

Thermal stability of novel polyurethane adhesives investigated by TGA

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Abstract: The objective of the work was an assessment of thermal stability of novel polyurethane wood adhesives by means of TGA. Hyperbranched polyglycerols of various structures were used as polyol components cured with polymeric methylenediphenyldiisocyanate (PMDI) or polymeric hexamethylenediisocyanate (PHDI). Resultant adhesives were thermally degraded in temperature range 20 - 500°C. Performance of polyurethane based on fully aliphatic polyglycerol was inferior to those based on polyglycerols bearing aromatic moieties. The differences in 50%-weight loss temperature achieving 27 - 39°C as well as residual weights at 480 °C indicate the contribution of aromatic unit's presence within the macromonomer structure to increased thermal stability of polyurethane upon thermal degradation. Furthermore, temperature of 50% weight loss revealed that thermal stability of the developed hyperbranched polyglycerol-based adhesives was comparable to that of the commercial PUR adhesive.

Keywords: hyperbranched polyglycerol, polyurethane adhesive, thermal stability, TGA.

Introduction

A growing interest in extending the area of utilization of renewable resources and their application in wood adhesives have been observed for years. Detailed reviews on that field can be found in the literature^{1,2}. However, many research reports have also been published. The main resources attracting researches attention are tannins³⁻⁶ and lignin⁷⁻⁹. Attempts of involving carbohydrates¹⁰, plant oils¹¹, proteins¹² or liquefied wood¹³ in polyurethane adhesives were reported, too. New findings on the performance of the innovative nanomaterial-modified polyurethane adhesives were described in the recent literature¹⁴⁻¹⁶. There are few works regarding glycerol-derived polymers as components of wood adhesives. Recently, Mamiński et al.^{14,15} described applicability of hyperbranched polyglycerols as polyol components of PUR adhesives for wood bonding. It was shown that benzyl-functionalized HBP might provide excellent performance of the bond line. A variety of polyols and diisocyanates provide great set of combinations and variety of polyurethane properties. In consequence, resulting polymers may contain ester, ether, urea, alkyl or aryl units that influence thermal stability of the material. It is reported in the literature that

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urethane stability is affected by the concentration of urethane groups, cross-linking density or either primary or secondary hydroxyl formed urethane¹⁹⁻²¹.

As reported by Dombrow²² urethane thermal stability decreases in the order as follows: alkyl isocyanate - alkyl alcohol (250°C), aryl isocyanate - alkyl alcohol (200°C), alkyl isocyanate - aryl alcohol (120°C). Moreover, temperatures of thermal decomposition of substructures present in polyurethanes vary from 250°C for urea, 135 - 140°C for biuret to 106°C for allophanate^{23,24}.

In this paper TGA investigations of thermal stability of cured hyperbranched polyglycerol-based polyurethane wood adhesives were presented. That class of adhesives is new and not fully characterized, therefore TG analysis is a new contribution to its description.

Experimental Section

Hyperbranched polyglycerols (HBPs) used in the studies were synthesized from environmentally friendly monomer glycerol carbonate and core molecule (Bisphenol A or 1,1,1-tris(hydroxymethyl)propane). Structures are shown in Figure 1. In polyglycerol Bz-S 62% hydroxyl groups were randomly benzylated. Bis51 and Bis101 were synthesized at core: glycerol carbonate ratio, 1:5 and 1:10 (mol / mol), respectively. HBPG was synthesized at core: glycerol carbonate molar ratio 1:10. Detailed synthetic procedures and characterization of the HBPs were given elsewhere^{17,18}. Average hydroxyl functionality in Bz-S, Bis51 and Bis101 were 5.5, 7 and 12 respectively. Polyurethanes were cured at ambient temperature with PMDI (Huntsman Co.) or PHDI (Aldrich) at NCO/OH ratio 1.0 and 0.6, respectively, in the presence of 0.2% wt tin dibutyldilaurylate.

Thermogravimetric analysis (TGA) was performed on a Q500 (TA Instruments) apparatus in air (90 mL·min⁻¹) in temperature range 20 - 500°C at heating rate 10°C·min⁻¹. Samples of 20 mg were tested in triplicates. A commercial one-component PUR adhesive was used as a reference. The main components of the prepolymer were methylenediphenyldiisocyanate (MDI) and polyester polyols bearing aromatic moieties and amine-based catalysts.

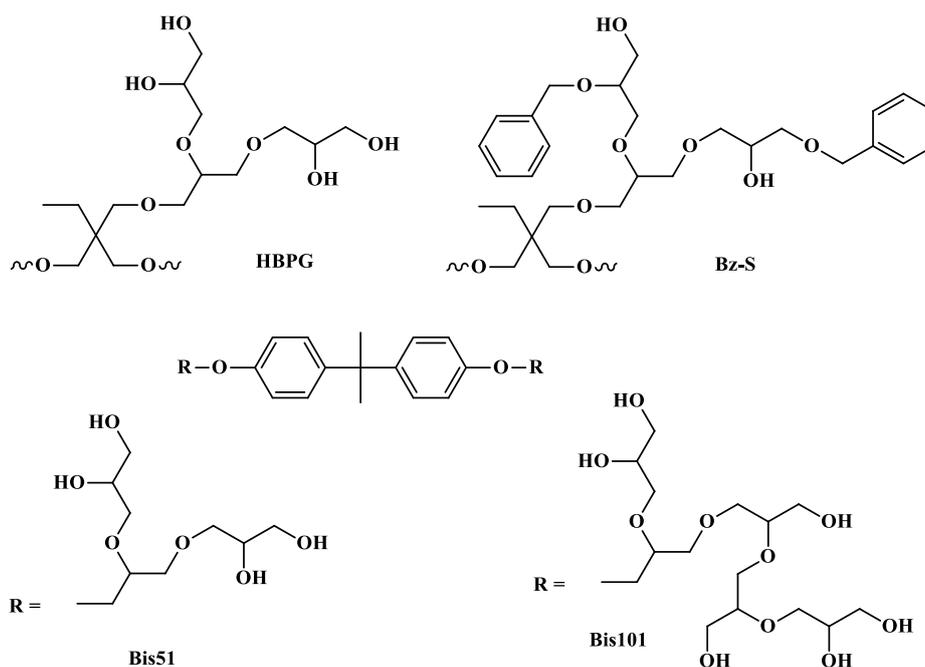


Figure 1: Structures of the polyglycerols used as polyol components of PUR adhesives.

Results and Discussion

In Fig. 2 representative TG and DTG curves of the investigated adhesive systems were presented, while in Table 1 additional data on respective PHDI-cured systems was shown.

As reported in the literature²⁵⁻²⁶ thermal degradation of a polyurethane goes through two or three stages. The first step is associated with the decomposition of hard segments and urethane linkages, while the second and third come from decomposition of soft segments. The curves in Figure 2 show two and three steps of degradation, however for Bis51-PMDI and HBPG-PMDI systems (Figs. 2 A,C) - unlike for Bz-S-PMDI (Fig. 2B) - monotonic weight loss is observed from low temperatures which might possibly result from higher volatiles content (e.g. occluded carbon dioxide liberated on curing)²⁸. The first degradation step occurring at ca. 200°C is in accordance with the literature data. Moreover, it was found that the temperature of first degradation for 7-functional Bis51 was 200.7°C, while that of 12-functional Bis101 was 205.3°C (TG curve not shown). The increase remained coherent with the statement that higher crosslink density provided higher thermal stability of a polyurethane¹⁹. In case of the system based on the benzylated polyglycerol (Figure 2 B) there are just two steps of degradation with maxima at 318°C and 383°C. According to Wang et al²⁷, first maximum occurs in the region of polyurethane degradation, while the second one might come from polyol degradation. High stability of the polyurethane based on benzylated polyglycerol is surprising, since degradation preferentially starts by scission of side chains²⁸, so benzyls should have been degraded first. Therefore, an explanation of increased thermal stability might possibly be formation of isocyanurate units degrading above 270°C²³, since the presence of the unreacted NCO groups in the cured polyurethane had been found as reported elsewhere^{17,18}.

In Table 1, 50% - and 80% - weight loss temperatures as well as sample residual weights at 480°C are shown. Based on these estimators, it is apparent that PMDI - crosslinked adhesives exhibited higher thermal stability when compared to those for PHDI - crosslinked series.

Table 1: Thermal stability estimators for the investigated PUR adhesives (air 90 mL·min⁻¹, heating rate 10°C·min⁻¹).

| Entry | polyglycerol | isocyanate | weight loss | | residual weight at 480°C |
|-----------|----------------|------------|-------------|----------------|--------------------------|
| | | | 50% | 80% | |
| | | | [°C] | | [%] |
| 1. | Bis51 | PMDI | 398.9 | — ^a | 38.6 |
| 2. | Bz-S | PMDI | 387.2 | — ^a | 39.5 |
| 3. | HBPG | PMDI | 372.3 | 463.3 | 7.9 |
| 4. | Bis101 | PMDI | 324.8 | — ^a | 36.2 |
| 5. | Bis51 | PHDI | 305.9 | 451.1 | 19.0 |
| 6. | Bis101 | PHDI | 294.7 | 468.9 | 19.2 |
| 7. | HBPG | PHDI | 266.1 | 394.3 | 2.9 |
| reference | commercial PUR | | 400.3 | 481.1 | 34.2 |

^a not achieved in temperature range 20 - 480°C

The phenomenon is not obvious since, as mentioned above, aliphatic polyurethanes are more stable than those bearing aromatic moieties. One can see that in both series the performance of adhesives containing fully aliphatic polyglycerol HBPg was inferior to those based on Bis51 and Bz-S bearing aromatic core. The differences in 50% weight loss temperatures achieving 27 - 39°C (entries 1-3 and 5-7 in Table 1) indicate the role of aromatic units fixed within the macromonomer structure.

The values of residual weights of the polyurethanes based on Bis51 and Bz-S polyglycerols (38.6% and 39.5%) were comparable to those of the reference (34.2%). Furthermore, temperature of 50% weight loss confirmed thermal stability of the developed hyperbranched polyglycerols based adhesives comparable to that of the commercial PUR adhesive.

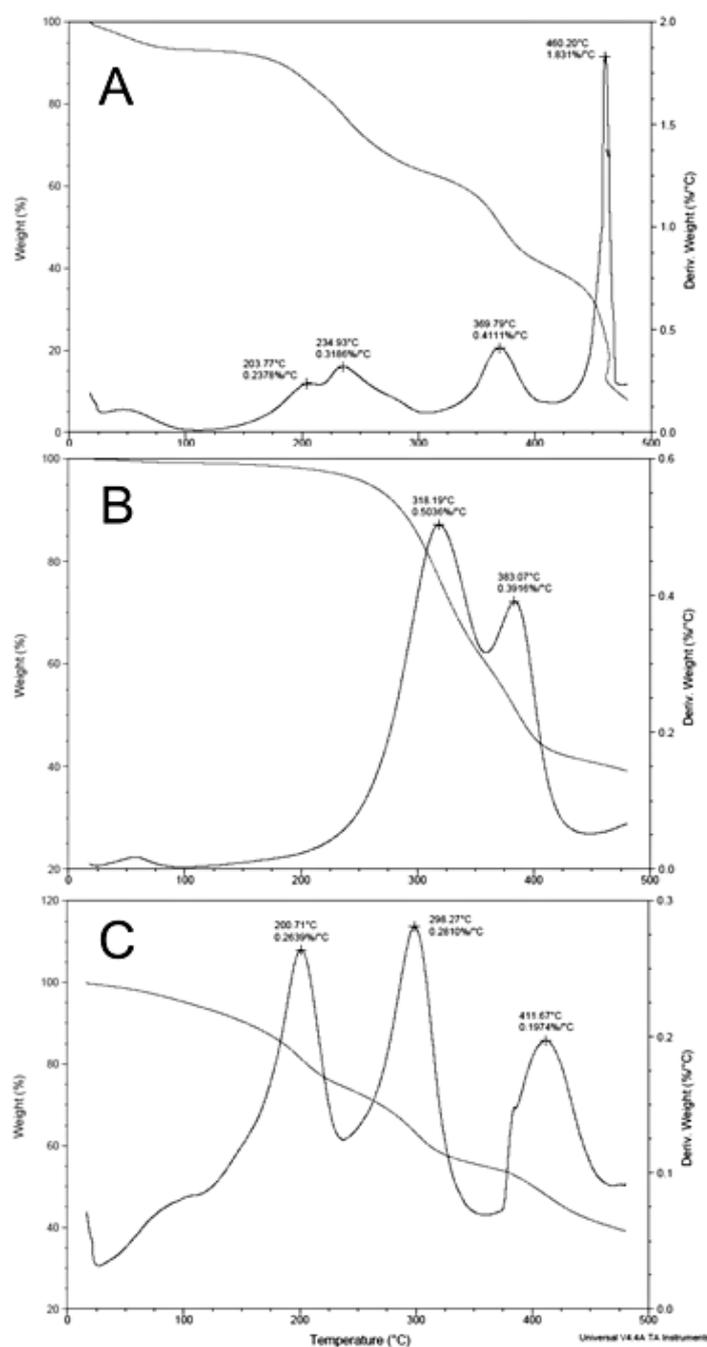


Figure 2: TG and DTG curves: A - HBPg-PMDI, B - Bz-S-PMDI, C - Bis51-PMDI.

Conclusion

The performed thermogravimetric analyses of the novel hyperbranched polyglycerols-based polyurethane adhesives revealed their thermal stability comparable to that of the commercial adhesives. Observed multi-step degradation was typical for polyurethanes²⁹⁻³¹. It was possible to show the effect of aromatic moieties present in polyol macromolecule on increased stability of PMDI-cured polyurethane. The observed thermal stability was slightly lower than that of the commercial adhesive bearing aromatic isocyanate - aromatic polyester polyol structure. The decrease might have come from large portion of aliphatic character borne by polyglycerol backbone. The observations remain in discrepancy with the literature data on fully aliphatic polyurethanes which are considered more stable on thermal degradation. Thus, further investigations on the decomposition at the temperatures above 500°C and under nitrogen instead of air would shed some light on that matter.

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