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RHEOLOGICAL AND THERMOGRAVIMETRIC ANALYSIS OF UNMODIFIED AND MODIFIED ALIPHATIC HYPERBRANCHED POLYESTER

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Abstract

The influence of the type of end groups on the rheological and thermal properties of aliphatic hyperbranched polyesters (AHBP) was investigated in this work. Unmodified, hydroxy-functional AHBP sample of third pseudo generation (AHBP-3) and the same sample whose end –OH groups were modified with stearic acid (AHBP-3SA) were examined. The presence of the long alkyl chain ends, instead of the polar –OH groups, has reduced the possibility for H-bonding and value of the glass transition temperature. On the other side, by modification of the end –OH groups with stearic acid, thermal stability of AHBP has been improved.

Introduction

The specific and unique features of hyperbranched polymers (HBP) have generated increasing scientific attention over the last years [1,2]. Their compact structure and presence of a large number of functional end groups enable a spectrum of unusual properties in comparison with analogue linear polymers.

Unmodified, hydroxy-functional aliphatic hyperbranched polyester (AHBP) of third pseudo generation (AHBP-3) and the same sample whose end –OH groups were modified with stearic acid (AHBP-3SA) were investigated in this work. The influence of the nature of end groups on the rheological and thermal properties of these AHBP was examined.

Experimental

The sample AHBP-3 was synthesized starting from 2,2-bis(hydroxy-methyl)propionic acid (AB_2 monomer) and di-trimethylolpropane (B_4 core molecule), using acid-catalyzed polyesterification reaction and pseudo one-step procedure. A detailed description of the procedure for the synthesis of AHBP-3, as well as, modification of end –OH groups with stearic acid are presented elsewhere [3].

^{13}C NMR spectra of AHBP samples were recorded on Bruker (250 MHz) NMR spectrometer in DMSO-d_6. The degree of branching, *DB*, was calculated using equations developed by Fréchet [4]. Rheological properties of AHBP were determined by Carri-Med CSL-100 stress controlled cone and plate rheometer (TA

Instruments), fitted with a 2 cm diameter cone of 2º cone angle. The thermal stability of HB polyesters was determined by nonisothermic thermogravimetric (TG) analysis, using a NETZSCH TG 209 instrument in nitrogen atmosphere, at heating rate of 5 ºC/min (flow rate of N_2 was 25 cm^3/min).

Results and Discussion

Some important properties of investigated AHBP samples are listed in Table 1. From these results and results presented in Fig. 1 it can be seen that value of the glass transition temperature, T_g, (determined from the maximum of loss modulus temperature dependence) and complex viscosity, η^*, are lower for the sample AHBP-3SA than for AHBP-3. This indicates that the presence of such long terminal alkyl chains (C18) instead of polar –OH groups, reduces to a certain amount the possibility for the H-bonding, but at the same time can induce crystallinity in the AHBP sample [5]. The sudden decrease of the η^* values at around 37 ^oC for the AHBP-3SA is ascribed to the melting of this sample, while non-Newtonian behaviour up to the 40 ^oC is probably due to the interpenetration of end alkyl groups from the surrounding molecules.

Table 1. The theoretically expected values of the molar mass, M_{theor}, values of degree of branching, *DB*, glass transition temperature, T_g, and characteristic temperatures of thermal degradation for the investigated AHBP samples

Sample	M_{theor}, g/mol	*DB*	T_g, ºC	T_5, ºC	T_{20}, ºC	T_{50}, ºC	T_{80}, ºC
AHBP-3	3498	0.45	38	240	274	297	328
AHBP-3SA	29482	0.45	29	246	285	334	388

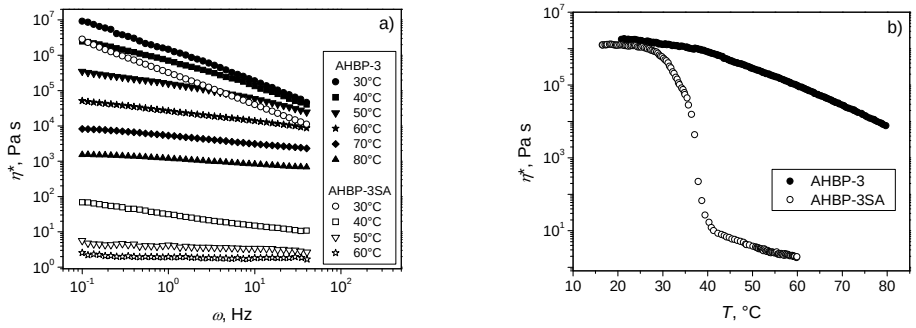

Fig. 1. (a) Frequency and (b) temperature dependences of the complex viscosity, η^*, of investigated AHBP

From the TG curves presented in Fig. 2 it can be observed that under the given experimental conditions a measurable mass loss of investigated AHBP is detected at around 220 °C. Beside that, obtained results show that the thermal stability of the AHBP increases significantly by modification of the end –OH

groups with stearic acid. This can also be seen from the results listed in Table 1, where temperatures obtained for mass losses of 5, 20, 50 and 80 wt. % (T_5, T_{20}, T_{50} and T_{80}, respectively) are listed.

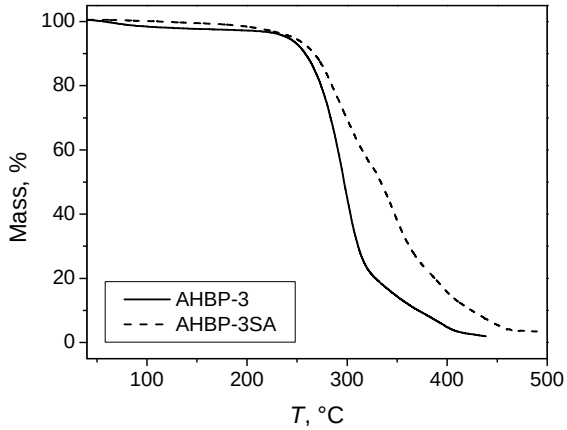

Fig. 2. TG curves of investigated AHBP, determined in nitrogen atmosphere at heating rate of 5 °C/min

Conclusions

According to the results presented in this work it may be concluded that the nature of end groups have marked influence on the rheological and thermal properties of AHBP samples. By modification of the end –OH groups with stearic acid, the values of the complex viscosity and glass transition temperature has been reduced, while thermal stability has been improved.

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