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SYNTHESIS AND CHARACTERIZATION OF CROSSLINKED POLYURETHANES

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Abstract

Two polyurethane samples, crosslinked with aliphatic hyperbranched polyester, were synthesized and examined in this work. The sample PUPDMS-EO was prepared using ethylene oxide-poly(dimethylsiloxane)-ethylene oxide as macrodiol, while the synthesis of PUPTMO was performed using poly(tetramethyleneoxide). The obtained results show that thermal stability of these networks can be improved by introducing the siloxane sequences. However, the sample PUPDMS-EO has at the same time much lower crosslinking density than PUPTMO.

Introduction

Crosslinked polyurethanes (PUs) are important class of PU family, due to their interesting physical and chemical properties and extensive applications in the manufacture of coatings, elastomers, foams, etc. Two types of network are usually present in crosslinked PUs: physical (created by the H-bonds) and chemical. The nature of the chemical network and properties of crosslinked PUs strongly depend on the type of crosslinking agent. The use of hyperbranched (HB) polymers as crosslinker of PUs has attracted large scientific attention over the last years, because of their unique structure and properties and simple synthetic procedure [1,2].

In this work, the influence of the nature of macrodiol on swelling and thermal properties of two crosslinked PUs, PUPDMS-EO and PUPTMO, based on ethylene oxide-poly(dimethylsiloxane)-ethylene oxide and poly(tetramethyleneoxide), respectively, was investigated. Both samples were crosslinked by the hydroxy-functional aliphatic HB polyester of the second pseudo generation (BH-2, Boltorn[®]).

Experimental

The PU networks were synthesized in bulk using PDMS-EO ($M_n = 1200$ g/mol) or PTMO ($M_n = 1000$ g/mol) and 4,4'-diisocyanatodiphenylmethane (MDI) as monomers and BH-2 ($M_n = 1340$ g/mol, functionality $f_n = 12$ [3]) as crosslinking agent. The NCO/OH ratio was 0.8 for both samples. The crosslinked samples were obtained as yellow films.

IR spectra of the crosslinked PUs were recorded on ATR NICOLET 6700 IR spectrometer. Swelling behavior of square samples was investigated in N-methyl-2-pyrrolidinon (NMP) at room temperature. The thermal stability of samples was

determined by thermogravimetric (TG) analysis, using Setaram Setsys Evolution 16/18 instrument in argon atmosphere, at heating rate of 10 °C/min.

Results and Discussion

Some important properties of the synthesized PU networks are listed in Table 1. The soft segments content, SSC, calculated according to the feed mass ratio ($SSC\% = [W_{\text{Macrodiol}}/W_{\text{MDI}} + W_{\text{BH-2}} + W_{\text{Macrodiol}}] \times 100$), is similar for both samples. The course and the end of the reaction, as well as the chemical structure of both samples were determined by IR spectroscopy. As an illustration, in Fig. 1 is presented IR spectra of PUPTMO sample, determined at different times during the synthesis. In the IR spectra of final PU samples the diisocyanate $-N=C=O$ band ($2250-2275\text{ cm}^{-1}$) was not detected.

Table 1. The soft segments content, SSC, swelling degree, q , and characteristic temperatures of thermal degradation of synthesized crosslinked PUs

Sample	SSC, wt.%	q	T_{20} , °C	T_{50} , °C	T_{70} , °C	T_{80} , °C
PUPDMS-EO	59	4.8	351	400	438	457
PUPTMO	56	2.7	352	406	424	433

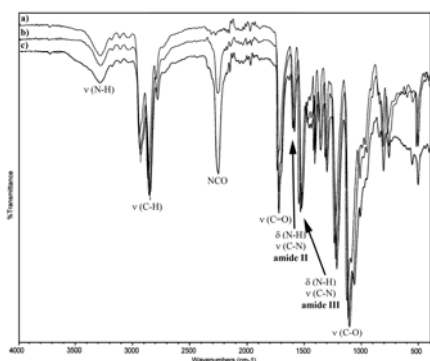


Fig. 1. IR spectra of PUPTMO sample determined at a) 26 h, b) 19 h and c) 0 h during the synthesis

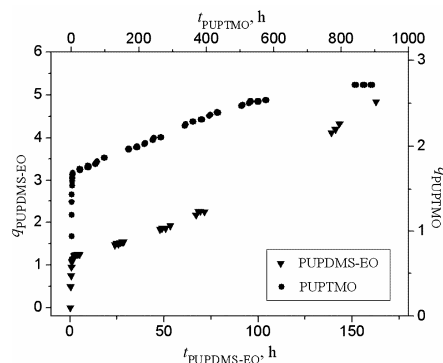


Fig. 2. The change of the swelling degree, q , with time for crosslinked PUs

The results obtained by investigation of swelling behavior of the synthesized crosslinked PUs in NMP at room temperature are presented in Table 1 and Fig. 2. Values of the swelling degree, q , were calculated using conventional gravimetric method, equation $q = (m - m_0)/m_0$ and values of the sample masses before, m_0 , and after swelling, m . The equilibrium swelling of the sample PUPTMO was accomplished after 35 days with q value of 2.7, while sample PUPDMS-EO broke up after 163 h of swelling, having q of 4.8. The reason of such big differences in swelling behavior in NMP between PUPTMO and PUPDMS-EO is the heterogene-

ity of the network composition of PUPDMS-EO, containing relatively low number of chemical cross-links and consequently much lower crosslinking density than the network of PUPTMO sample.

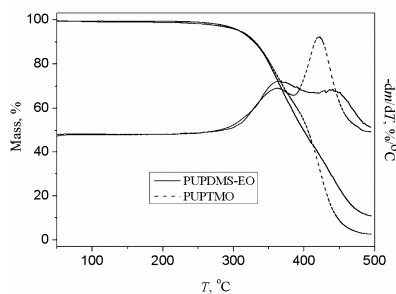


Fig. 3. TG and DTG curves of investigated crosslinked PUs, determined in argon atmosphere, at heating rate of 10 °C/min

From the results presented in Fig. 3 it can be observed that the thermal degradation of these crosslinked PUs is a two-step process in argon. This is clearly demonstrated from the thermogram derivative (Fig. 3). The thermal degradation of polyurethanes first goes via decomposition of urethane bonds, followed by breakage of the soft segment phase [4]. A measurable mass loss of investigated samples is detected between 250 and 270 °C. In Table 1 are listed temperatures obtained for mass losses of 20, 50, 70 and 80 wt. % (T_{20} , T_{50} , T_{70} and T_{80} , respectively). Up to the temperature corresponding to the mass loss of 60 wt. %, the thermal stability of PUPTMO and PUPDMS-EO is almost the same, while at higher mass loss temperatures PUPDMS-EO is more thermally stable than PUPTMO.

Conclusions

The results presented in this work show that the nature of monomer can have significant influence on the properties of PU networks. Crosslinked PU synthesized using PDMS-EO as macrodiol has much lower crosslinking density than PUPTMO sample. However, by introducing the siloxane sequences in these crosslinked PUs, thermal stability increased.

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