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Rheological behaviour of polymer blends containing only hyperbranched polyesters of varying generation number

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Abstract

Rheological features of melt processed hyperbranched polyesters and their blends are presented in this study. The hyperbranched polyesters showed shear-thinning behaviour for lower generation samples, whilst the higher generation ones exhibited Newtonian behaviour. This distinct shift from shear-thinning behaviour to Newtonian behaviour was also observed in the previous study for their unprocessed counterparts. This indicates that there is little change in the molecular structures during processing. The striking finding is that the blends consisting of two hyperbranched polyesters showed only Newtonian characteristics in both steady shear and oscillatory shear conditions if at least one of the components is Newtonian. This behaviour is seldom observed in polymer mixtures.

Keywords: Hyperbranched polyester; Blend; Rheology

1. Introduction

Hyperbranched polymers are members of a polymer family called dendritic polymers which have attracted great attention recently due to their intriguing molecular structures and potential applications [1–4]. Dendritic polymers are characterized by their highly branched molecular architectures and are thus capable of possessing a high peripheral functionality and can be constructed from molecules possessing two different functional groups which react with each other, such as AB_x. Each layer in the dendritic structure is called a generation. Hyperbranched polymers are much easier and cheaper to make compared to dendrimers which require the use of highly purified chemicals and complicated polymerization steps to ensure a perfect molecular structure and thus no linear sequences present [2]. Many dendritic materials have been studied in terms of their syntheses and characterization [5].

Despite the vast amount of literature appearing recently relating to these materials, rheology (and melt rheology in particular) has drawn less attention. Early work in dendrimer and hyperbranched polymer rheology showed only Newtonian features in their flow curves and the Cox–Merz rule, which correlates steady shear and oscillatory shear viscosities, has been reported to be valid [4–7]. However, our recent work on melt rheology of certain commercial aliphatic hyperbranched polyesters indicates that such materials with lower generations may exhibit shear-thinning behaviour due to the interactions between the functional groups on the molecular periphery, whilst Newtonian behaviour is observed for materials with larger molecular weights (higher generations) [8]. We proposed that lower generation hyperbranched materials showed less inward chain folding of the terminal hydroxyl groups and, along with a higher concentration of hydroxyl end groups per mass of polymer for smaller generations, had greater interactions which leaded to non-linear flow affects with shear. It should be noted that there have been reports that heat treatment of these materials above the glass transition, in the region where they flow, can lead to the formation of developed associated structures which are sometimes thermally-reversible [9]. Nonetheless, we recently found that similar rheological behaviour was observed for the materials of various generations, even if powdered hyperbranched materials were introduced to the heated plates of the oscillatory rheometer, without having being previously compression moulded into plaques [10]. Non-Newtonian phenomena has also been observed recently in Uppuliri et al. [11] with supermolecular interdendrimer hydrogen bonding

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also proposed. Such non-Newtonian behaviour occurring at lower shear rates for dendrimers was recently predicted by Brownian dynamic simulations [12].

The work by Uppuluri et al. [11] in PANAM seems to indicate that at generations greater than four, the dendrimers do not move as a single kinetic unit but that motions of individual dendrons or multiples of them (but not the whole dendrimer) become important. Recent work by Lylulin et al. [12] indicates that at very high generations, segments of the highest generation can be found to be dispersed throughout the whole dendrimer. Likewise, solid state nuclear magnetic resonance (NMR) experiments of labeled components indicate, for example, that in a generation 5 dendrimer, a large fraction of the internal, third generation units are close to the surface [13]. Thus there are many interesting structure–property relationships to be investigated in these materials as they are increasingly synthesised in sufficient quantities for melt rheological measurement.

In this work we present what is, to the best of our knowledge, the first data of the rheological properties of hyperbranched polymer — hyperbranched polymer blends. The emphasis is to examine the types of flow curves, shear-thinning or Newtonian, shown by blends consisting of rheologically-different components, for example, blends of a lower generation hyperbranched polymer and a higher one. As mentioned, the resultant blend behaviour is potentially interesting given the different appearance of Newtonian or shear-thinning behaviour of the high and low generation component materials in the blend. Furthermore, we seek to make a comparison between the above-mentioned blends with its single-component equivalent (e.g. a comparison between flow properties of a 50 wt% blend of generation 3 and 5 with the polymer of generation 4 will be made).

2. Experimental

Hyperbranched polymers used are commercial aliphatic polyesters supplied by Perstorp, Sweden, under the trade name as Boltorn Hx series dendritic polymers. For their designations, Boltorn H20 indicates that it contains two generations statistically, whilst Boltorn H50 is the hyperbranched polymer with five generations (as the chemical structures are not as precise as for dendrimers they often known as 'pseudo-generations'). Their details can be found elsewhere [8].

Blends of Boltorn polymers of different generations were prepared using a Haake Rheomix 600 internal mixer equipped with two sigma rotors. In order to limit the chemical reaction taking place, a 0.2% transesterification inhibitor (based on total weight of the blend), Irganox 1098 obtained from Ciba-Geigy, was dry blended with the polymer pellets before processing. The mixture of two kinds of Boltorn polymers with a weight ratio of unity was then blended at 110°C for five minutes with a rotor speed of 20 rpm. Neat Boltorn polymers were also processed the same way as their blends so they underwent the same mechanical and thermal history. Because Boltorn polymers are hygroscopic, they were dried in a vacuum oven at ambient temperature for 24 h before processing and measurements.

A Rheometrics Dynamic Analyser II (RDAII) rotational rheometer was used to determine rheological properties under steady shear and oscillatory shear conditions. 25 mm parallel-plate fixtures were used with a constant gap setting of 0.9 mm for all measurements. The sample was placed between the two preheated fixture plates located inside of an environmental chamber purged with dry nitrogen. Ten minutes were allowed for gap setting, removal of excessive melt and thermal equilibrium before the test started. Dynamic measurements were performed within the linear viscoelastic region determined by strain sweep tests and no preshear was applied to the sample.

3. Results and discussion

Fig. 1 shows the steady shear viscosity of the Boltorn polymers at 110°C. Boltorn polymers with lower generation like H20 and H30 exhibit shear-thinning characteristics and in contrast, H40 and H50 are Newtonian. Their behaviour under oscillatory shear is also the same, which is not shown here to avoid repetition, and the Cox–Merz rule does not

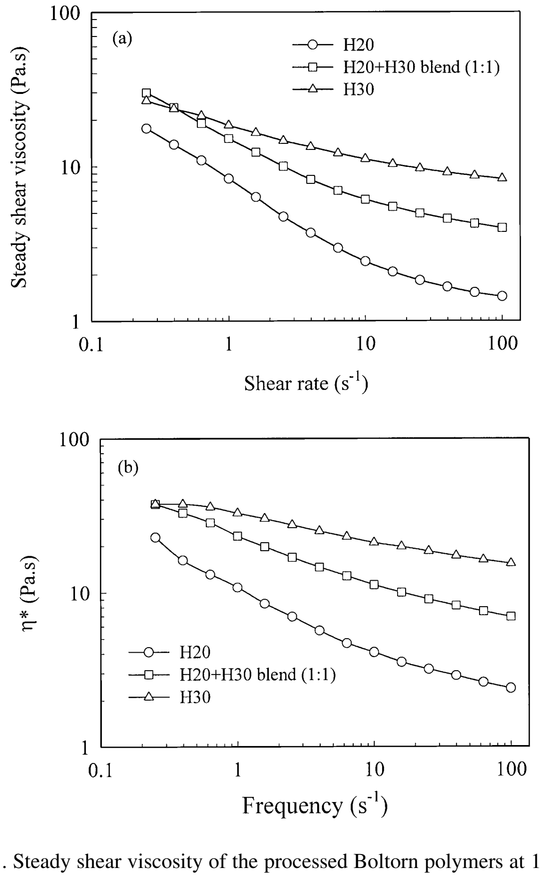

Fig. 1. Steady shear viscosity of the processed Boltorn polymers at 110°C.

apply. These results are very similar with those of their unprocessed counterparts reported in the previous study [8], although the viscosity values are not precisely the same due to the different thermo-mechanical experience undergone. The similarity in flow behaviour between processed and unprocessed materials indicates that there is little change in the molecular structures in the duration of processing. It has been proposed that lack of entanglements in the dendritic materials is the cause of their Newtonian features [5–7] which are commonly reported in the literature to date. However, melts of most flexible thermoplastics which possess numerous entanglements have been known to be Newtonian at low to intermediate deformation rates, whilst polymers with far less entanglements such as thermotropic liquid crystalline polymers (TLCPs) frequently show strong shear-thinning behaviour even at extremely low shear rates [14]. Dependence of shear viscosity on applied deformation rates, especially shear-thinning, have been known as a rheological feature for the structured fluids such as LCP and suspensions.

Fig. 2(a) shows steady shear viscosity of H20, H30 and their blend as a function of shear rates at 110°C. The blend displays a shear-thinning feature as its parent polymers. Except for shear rates below 1 s^{-1}, the blend viscosity lies between those of H20 and H30 and approximately follows the rule of addition. The oscillatory results of these samples lead to the same conclusion, except that the blend exhibits intermediate dynamic viscosity within the whole frequency range measured, which can be seen in Fig. 2(b). The flow characteristics of the blends determined by steady shear, as well as oscillatory shear, are also listed in Table 1.

Fig. 3(a) depicts steady shear viscosity of H20, H30, H40 and the blend of H20 and H40 versus shear rate at 110°C. Although H20 and H40 demonstrate different flow characteristics in which H20 behaves shear-thinning, whilst H40 is Newtonian, their blend shows Newtonian behaviour only. The Boltorn polymer with the approximate molecular weight equivalent of the blend, H30, however, is shear-thinning and is more viscous than the blend within the shear rates investigated. The influence of H20 on the viscosity of the blend is seen in the reduced viscosity compared to neat H40. The similar rheological findings can also be observed when oscillatory shear is applied to the samples, which is shown in Fig. 3(b). This Newtonian dominance is rarely observed for polymer blends consisting of components with different rheological characteristics. The opposite (shear-thinning dominance) has been frequently reported, for example, for blends of TLCP and flexible polymers [15]

Fig. 4(a) shows steady shear viscosity of H30, H40, H50

Table 1
Flow characteristics of hyperbranched polyester blends under steady and oscillatory shears

Blend pair	Steady shear	Oscillatory shear
H20 + H30	Shear-thinning	Shear-thinning
H20 + H40	Newtonian[a]	Newtonian[a]
H20 + H50	Newtonian	Newtonian
H30 + H40	Newtonian	Newtonian
H30 + H50	Newtonian[b]	Newtonian[b]
H40 + H50	Newtonian	Newtonian

[a] H30: Shear-thinning.

[b] H40: Newtonian (for comparison with blends).

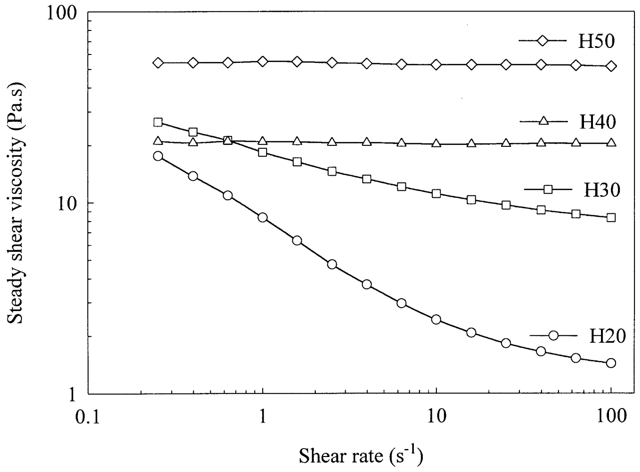

Fig. 2. (a) Steady shear viscosity and (b) oscillatory shear viscosity of H20, H30 and H20 + H30 (1:1) blend at 110°C.

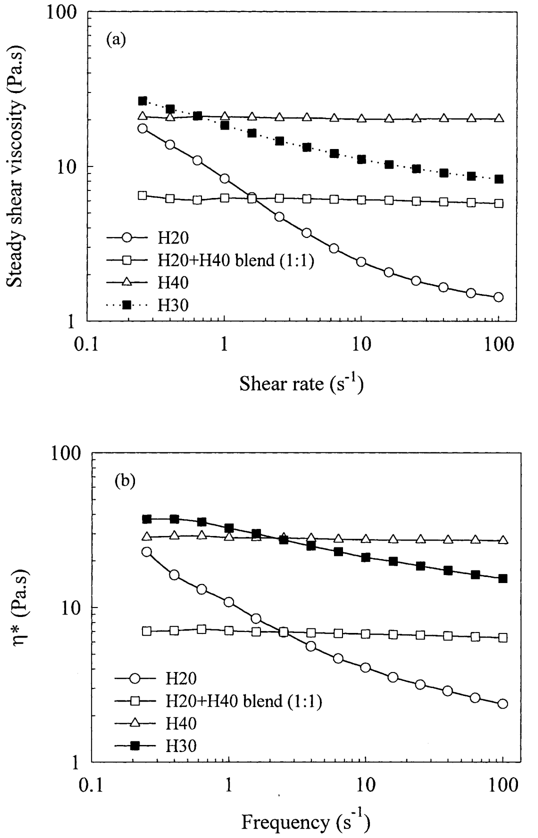

Fig. 3. (a) Steady shear viscosity and (b) oscillatory shear viscosity of H20, H30, H40 and H20 + H40 (1:1) blend at 110°C.

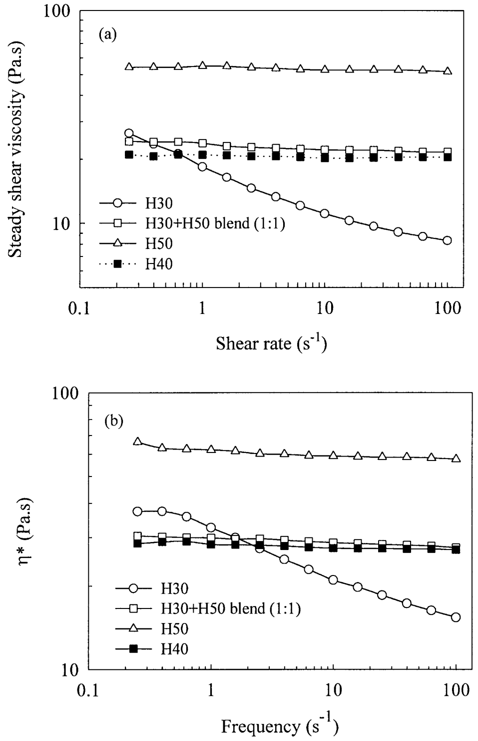

Fig. 4. (a) Steady shear viscosity and (b) oscillatory shear viscosity of H30, H40, H50 and H30 + H50 (1:1) blend at 110°C.

and the blend of H30 and H50 at 110°C. Once again, the blend behaves as a Newtonian fluid although it contains 50% of shear-thinning H30. As H40 is also Newtonian, it is more straightforward to compare viscosity of H40 and the blend. The blend is slightly more viscous than H40 within the shear rate range studied. As shown in Fig. 4(b), the oscillatory data gives the similar results as the steady shear data.

In order to confirm that the dominant behaviour of the Newtonian components in the blends containing two Boltorn hyperbranched polyesters where one is non-Newtonian does not exist only in those blend combinations discussed above, other blend pairs were also prepared and their rheological behaviour determined. Table 1 lists the results of all the blends studied. It is found that a shear-thinning blend is observed only when both component polymers are shear-thinning in nature. Otherwise, the blends predominantly display Newtonian behaviour within the deformation rate range measured. The cause of this phenomenon is not yet fully understood. As this is believed to be the first study on such blends, no directly related literature is available to offer any insight towards this somewhat unusual observation and an explanation must be sought from rheology of other materials. A polydisperse suspension of particulates, for example, which is bimodal (i.e. a colloidal fine fraction and a non-colloidal coarse fraction) gives an opposite result [16]. According to the bimodal model, the fine fraction imparts to the suspension its non-Newtonian characteristics and behaves independently of the other fraction, whilst the coarse component only contributes to an increase in the suspension viscosity. By contrast, it was observed in the present study that the higher-generation component of the Boltorn blend dictates the flow characteristics and the lower-generation portion largely affects the blend viscosity.

4. Conclusions

Blends containing only hyperbranched polyesters were prepared by melt blending and their rheological properties measured. The neat components were processed the same way as their blends for the purpose of comparison with their unprocessed counterparts [8] as well as with their molecular weight equivalent blends in terms of rheological behaviour. The similar rheological features found between the processed blend components and those that are unprocessed indicates that there is little change in the molecular characteristics during blending since the distinct change in rheology from generation 3 to generation 4 remains. Newtonian behaviour is found to be the dominant flow characteristic among the blends prepared if the components are not both shear-thinning. This phenomenon is seldom observed since it is more frequent to find that the addition of shear-thinning components into Newtonian fluids results in shear-thinning mixtures, such as blends of thermoplastics and TLCPs and suspensions.

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