethyl ketone (MEK) both were purchased from Vas Chemical Reagent Corp. (Beijing, China) and were used after they were stored over type 4-Å molecular sieves. Exolit OP550 was purchased from Clariant Chemical Co., and its hydroxyl number was 170 KOH mg/g. It was dried *in vacuo* at 90°C for 2 h before use.

### Preparation of the organophosphonate-containing WPUs

PPG, DMPA, and toluene diisocyanate were reacted in a 250 mL, four-necked flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, and condenser at 85°C for 0.5 h with 0.1 wt % catalyst (stannous octanoate); then, Exolit OP550 was added to the compound, and the mixture was reacted until the percentage of NCO was nearly the theoretic value. MEK was then added to the flask to adjust the viscosity of the prepolymer. The WPUs were prepared by the mixture of this prepolymer with an aqueous solution of triethylamine at a high shear rate. The final WPUs had a solid content of about 28% after MEK was distilled off. This synthesis process is shown in Scheme 1.

### Preparation of the test WPU films

The WPU films were cast and air-dried from a WPU dispersion on a polytetrafluoroethylene plate mold

at room temperature and then dried *in vacuo* at 75°C for 2 days. WPU films about 0.3 mm thick were finally obtained; during the whole process, no additives were used to favor the films' formation.

### Characterization

#### Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were obtained with a Nicolet (Boston, MA) 8700 FTIR spectrometer. We cast the prepolymer films on KBr discs.

#### <sup>1</sup>H-NMR

<sup>1</sup>H-NMR spectra were recorded on a Varian (Palo Alto, CA) Mercury-Plus 400 spectrometer, and dimethyl sulfoxide-*d*<sub>6</sub> was used as a solvent. The prepolymers were dissolved by dimethylformamide and deposited to remove unreacted monomers. The deposits were dried *in vacuo* at 75°C and then used for NMR testing.

#### Thermal analysis

Differential scanning calorimetry (DSC) measurements were performed on a DSC TA60 instrument (Shimadzu Corp., Kyoto, Japan). The weights of the films were about 10 mg, and the heating rate was set 10°C/min under a nitrogen atmosphere. Thermogravimetric analysis was performed on a Q50 V20.6 Build 31 thermogravimetric analyzer (Thermo-Fisher Scientific, Waltham, MA) at a heating rate of 10°C/min under a nitrogen atmosphere.

#### Transmission electron microscopy (TEM)

The WPU for TEM was diluted, dyed with phosphotungstic acid, and observed on a Hitachi (Japan) H-700 instrument.

#### Flame retardancy

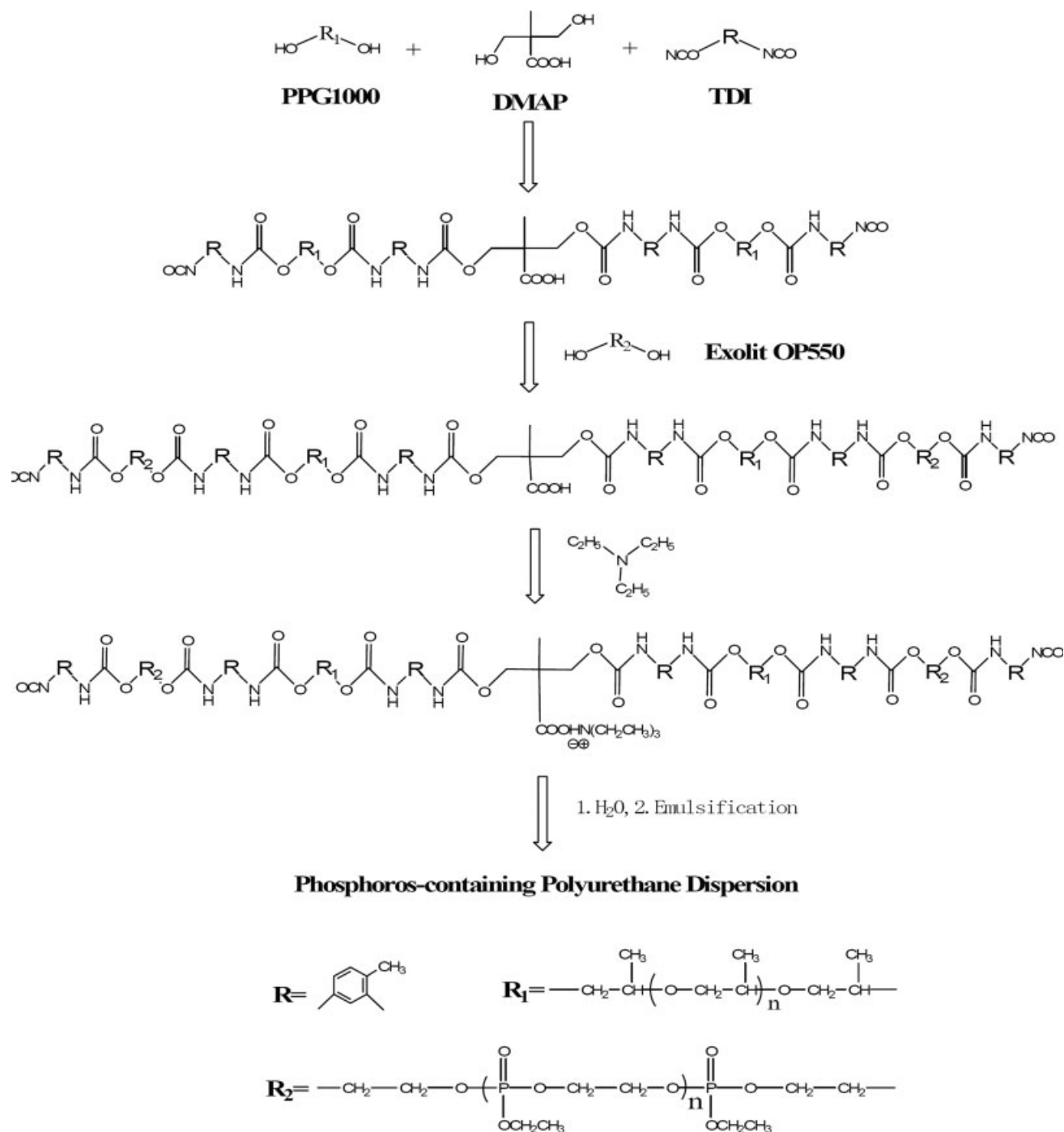
Flame retardancy was evaluated by LOI according to GB/T2406-93 testing procedures. LOI values were measured on a Stanton Redcroft (England) flame meter.

#### Mechanical testing

The mechanical properties were measured in tension mode with an AGS-J instrument (Shimadzu Corp) according to GB/1040-79 with a speed of 250 mm/min. Five specimens were tested for each sample, and we used the average of the three closest results.

#### Static contact angle testing

The static contact angles of distilled water on the air-side surfaces of the WPU films were measured



**Scheme 1** Preparation of the phosphorus-containing polyurethane dispersion.

on a JGW-360° static contact angle meter (Chengde Testing Machine Co., China), and at least 10 measurements of each sample were taken. The 8 closest results were chosen and averaged for a mean value.

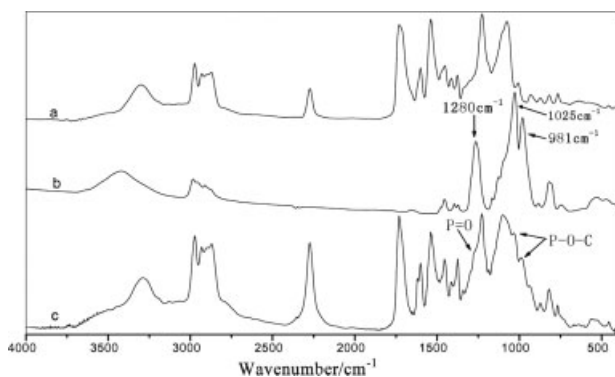
#### Water uptake

Water uptake was tested by a general gravimetric method. Dry WPU films with dimensions of  $2 \times 2 \text{ cm}^2$  were immersed in distilled water at  $40^\circ\text{C}$ .

Twenty days later, the weight of each sample was recorded after excess surface water was wiped off carefully with filter paper. The water uptake ( $W$ ) was calculated by the following equation:

$$W(\%) = \frac{W_1 - W_0}{W_0} \times 100\%$$

where  $W_0$  is the initial weight of the dried film and  $W_1$  is the weight of the film after the absorption of water.



**Figure 1** FTIR spectra of (a) PU0, (b) Exolit OP550, and (c) PPU2.

Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) analysis (SEM-EDS) of the WPU films were done with a model S-4800 Hitachi scanning electron microscope and energy-dispersive spectrometer. The electron beam energies were 15 keV. Data were collected from a scanned region of approximately  $100 \times 50 \mu\text{m}^2$ .

## RESULTS AND DISCUSSION

### Synthesis and structural characterization of the WPUs

A series of WPUs containing different contents of organophosphonate were prepared. For the sake of expression, PPU1, PPU2, PPU3, and PPU4 are used to represent the WPU segments of Exolit OP550 with contents of 5, 10, 15, and 20 wt %, respectively, and PU0 indicates the WPU prepared the same way without organophosphonate.

The chemical structures of the resulting compounds were characterized by FTIR and  $^1\text{H-NMR}$  spectroscopy. Figure 1 displays the FTIR spectra of PU0, the organophosphonate oligomer (Exolit OP550), and an organophosphonate-containing WPU (PPU2). The peaks appearing at  $1282 \text{ cm}^{-1}$  ( $\text{P}=\text{O}$ ) and  $1025$  and  $981 \text{ cm}^{-1}$  ( $\text{P}-\text{O}-\text{C}$ ) in the IR spectrum of Exolit OP550 were attributed to the organic phosphorous groups. Similar absorption peaks were observed in PPU2, although they did not appear in PU0. The absorptions at  $3299$  and  $1550 \text{ cm}^{-1}$  in the PPU2 and PU0 IR spectra were caused by the stretching vibrations and bending vibrations of  $\text{N}-\text{H}$ ; the peaks at  $2979$ – $2872 \text{ cm}^{-1}$  belonged to the stretching vibrations of  $\text{C}-\text{H}$  in  $\text{CH}_2$  and  $\text{CH}_3$ . Those at  $2272$  and  $1735 \text{ cm}^{-1}$  were assigned to  $\text{N}=\text{C}=\text{O}$  and  $\text{C}=\text{O}$  stretching vibrations, respectively. The  $1602 \text{ cm}^{-1}$  absorption peak was produced by the stretching vibrations of  $\text{C}=\text{C}$  in the aromatic ring. The  $1228$  and  $1082 \text{ cm}^{-1}$  absorption peaks were assigned to the stretching vibrations of  $\text{C}-\text{O}-\text{C}$  in urethane bonds and ether bonds, respectively.

The  $^1\text{H-NMR}$  spectra of Exolit OP550, PPU2, and PU0 are shown in Figure 2 along with the assignments of their protons. In Figure 2(a,b), the resonance peaks were attributed to the protons in molecular structures I and II, respectively. From the comparison of Figures 2(a), 2(b), and 2(c), the main proton resonance peaks in the spectrum of Exolit OP550 were clearly found in PPU2, such as protons 2, 4, and 6 in the repeat unit of structure I. Some peaks overlapped in the spectrum of PPU2 [Fig. 2(b)]; for example, proton 2 in the Exolit OP550 segments had a similar chemical shift as proton 7 in the DMPA compound. These facts confirmed that the organophosphonate oligomer was successfully segmented into the WPU macromolecule.

### TEM of the WPU emulsion

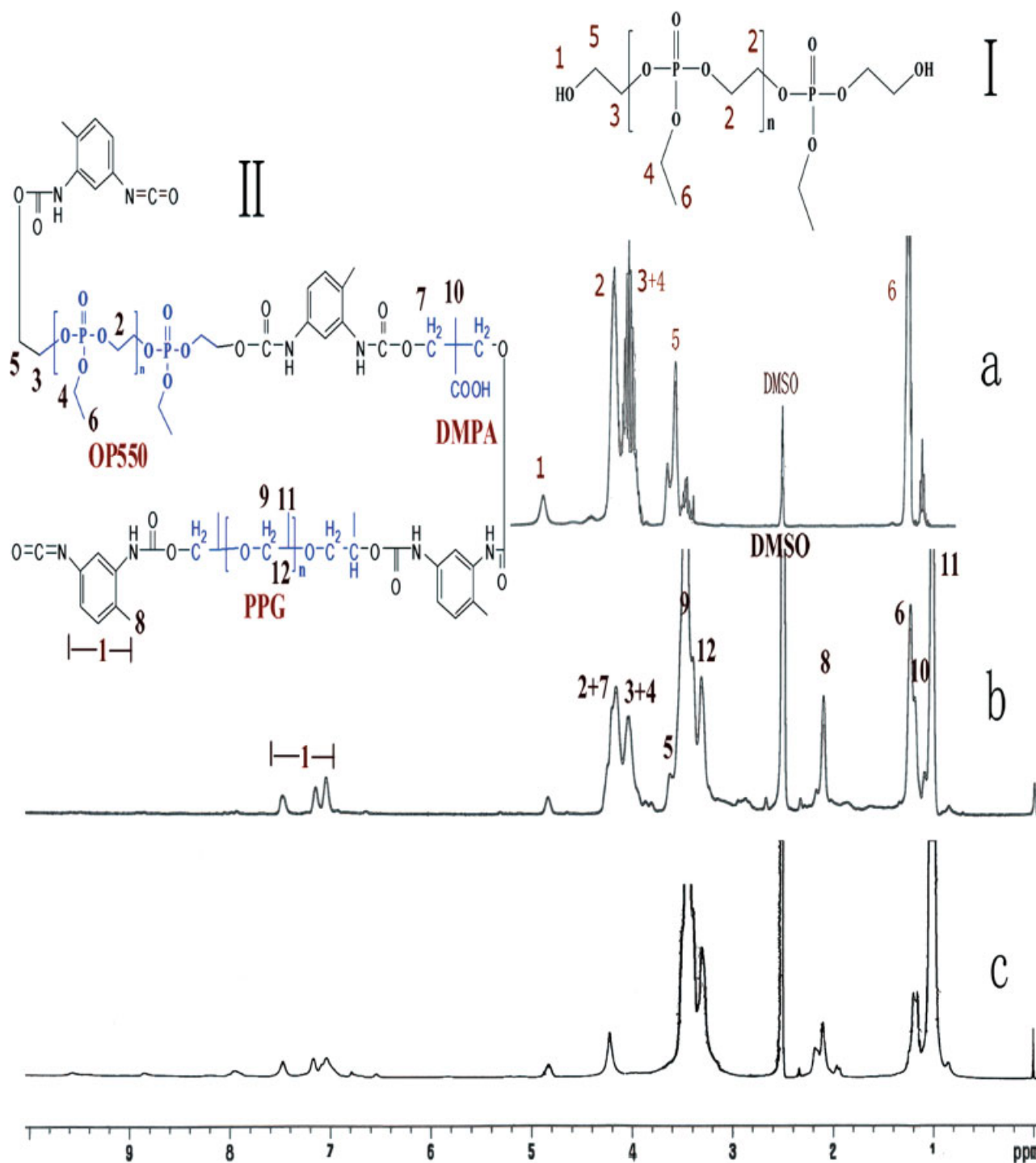
WPU was observed as a white emulsion with blue light. As shown in Figure 3, TEM photomicrographs showed that PPU2 particles were spherical in shape with diameters in range 80–100 nm.

### Thermal analysis

#### Thermal stability

The thermal stability of polymers PU0, PPU1, PPU2, PPU3, and PPU4 were investigated by means of thermogravimetry (TG) and derivative thermogravimetry (DTG), and the curves of TG and DTG are shown in Figure 4. A two-step thermal decomposition process was revealed by the TG and DTG data, in which the two steps corresponded to the weight loss of the hard and soft segments, respectively. The decomposition process was characterized by the onset and maximum degradation temperatures of the first and second steps, as summarized in Table I. All of the characteristic temperatures of the organophosphonate-modified WPUs were lower than those of PU0 and decreased with increasing organophosphonate content. This was probably because the bond strength of phosphorus–oxygen ( $\text{P}-\text{O}$ , 149 K/mol) in the phosphorous polyol was significantly lower than that of  $\text{C}-\text{O}$  (257 K/mol) in the PPG polyol;<sup>22</sup> therefore, the onset degradation temperature of the organophosphonate-modified WPUs decreased compared with those of PU0. The maximum degradation temperature decrease might be have been caused by the acid produced by the degradation of organophosphonate, which could have catalyzed both the depolymerization of urethane in the first stage and the dehydration of polyol in the second stage.<sup>23</sup> In addition, the introduction of the phosphorous segment significantly improved the char residue in the TG test, which was almost 0% in PU0 but reached 8.0% in PPU2 at  $400^\circ\text{C}$ . This was





**Figure 2** Molecular structures of (I) OP550 and (II) PPU2 and  $^1\text{H-NMR}$  spectra of (a) Exolit OP550, (b) PPU2, and (c) PU0. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

consistent with the observations of Park et al.<sup>24</sup> that the introduction of phosphorus into SPU could lower the decomposition starting temperature but accelerate the formation of char at high temperatures. According to the theory proposed, the char layer provides resistance to both mass and heat transfer and retards the degradation of the underlying materials.<sup>25</sup>

#### DSC analysis

As shown by the DSC data in Table II, two glass transitions were observed, and the absent of melting points indicated that no crystallization phase existed in the WPU films. Generally, the glass-transition temperature of the soft segment ( $T_{gs}$ ) is used to determine the degree of microphase separation,<sup>26</sup>

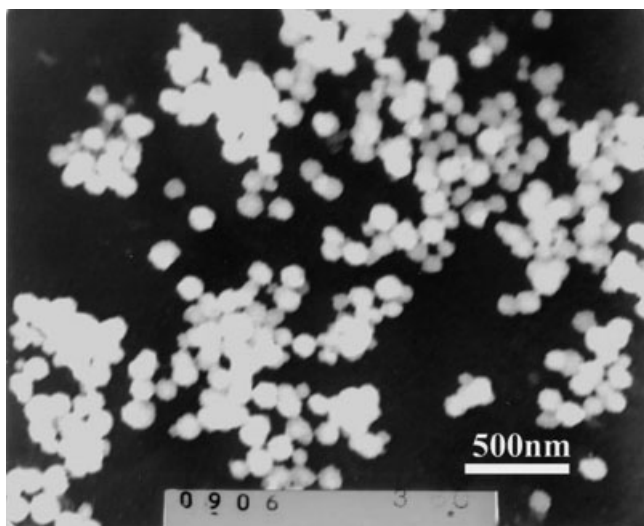


Figure 3 TEM image of particles in the WPU PPU2.

which increases with the decreasing offset of  $T_{gs}$  and the glass-transition temperature of the pure soft segment. As observed,  $T_{gs}$  tended to increase with increasing organophosphonate content. Usually, the  $T_{gs}$  of polyurethane (PU) is affected by the following factors: the number-average molecular weight of the soft segment, the amount of hard segment dispersed in the soft-segment phase, the capability of the urethane segments to form interurethane hydrogen bonds, and the steric hindrance for rotation.<sup>27</sup> Herein, the number-average molecular weight of the polyol PPG used in all of the experiments was 1000, and the hard-segment content varied slightly, as summarized in Table II. Thus, we speculate that the change in  $T_{gs}$  might have primarily caused by the latter two factors. The organophosphonate oligomer Exolit OP550 structure was rich in oxygen atoms, which could form more hydrogen bonds with urethane than could PPG in the phosphorus-free PU; this, consequently, enhanced the interaction between the soft segment and hard segment and improved the compatibility of the two segments. In addition, Exolit OP550 possessed a more rigid structure than PPG to retard the steric rotation of the molecular

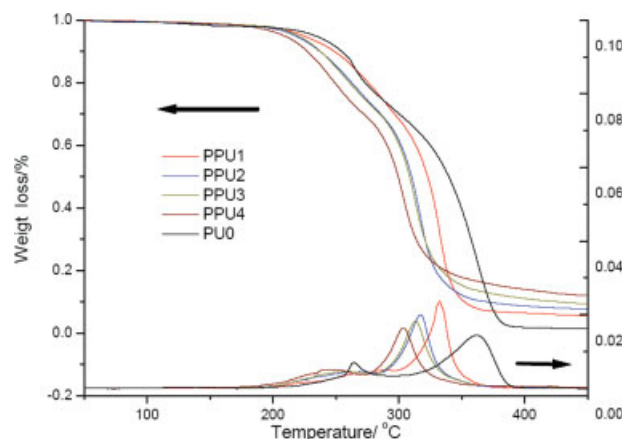


Figure 4 TG and DTG curves of PU0, PPU1, PPU2, PPU3, and PPU4. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

chain. Therefore, the incorporation of phosphorous polyol segments induced an increase in  $T_{gs}$  and lowered the degree of microphase separation in WPU films.

The endotherm of the glass-transition temperature of the hard segment ( $T_{gh}$ ) always displays as a small peak or change in slope of the DSC line, which is ascribed to short-range ordering of the hard segments.<sup>28</sup> Chen et al.<sup>29</sup> studied endothermic behavior of short-range ordering dissociation in SPU based on 4, 4'-diphenylmethane diisocyanate and 1, 4-butane-diol and suggested that the nature of the behavior was typical of enthalpy relaxation and resulted from the physical aging of the amorphous hard segment. Shu et al.<sup>30</sup> verified that the easy physical aging of the amorphous phosphorous hard segment led to a higher temperature of short-range ordering dissociation. In this study, the phosphorous segments served as soft segments in the WPU films, and  $T_{gh}$  shifted to higher temperatures with the incorporation of this segment, as summarized in Table II. That the mobility of the hard segments inside the soft domain have a strong effect on the morphology of SPU was proven by Chen et al.,<sup>31</sup> in which an increase in the

TABLE I  
Characteristic Decomposition Temperatures for the WPU Films

Sample	$T_{1on}$ (°C)	$T_{1m}$ (°C)	$T_{2on}$ (°C)	$T_{2m}$ (°C)	Char yield at 400°C (wt %)
PU0	268.1	284.7	359.2	382.0	0.6
PPU1	256.8	287.8	342.1	352.6	5.8
PPU2	244.8	278.6	325.5	336.8	8.0
PPU3	243.2	272.7	321.6	333.4	9.9
PPU4	236.6	260.8	312.9	323.7	12.5

$T_{1on}$  = onset degradation temperature of the first step;  $T_{1m}$  = maximum degradation temperature of the first step;  $T_{2on}$  = onset degradation temperature of the second step;  $T_{2m}$  = maximum degradation temperature of the second step.

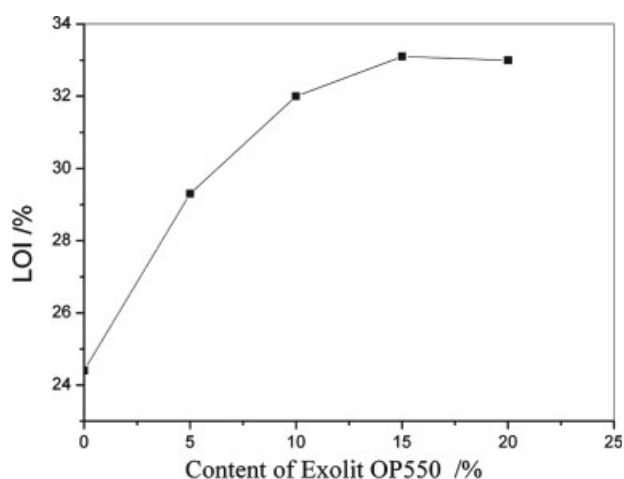
**TABLE II**  
DSC Data for the WPU Films

Sample	$T_{gs}$ (°C)	$T_{gh}$ (°C)	Hard-segment content (wt %)
PU0	-17.0	60.6	30.2
PPU1	-15.9	75.3	30.7
PPU2	-14.2	71.8	31.2
PPU3	-7.0	72.6	31.7
PPU4	-4.2	96.8	32.0

polyester with  $-\text{CH}_3$  side chains leads to an increase in the free volume of the soft-segment domain and, therefore, to a higher mobility of hard-segment molecules inside the soft domain. Accordingly, we believed here that the  $-\text{OCH}_2\text{CH}_3$  side chain of the phosphorus-containing polyol had a similar effect on the hard segment. The hard segments with higher mobility moved relatively easily out of the soft domain and aggregated into a better short-range ordering, which required more energy for dissociation and, consequently, raised  $T_{gh}$ .

### Flame retardancy

The flammability of the WPU films was characterized by the LOI. As depicted in Figure 5, the LOI value greatly improved with the introduction of Exolit OP550, even at a low content of 5% for PPU1, and increased with increasing Exolit OP550 content. PPU3, with 15% Exolit OP550, presented the highest flame-retardant capacity, with a LOI of 33.1%. However, the LOI value of the films of PPU4, with 20% Exolit OP550, was 33.0% and remained constant above 15% organophosphonate content (the error on the LOI test was  $\pm 0.1$ ).



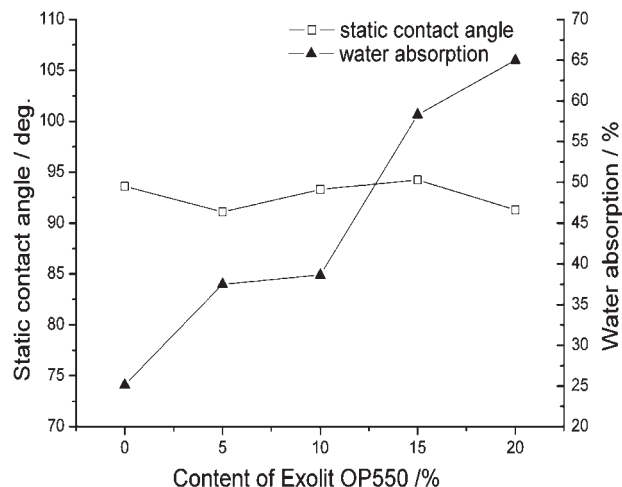
**Figure 5** LOI values of PU0 and PPU with different Exolit OP550 contents.

**TABLE III**  
Mechanical Properties of the WPU Films

Sample	Tensile strength (MPa)	Elongation at break (%)	Elastic modulus (MPa)
PU0	2.975	788	0.503
PPU1	2.562	575	0.512
PPU2	2.402	502	0.526
PPU3	2.298	398	0.573
PPU4	2.123	255	0.622

### Mechanical properties

As listed in Table III, the tensile strength and elongation at break of phosphorus-free WPU film (PU0) were 2.975 MPa and 788%, respectively, whereas these values decreased to 2.123 MPa and 255% when WPU was segmented with 20 wt % Exolit OP550 (PPU4). Both values decreased with increasing organophosphonate content. At the same time, the elastic modulus increased very slightly. However, these kinds of changes were very small and rarely affected the flexibility of the films. Usually, the mechanical properties of PU are profoundly affected by the content of hard segment and degree of phase separation. PUs containing higher hard-segment content possess better tensile strength because the hard segment behaves as a physical crosslink and imparts stiffness and reinforcement. A low degree of micro-phase separation would decrease the tensile strength of PU. As discussed previously, the hard-segment content only increased slightly from 30.2 to 32.1%, but the degree of phase separation decreased with increasing content of organophosphonate. Thus, the latter was supposed to be the main factor responsible for the decrease in tensile strength and the elongation at break of the WPU films.



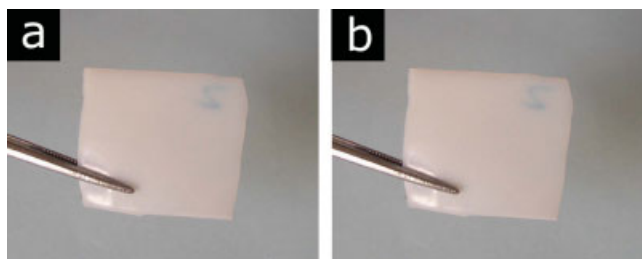
**Figure 6** Water absorption and static contact angle values of the PU0, PPU1, PPU2, PPU3, and PPU4 films.

### Water absorption and static contact angle

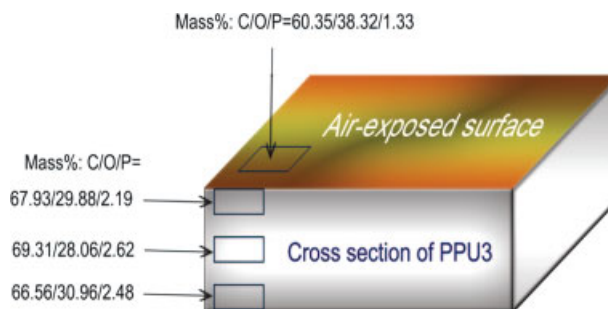
Because of the more polar and hydrophilic structure of Exolit OP550 compared to PPG, the organophosphonate modified waterborne polyurethane (PPU) films had higher water uptake values with the incorporation of the hydrophilic segment of organophosphonate, and these increased with the content of organophosphonate, as shown in Figure 6. Nevertheless, the PPU films still retained integrity and did not deform even after they were dipped in water for 2 months, as shown in Figure 7. The static contact angle was herein used to value the hydrophobic properties of the WPU film surfaces. The higher the contact angle was, the more hydrophobic the films were. However, as indicated in Figure 6, the static contact angles were hardly affected by the organophosphonate content and were all higher than 90°. A proposed explanation is that, during film formation, the lower polar segment tended to move to the surface, and the more polar segment moved to the bulk.<sup>32</sup> Thus, we suspect that the relatively low content of polar Exolit OP550 segments on the surface led to no evident change in the static contact angles.

### SEM-EDS analysis

To confirm that the organophosphonate chain tended to migrate to the bulk of the WPU film, the cross section and surface elemental analysis of the organophosphonate modified WPU films were measured with SEM-EDS. Figure 8 shows that the phosphorus content in the air-exposed surface was markedly lower than that in the cross section, and the place near to the air-exposed surface exhibited the lowest phosphorus content compared to the other places in the cross section. Because the SEM-EDS collected data for about a 10  $\mu\text{m}$  thickness of the surface, the phosphorus content in a real air-exposed surface might be lower. Therefore, the surface polarity of the organophosphonate-modified WPU films changed rarely, and the contact angles



**Figure 7** Photographs of (a) PU0 and (b) PPU2. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 8** SEM-EDS analysis results for PPU3. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

remained in the same level, although the water absorption increased.

### CONCLUSIONS

A series of flame-retardant WPU films were successfully prepared by the segmentation of organophosphonate Exolit OP550 and structurally characterized by means of FTIR,  $^1\text{H-NMR}$ , and spectroscopy. With the incorporation of this kind of phosphorous segment, TG and DTG indicated that the WPU films possessed lower onset and maximum degradation temperatures but higher char yields than the phosphorus-free ones. The degree of phase separation decreased with increasing organophosphonate content. Although the mechanical properties were depressed to some extent, the flame retardancy of the WPU films greatly improved with regard to the LOI results, which increased to 32.0% at a 10 wt % content of Exolit OP550 and to 33.1% at a 15 wt % content, in contrast to 24% for the phosphorus-free WPU films. SEM-EDS showed that it was reasonable for the phosphorus-containing films to retain good hydrophobic properties when the water absorption increased.

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