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Synthesis and Application of Water-Borne Linear Polyester-Ether-Urethane†

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The water-borne linear polyester-ether-urethane with alternating polyester and polyether as soft segment was synthesized by pre-polymerization and blocking reaction. The chemical structure of polyester-ether-urethane was characterized by FTIR and was proved no chemical crosslinking by dissolution experiments of N,N-dimethylformamide. The water dispersion and solubilization were analyzed by solid content, emulsion stability, surface tension and viscosity of hybrid latex. The results showed that the emulsion of polyester-ether-urethane with methyl diphenylene diisocyanate as hard block was the most stable and its maximum solid content was 6.5 %, the surface tension of water was reduced obviously by the polyester-ether-urethane emulsion, when the mass per cent of the polyester-ether-urethane, emulsion and the emulsion of polyester-urethane admixture was 8 %, polyether-urethane and polyester-urethane mass ratio of 1:1.

Key Words: Polyester-ether-urethane, Pre-polymerization, Emulsion, Solubilizing.

INTRODUCTION

Water-borne polyurethane was successfully developed for the first time in 1943, it with the medium of water is non-toxic, non-environmental pollution, non-combustible, energy saving and easy processing, which caused great attention of many scholars[1,2]. Recently, the growing requirements of environmental protection accelerated the pace of water-borne polyurethane industrial development out of the world[3,4]. The polyester-urethane has good mechanical properties but poor hydrolysis resistance, while the hydrolytic stability of polyether-urethane is better[5]. Therefore, some researchers[6-8] have been trying to get a kind of polyurethane emulsion with good mechanical properties and hydrolysis resistance performance. However, due to the difference of bond polarities of ether and ester, the hybrid emulsion of polyester-urethane and polyether-urethane is highly unstable. To obtain the polyurethane emulsion with excellent properties, the research of compatibility of different polyurethane emulsion becomes more and more urgent. A kind of water-borne linear multi-block polyester-ether-urethane was synthesized present studies. It has better solubility effect on hybrid latex of polyether-urethane and polyester-urethane.

EXPERIMENTAL

Hydroxyl group of polyether glycol (N-220), hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI), methyl diphenylene diisocyanate (MDI), polyester glycol (SP-202) were purchased from commercial sources, the polyether glycol and polyester glycol were vacumm dried at 120 ºC for 2 h before use.

Synthesis of polyester-ether-urethane: The isocyanate terminate pre-polymers were synthesized by the molar ratio 1:2 of N-220 to isocyanate group of different diisocyanate such as HDI , TDI , MDI, respectively. Then, the isocyanate-terminate pre-polymers were capped with N-220, polyester glycol (SP-202), respectively, as the molar ratio of 1:2 of isocyanate group to hydroxyl group. The product employed HDI as hard segment and polyether glycol (N-220) as soft segment was denominated HDI1, while the terminated product with HDI as hard segment and alternating polyester and polyether as soft segment was denominated HDI2. The TDI1, TDI2, MDI1 and MDI2 can be deduced by analogy. Then 3 % dodecyl sodium sulfate was added into the terminated products, respectively. The admixtures of polyurethane and dodecyl sodium sulfate were stirred homogenously, de-ionized water

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was added into the beaker and high-speed mechanical stirred at 50 ºC for 0.5 h. The products were stored for standby. Water-borne linear polyester-ether-urethane (as MDI2 for example) synthetic process **Scheme-I**.

RESULTS AND DISCUSSION

The FTIR spectra of water-borne linear polyester-ether-urethane (as MDI2 for example) was recorded at the resolution of 1 cm^{-1} and at 32 scans on a WQF-300 spectrometer (Second Optical Instrument Factory of Beijing, China). All samples for FTIR measurements were prepared by coating water-borne linear polyurethane solutions onto mono-crystalline silicon sheets.

Fig. 1 shows the FTIR spectra of as-synthesized water-borne linear polyurethane. The pre-polymerization reaction was characterized by absorption bands at 2262 cm^{-1} of NCO characteristic bands groups, 1100 cm^{-1} of ether bonds characteristic bands and 1727 cm^{-1} of carbonyl of amide and isocyanate characteristic bands. Stretching vibration bands at 1738 cm^{-1} of two carbonyls were presented and absorption bands at 2262 cm^{-1} of NCO groups characteristic bands were disappeared in the FTIR spectra of terminated pre-polymer. The FTIR spectra of Fig. 1 revealing the characteristics of the urethane group and alternating polyester and polyether polymerized with isocyanate.

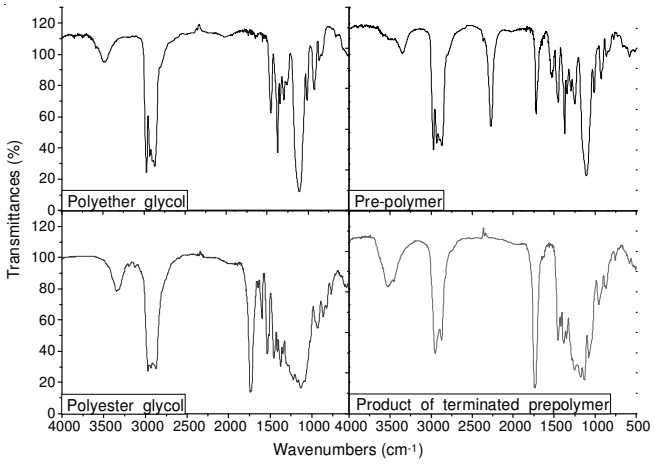


Fig. 1. FTIR spectra of water-borne linear polyester-ether-urethane

Using N,N-dimethylformamide (DMF) as solvent, the water-borne linear polyester-ether-urethanes were used in the solubility tests, the results showed that it can be completely dissolved in DMF and do for the linear structure, no cross-linking[9,10].

A certain amount of water-borne linear polyurethane emulsion was dried in an oven until the weight was constant and then calculated the solid content of each emulsion, the disposed data was showed in Table-1.

TABLE-1
SOLID CONTENT OF DIFFERENT POLYURETHANE EMULSIONS

Emulsions	HDI1	HDI2	TDI1	TDI2	MDI1	MDI2
Solid contents (%)	11	8.5	9.5	8.0	8.5	6.5

The effect of molecular chain of polyester and structure of rigid benzene ring on the solid content of emulsions was showed in Table-1. The solid content of emulsion reduced with increasing of molecular chain of polyester and structure of rigid benzene ring. The reason is that the hydrogen bonds of ester enhance the interaction of molecules and hindered the emulsification of polyurethane and benzene ring is hydrophobic group, so that more hydrophobic groups of polymer molecular chain, the more difficult to be emulsified.

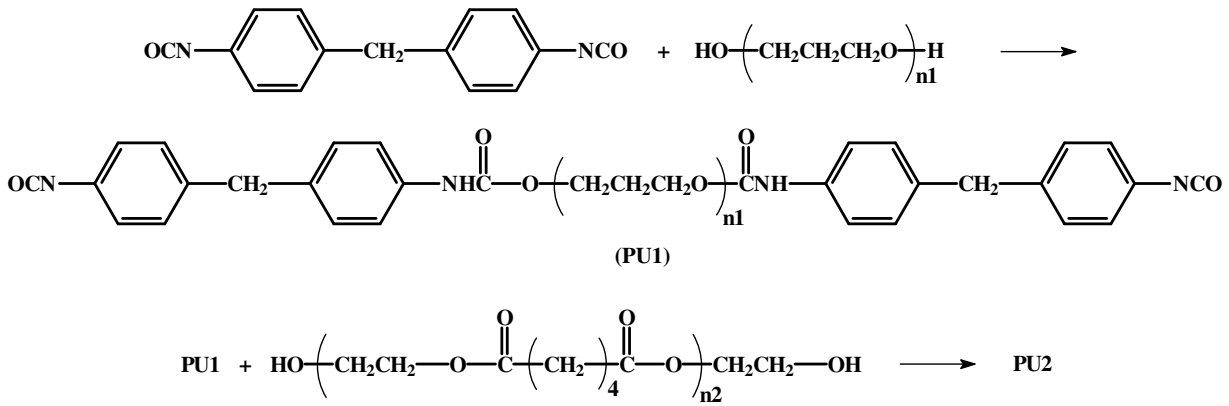
The solid contents of emulsion were transferred to 5 % with de-ionized water and kept at 35 ºC for 48 h, the phenomena of emulsion were showed in Table-2.

TABLE-2
STABILITY OF WATER-BORNE LINEAR POLYURETHANE EMULSIONS

Emulsions	HDI1	HDI2	TDI1	TDI2	MDI1	MDI2
Phenomena	A lot of deposit	A little of deposit	A lot of deposit	A little of deposit	A lot of deposit	Homogeneous

It was discovered that there are deposits in the HDI1, HDI2, TDI1, TDI2 and MDI1, but none in the emulsion of MDI2 in Table-2. The phenomena showed the emulsion of water-borne linear polyester-ether-urethane with MDI as hard block was the most stable.

The various types of polyesterurethane emulsions with 5 % solid content were prepared by adding 3 % dodecyl sodium



Scheme-I: Synthetic process of polyester-ether-urethane

TABLE-4
VISCOSITIES AND PHENOMENA OF THE HYBRID EMULSIONS

Properties	Parameters					
	0 (%)	2 (%)	4 (%)	6 (%)	8 (%)	10 (%)
Phenomena	Phase separation	Phase separation	Phase separation	Phase separation	Homogeneous	Homogeneous
Viscosities (Pa S)	1.26	1.08	0.99	0.95	0.92	0.91

sulfate into the various types of polyurethane and stirring homogenously, then adding de-ionized water into the beaker and high-speed mechanical stirring for 0.5 h, the water solution of blank sample contains the same amount of dodecyl sodium sulfate with polyester-ether-urethane emulsions. The surface tensions of emulsions were measured by the maximum bubble method at 30 ºC. The results were showed in Table-3.

TABLE-3
SURFACE TENSIONS OF WATER SOLUTION AND DIFFERENT POLYESTER-ETHER-URETHANE EMULSIONS

Emulsions	Water solution	HDI2	TDI2	MDI2
Surface tensions (dyne cm^{-1})	67.57	60.52	58.06	59.09

The surface tension of water was significantly reduced with the addition of various types of polyurethane emulsions, but the difference of surface tensions among various polyurethane emulsions was all the same in Table-3, which demonstrated that the polyester-ether-urethane is surface active agents.

A certain amounts of water-borne linear polyurethane with MDI as hard segment emulsion was added into the hybrid emulsion of polyester-urethane and polyether-urethane, polyether-urethane and polyester-urethane of the mass ratio was 1:1. The viscosities of polyurethane hybrid emulsions were measured by NDJ-1 Rotation Viscometer (Changji Geological Instrument Ltd. of Shanghai, China) at 35 ºC, the viscosities of the hybrid emulsion and the phenomena of hybrid emulsions that were stored at 35 ºC for 24 h, were showed in Table-4.

It can be found that the solubilization of water-borne linear polyester-ether-urethane with MDI as hard block was quite obvious. The viscosities of emulsions of hybrid emulsion were declined with the increasing of water-borne linear polyester-ether-urethane (Table-4). The reasion is the solubilization of polyester-ether-urethane.

Conclusion

A series of water-borne linear polyester-ether-urethane with different diisocyanates as hard segment was prepared successfully, the water-borne linear polyester-ether-urethane with MDI as hard segment has positive solubilizing effect on the emulsion of polyether-urethane and polyester-urethane admixture. However, much work needs further study.

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