



Synthesis and Properties of Polyurethane Elastomers from a Phosphorus-Containing Chain Extender†

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A series of phosphorus-containing polyurethane elastomers (P-PU) were prepared, which are based on synthesized *bis*(3-hydroxy phenyl)phenyl phosphate (BPP) as chain extender and phosphorus resource reacting with NCO-terminated polyurethane prepolymers from 4,4'-diphenylmethane diisocyanate (MDI) reacting with different soft segments of polyether polyols, polytetrahydrofuran ether glycol, polyester polyols, respectively. The *bis*(3-hydroxy phenyl)phenyl phosphate and phosphorus containing polyurethane elastomers structures were confirmed by FTIR spectroscopy. The properties of polyurethane elastomers of hydrophilicity, thermo-stability and mechanical property were analyzed. The results showed that the hydrophilicity of phosphorus containing polyurethane elastomers was enhanced with the increased amount of phosphorus containing; the soft segments content and types definitely influence the phosphorus containing polyurethane elastomers thermal stability.

Key Words: Phosphorus-containing polyurethane, *Bis*(3-hydroxy phenyl)phenyl phosphate, Synthesis, Properties.

INTRODUCTION

The main chain of polyurethane (PU) is composed by soft segments and hard segments^{1,2}. Because of the outstanding performance, polyurethane in different fields such as health care, machinery, building *etc.* was awarded a wide range of applications. Now, polyurethane has been seen as a universal polymer materials used as rubber, plastics, fiber, or paint as the progress of segments design and synthesis technology. It is well known that many factors such as the change of the hard segment and soft segment of the chemical structure, extender chain and crosslinking agent type, *etc.*, will be decided to polyurethane materials of phase structure and performance.

The research on phosphorus containing materials has got great attention at its potential application in fireproof materials, UV protection materials and bio-compatible materials *etc.* Also, using the phosphorus to improve the properties of polyurethane had been widely reported³⁻⁷. But, higher the phosphorus-containing polyurethane is hard to synthesize due to difficult to choice of a mature phosphorus monomer. Meanwhile, selected inorganic polymer modification polyurethane gets more widely used. But due to the bad compatibility, the work ability of inorganic polymer modification polyurethane is not good enough, what is worse the property of inorganic

polymer modification polyurethane will decrease as time go by.

In this paper, phosphorous element introduced to polyurethane main chain skeleton through chain extender reaction has been investigated. The influence of different soft segments structure, hard segments and phosphorus containing on the thermal behaviour and mechanics properties of phosphorus-containing polyurethane elastomers (P-PU) were studied.

EXPERIMENTAL

Chemically pure, phenyl phosphorodichloridate (PPD), was purchased from Wuhan-Jiakai Chemical Co. Ltd.; resorcinol, was obtained from Shanghai-zhongyi Chemical Co. Ltd.; 4,4'-methane diphenyl diisocyanate (MDI), was provided from Shandong-Yantai Chemical Co. Ltd.; polyethylene polyols (N210, Mn = 1000; N220, Mn = 2000), were purchased from Zibo-Dexin Chemical Co. Ltd., vacuum dehydration at 110 °C for 2 h; poly(tetramethylene glycol, Mn = 1000, 2000) (PTMG) were obtained from Yantai-Yutian Chemical Co. Ltd., vacuum dehydration at 110 °C for 2 h; polyester polyols of aromatics (PAE Mn = 1000, 2000) were purchased from Nanjing KSD Chemical Co. Ltd., vacuum dehydration at 110 °C for 2 h; dibutyltin dilaurate (DBTD), chemically pure, were obtained from Shanghai-Chemical reagents Co. Ltd.

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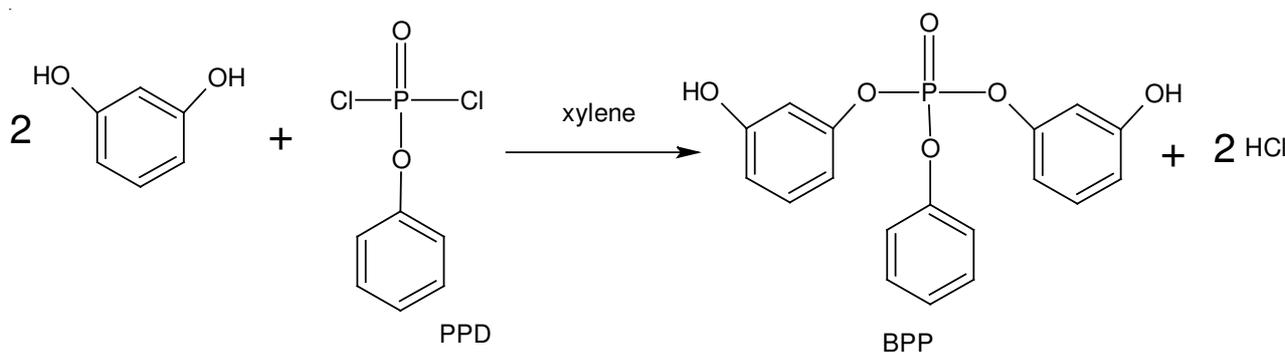
Synthesis: Adding a certain amount of resorcinol and corresponding amount of xylene in four-neck reaction vessel with the thermometer and mechanical stirrer and reflux condenser was heated up to 125 °C slowly. Then, adding stoichiometric amount of PPD according to the **Scheme-I** continuously in to the reaction system by syringe, keep stirring at 125 °C until no HCl escaping, in succession, wash the reaction liquid for many times in order to take away the undesired resorcinol. After circumsgrate evaporator, the xylene can be eliminated⁸⁻¹⁰. Purple coloured viscous *bis*(3-hydroxy phenoxy)-phenyl phosphate (BPP) product was obtained. The reaction equation is shown in **Scheme-I**.

Prepare the NCO-terminated prepolymer: The polyurethane prepolymer was prepared from 4,4'-diphenylmethane diisocyanate as hard segments and polyester glycol (or instead of polyethylene glycol or PTMG) as soft segment. The molar ratio between -NCO of 4,4'-diphenylmethane diisocyanate and -OH of polyol was selected here to be 2.02/1. Before the reaction, the soft segment was preheating and vacuuming at 60 °C for 2 h, then, put into the reaction mixture of 4,4'-diphenylmethane diisocyanate and dibutyltin dilaurate, keep the reaction mixture at 65 °C until the content of NCO wt. % reaching the design value by analyzed with the two *n*-butyl amine methods¹¹.

Preparation of polyurethane elastomer: Certain amounts of *bis*(3-hydroxy phenyl)phenyl phosphate dissolve in DMF and then react with NCO-terminated prepolymer at room temperature. The reaction mixtures were stirred sufficiently and poured into polyfluortetraethylene plate. After removal of the solvent by vacuum pumping, all reaction system were put in the oven at 100 °C for 6 h. The phosphorus-containing polyurethane elastomers (P-PU) were obtained. The formula of P-PU is listed in Table-1.

TABLE-1
P-PU MATERIALS FORMULATIONS

Specimen	Soft segments	Hard segments contents (%)	Phosphorus contents (%)
P-PU1	–	100	5.13
P-PU2	PEG (N210)	46.06	1.67
P-PU3	PEG (N220)	29.92	1.09
P-PU4	PTMG1000	46.06	1.67
P-PU5	PTMG2000	29.92	1.09
P-PU6	PU1000	46.06	1.67
P-PU7	PU2000	29.92	1.09



Scheme-I: Synthetic route of *bis*(3-hydroxy phenyl)phenyl phosphate (BPP)

Measurement and characterization

FTIR analysis: FTIR spectra were recorded using a Nicolet6700 FTIR spectrometer with smart iTR diamond mode at 0.2 cm⁻¹ resolution and 32 scans.

Rate of water absorption test: The samples of P-PU were immersed into the distilled water for 24 h at the room temperature. Then take the samples from the distilled water and have them weighted after removing the free water with filter paper immediately. The water absorption rates are given below equation as follows:

$$W_p = \frac{m_2 - m_1}{m_2} \times 100 \%$$

where the term W_p is the water absorption rate and m_1 or m_2 represents the weight of the sample which be immersed into the water before or after, respectively.

Mechanics test: The mechanics properties of the samples of P-PU were carried out at Ruigeer Model 3010 at 100 mm/min stretch speed, 25.5 °C and 62 % RH according to the GB/T 528-92 standard.

Hardness test: The hardness was tested on LX-A Rubber durometer according to GB513283 for all P-PU samples.

Thermal analysis: Thermal properties of P-PU samples were analyzed using the NETZSCH STA 409PC/PC and the Model DSC1 METTLER TOLEDO, under the nitrogen atmosphere at 10 °C/min heating rate.

RESULTS AND DISCUSSION

Synthesis of phosphorus-containing polyurethane: The FTIR spectra of P-PU samples are shown in Fig. 1. The structure of P-PU is confirmed by three characteristic groups of N-H vibration group absorption bands (3298 and 1535 cm⁻¹), CH₃- and CH₂- group vibration absorbance bands 2977-2830 cm⁻¹, C=O stretching vibration band 1721 cm⁻¹. The group of P=O stretching vibration band 1224 cm⁻¹ and P-O-Ar stretching vibration band 1108 cm⁻¹ belonging to *bis*(3-hydroxy phenyl)-phenyl phosphate are observed (Fig. 1), which proves that the structures of P-PU were formed. It is implied that the stretching vibration peak of -OH at 3396 cm⁻¹ of the *bis*(3-hydroxy phenyl)phenyl phosphate spectrogram disappears in P-PU spectra due to -OH reacting -NCO in the process of preparing polyurethane^{12,13}. The appearance and the disappearance of these peaks prove that the *bis*(3-hydroxy phenyl)phenyl phosphate had been successfully introducing into the molecular chain of polyurethane.

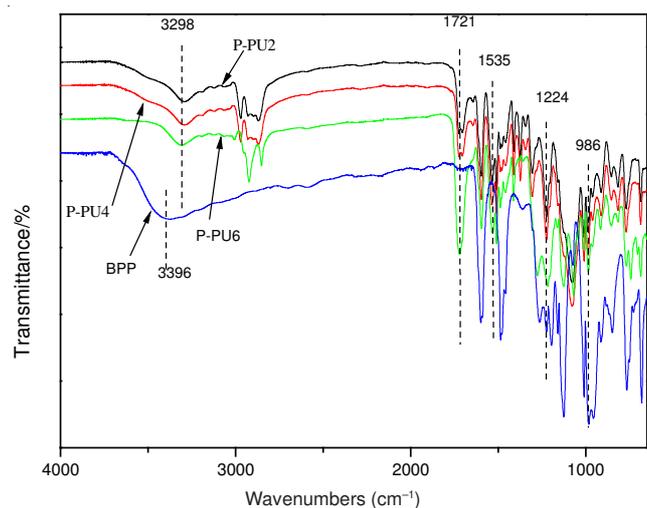


Fig. 1. FT-IR spectra of the samples of P-PU and *bis*(3-hydroxy phenyl)phenyl phosphate

Water resistance: The hydrophobic properties of the samples of P-PU were characterized by measuring the water absorption rate (W_p) of materials. The results are listed in Table-2.

Sample	P-PU1	P-PU2	P-PU3	P-PU4	P-PU5	P-PU6	P-PU7
W_p (%)	17.36	5.26	4.67	4.59	3.57	3.47	3.26

From Table-2, the water absorption results indicate the introduction of soft segments can be better to enhance its hydrophobic properties. Compared with the same series of soft segments, the sample's W_p showed increasing gradually as the phosphorus content improve, which indicate the introduction of phosphorus can increase the hydrophilic ability of polyurethanes. The results also show that P-PU from the soft segment of polyarylester (PU1000, PU2000) with the best properties of water-proof.

Mechanical properties: The chemical bonds, the main intermolecular forces and chain segment of rigidity and crystallinity of polyurethane materials decided to the performance of mechanical properties of P-PU. The main key role factor of polyurethane's is soft and hard segment for the type and proportion. Table-3 is listed the mechanical properties of the pure phosphorus-containing polyurethane. The results show that the rupture elongation of P-PU increased with lower phosphorus content in the same soft segment, the P-PU's tensile strength with polyethylene polyols (except PTMEG) soft segment decreased to that's of polyarylester polyols with lower phosphorus content. Most polyurethane elastomers are relatively high tensile strength and improved with hardness increase. In the same phosphorus content of the P-PU samples, the rupture elongation of different soft segments of P-PU is in the order of PEG > PTMG > polyarylester polyols and the change trend of tensile strength of P-PU is as follows: PTMEG > polyarylester polyols > PEG.

Sample	Rupture elongation (%)	Tensile strength (Mpa)	Hardness (Shore A)
P-PU2	504.3	12.40	57.2
P-PU3	512.6	9.35	51.5
P-PU4	382.5	25.03	60.8
P-PU5	491.9	43.50	63.2
P-PU6	365.3	13.03	65.7
P-PU7	438.2	9.65	59.9

Thermoproperties analysis: Fig. 2 shows the TG curves of the samples of P-PU and the characteristic thermal decomposition temperatures are listed in Table-4.

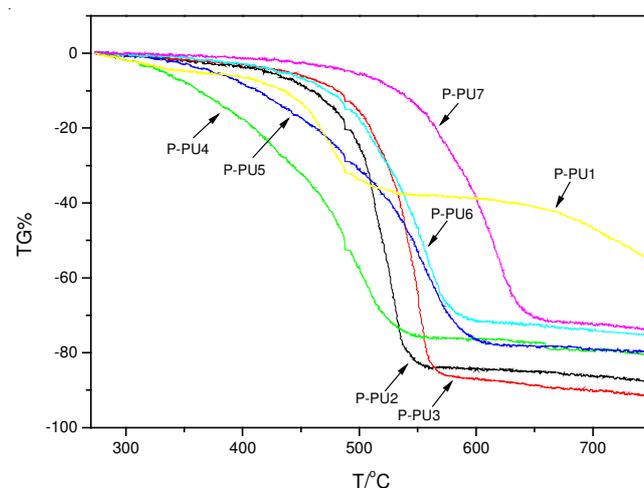


Fig. 2. TG curves and DTG curves of P-PU

Sample	V_T (°C/min)	$C_{H,S}$ (%)	T_{10} (°C)	T_{50} (°C)	T_{max} (°C)
P-PU1	10	100	437	718	469.5
P-PU2	10	46.06	459	519	519.28
P-PU3	10	29.92	481	541	546.21
P-PU4	10	46.06	361	487	538.3
P-PU5	10	29.92	412	546	550.29
P-PU6	10	46.06	469	553	601.69
P-PU7	10	29.92	533	615	605.77

V_T : Heating rate, $C_{H,S}$: hard segment content.

From Fig. 2 and Table-4, it can be compared the samples of P-PU of representative thermal decomposition temperatures. Compared P-PU's TG curves and T_{50} show the 100 % hard segments of P-PU has the best thermal stability in all P-PU samples, because of the hard segment have a higher cohesive energy than the soft segments. But, the P-PU with larger soft segments can get to enhance the thermal stability of polyurethane at the same soft segment. Compared P-PU2 and P-PU3, P-PU4 and P-PU5, P-PU6 and P-PU7, the data of T_{50} raised with the hard segment content decreased, it is because of the reaction system of higher hard segments containing results in more groups of allophanate and biuret with less thermal stability. Compared the samples of P-PU2, P-PU4 and P-PU6, the order of the T_{10} of thermal decomposition temperature shows P-PU6 > P-PU2 > P-PU4, which is due to the stability of difference soft segments. It can be explained by the cohesive

energy density (CED) of polyurethane, as we known, CED polyarylester > CED_{PEG} > CED_{PTMG}. Therefore, to improve the thermal stability of polyurethane elastomer, we should not only proceed from the hard segment, but also to choose a high thermal stability of the soft segment.

DSC analysis: The DSC curves of the samples of P-PU were show in Fig. 3, which were presented the T_g of the hard segment of P-PU1 in 54 °C and P-PU2's T_{g1} in -18 °C and T_{g2} in 101 °C, P-PU3's T_{g1} in -45 °C and T_{g2} in 83 °C, which T_{g1} belongs to the soft segment and T_{g2} belongs to the hard segment. The glass transition temperature of the hard segment in P-PU2 and P-PU3 is different from P-PU1 and the hard segment T_g was increased after access the soft segment. It is implied that the hard segment and soft segment in P-PU2 and P-PU3 has a certain incompatibility. Comparing the T_{g1} and T_{g2} of P-PU2 and P-PU3 reflects have a certain influence on the compatibility of hard and soft segments with the phosphorus containing of P-PU changes. The results show that longer soft segment is beneficial for soft segments phase separation from hard segments microarea of structure of P-PU. About P-PU further performance of the research work is in progress.

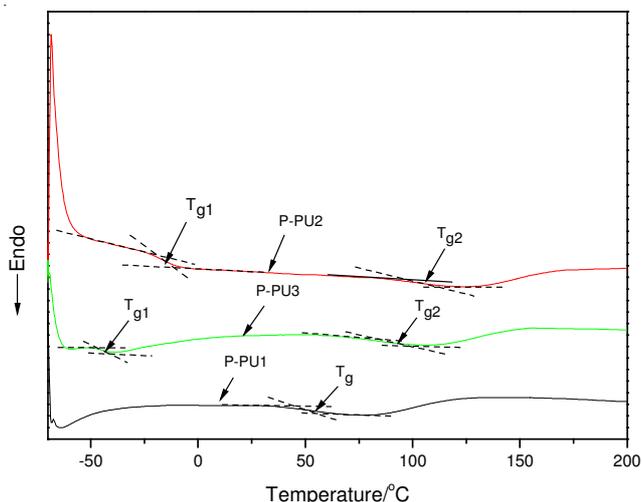


Fig. 3. DSC curves of P-PU1, P-PU2 and P-PU3

Conclusion

Phosphorus containing polyurethane elastomer based on prepared chain extender agent *bis*(3-hydroxy phenyl)phenyl phosphate and with other convention raws of 4,4'-diphenylmethane diisocyanate, PTMG, polyether polyols, polyarylester polyols. FTIR confirmed that the P-PU structure was obtained. DSC confirmed that P-PU with soft segment have two glass transition temperature. Research found that the introduction of the soft segment of polyurethane thermal stability will be enhanced. With the hard segment content decreased, the thermal stability of polyurethane to be strengthened. Select the appropriate soft segment can be significantly improved thermal stability of polyurethane.

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