Crystalline Hyperbranched Polyesters for Toners

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Abstract

Fusing and hot offset performance are dependent on the rheological properties of the toner. In this study, the influence of crystalline hyperbranched polymers on these properties is investigated. Toner resin blends containing these polymers exhibit a low melt viscosity for improved fusing and increased high temperature storage modulus for good hot offset resistance. In contrast to linear resins, these polymers exhibit rapid crystallization behavior and do not plasticize the primary toner resin.

Introduction

To improve fusing performance, toners which contain up to 20% of crystalline polymers have been evaluated.[1-3] These crystalline polymers typically are low in molecular weight and have a linear or lightly branched structure.[4] However, using these polymers can plasticize a toner by decreasing the glass transition temperature (T_g) of the primary toner resin. This results in poor toner storage stability and poor block resistance of printed sheets. The reason for this behavior is that crystallization during cooling is usually diffusion controlled and is dramatically affected by the presence of the primary toner resin.

Increasing the melt point of the crystalline polymer will improve storage stability and block resistance. However, due to the higher temperature required before polymer mobility occurs, the improvement in fusing is reduced.

A crystalline polymer should have a relatively low melt point and decrease the toner viscosity at low temperature for improved fusing. However, it should not decrease the storage modulus of the toner at high temperature. This would indicate a reduction of the internal cohesive force of the toner layer and could lead to a decrease in hot offset resistance. The crystalline polymer must not plasticize the primary toner resin and should crystallize rapidly upon cooling.

Hyperbranched polymers are highly branched and resemble dendritic or tree structures (Figure 1). They typically have a lower viscosity than linear polymers that have the same chemical composition. The number of chain end groups increase geometrically with increasing molecular weight. Reaction of the chain end groups with a crystalline monomer can give a polymer with a high concentration of crystalline groups per molecule. This results in a polymer that crystallizes by an intramolecular mechanism[5] and is independent of its rate of diffusion when used in a toner.

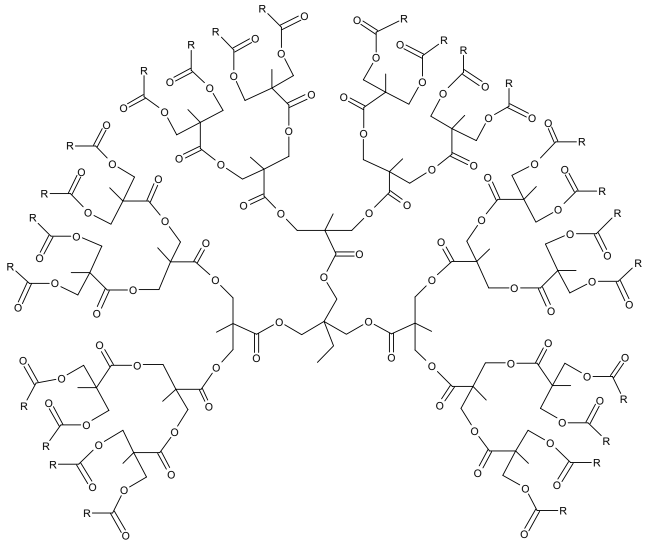

Figure 1. Idealized representation of an alkyl ester terminated hyperbranched polymer (R=alkyl group)

Preparation and Properties of Crystalline Hyperbranched Polyesters

Hydroxyl terminated hyperbranched polyesters were synthesized from the reaction of a core molecule, such as trimethylolpropane, and 2,2-dimethylolpropionic acid according to standard procedures.[6] The hydroxyl groups were then esterified with an aliphatic carboxylic acid to form alkyl terminated polymers. Crystalline hyperbranched polymers (CHBPs) were obtained when the alkyl chain contained at least 13 carbons.

The melting point of the CHBP can be changed by using different chain length alkyl end groups. Figure 2 shows the relationship of the aliphatic carboxylic acid used in synthesis and the melt point of the CHBP.

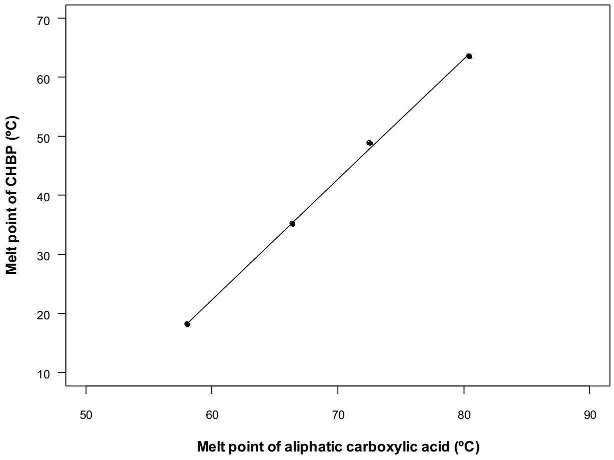

Figure 2. Influence of the melt point of aliphatic carboxylic acid monomer on the melt point of CHBP

Thermal Properties

Resin blends were prepared by melt mixing the CHBPs with a primary toner resin at 175°C in a glass reactor fitted with a paddle stirrer. The primary toner resin is a polyester based on the reaction of terephthalic acid and alkoxylated bisphenol A diol. This resin is amorphous and has a T_g of 65°C. The differential scanning calorimetry (DSC) thermogram of a blend containing 10 wt % CHBP is shown in Figure 3. For this study, a CHBP with a lower melt point was selected, so that transitions for both the CHBP and the primary toner resin could be clearly observed in both the heating and cooling cycles.

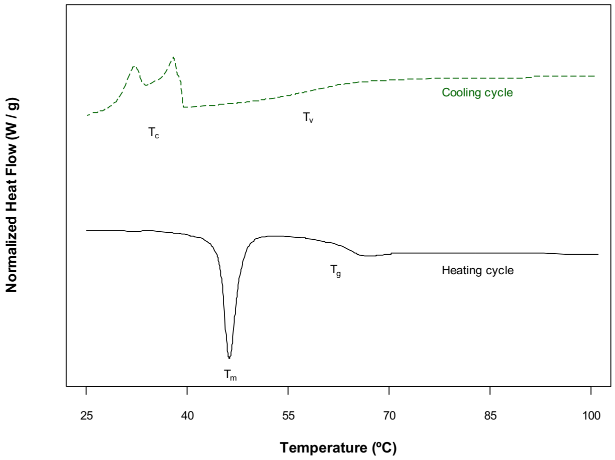

Figure 3. DSC thermogram of toner resin blend (10% CHBP)

The T_g of the primary toner polyester was almost unchanged when blended with a CHBP, even when incorporating up to 20% CHBP. In addition, the melt point of the CHBP was not affected by the primary toner resin. For comparison, blends were also prepared using an aliphatic linear crystalline resin, poly(1,6-hexylene adipate). This polymer has approximately the same melt point and molecular weight as the CHBP. Even at low use levels, blends using the linear resin resulted in a large reduction of the T_g of the primary toner resin, and only one thermal transition was observed. The results are shown in Figure 4.

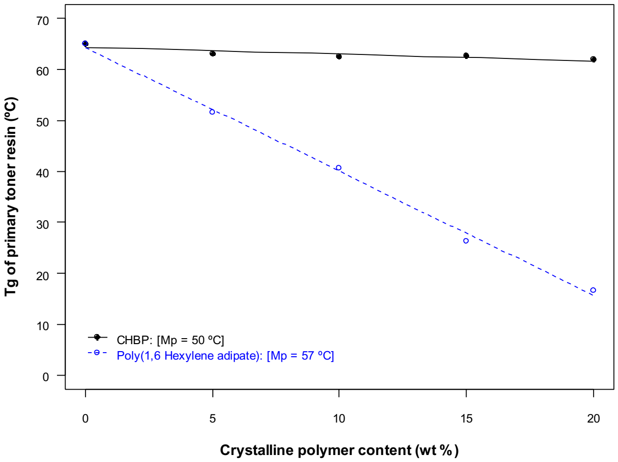

Figure 4. Glass transition temperature of toner resin blends

Rheological Properties

Despite having a higher molecular weight than the primary toner resin, CHBPs have a very low melt viscosity. At 80°C, the viscosity of the primary toner polyester is over 230,000 Pa-s, while that of the CHBP is only 0.4 Pa-s. Resin blends containing CHBPs closely follow the log viscosity mixing rule:

$$\log \eta_{blend} = \phi_1 \log \eta_1 + \phi_2 \log \eta_2 \qquad (1)$$

where η_{blend} is the melt viscosity of the resin blend, η_1 and η_2 are the viscosities of individual resins while ϕ_1 and ϕ_2 are the volume fractions of each resin.

Figure 5 shows the melt viscosity of resin blends at 105°C. Addition of 5 wt. % CHBP decreased the blend viscosity by approximately 30 %; 20 wt. % decreased it by almost 75 %.

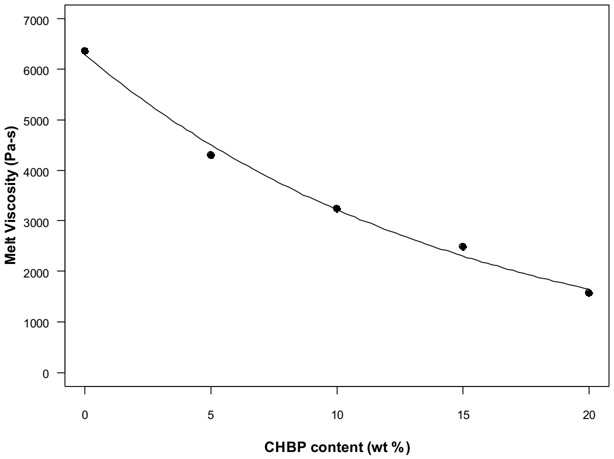

Figure 5. Melt viscosity of toner resin blends at 105°C

Typical linear crystalline toner resins have a low storage modulus and reduce high temperature storage modulus when used in a toner. CHBPs also have a low storage modulus. However, when incorporated into a resin blend, these materials result in an increase in storage modulus at high temperature. This effect is shown in Figure 6 and the extra elasticity is probably due to the shape relaxation of the dispersed phase driven by interfacial tension.[7]

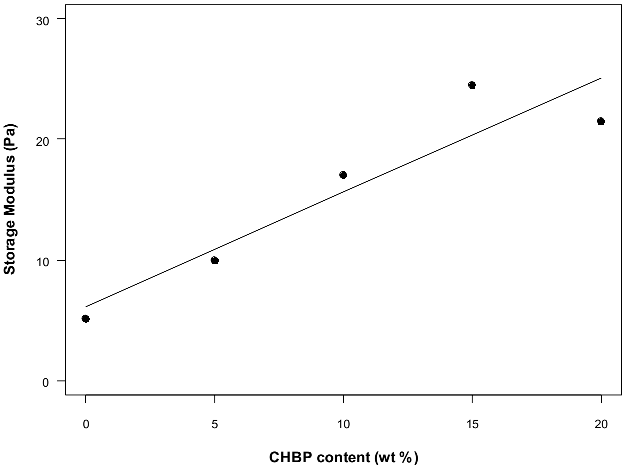

Figure 6 . Storage modulus of toner resin blends at 175°C

Kinetics of Crystallization

Because of the rapid crystallization behavior of the CHBPs, non-isothermal DSC was used to determine the crystallization kinetics upon cooling. Rate parameters were determined by fitting experimental data to the Avrami equation:

$$\theta_t = 1 - \exp[-(k_a t)^n] \quad (2)$$

where θ_t is the weight fraction of crystallized polymer at time t, k_a is the crystallization rate constant and n is a parameter that depends on the shape of the crystalline structures and the nucleation process. The total degree of crystallization (X_c) was calculated by comparing the enthalpy of crystallization during cooling to the original enthalpy of melting. CHBPs crystallize faster when the cooling rate is increased. The results for experiments using a cooling rate of 10°C per minute are listed in Table 1.

Table 1. Non-Isothermal Crystallization Kinetics

CHBP [wt %]	**k_a** [sec^{-1}]	**n**	**X_c** [a] [%]
100	0.0575	1.13	86.5
20	0.0371	1.32	90.9
15	0.0327	1.43	93.0
10	0.0282	1.69	90.1
5	0.0252	2.07	94.0

[a] Degree of crystallization during cooling cycle

Although there was a trend for a lower rate of crystallization with increasing amount of primary toner resin, the effect is not large. In each of the blends, the CHBP regained >90% of its crystalline structure during cooling. This is virtually identical to the behavior of pure CHBP. In contrast, poly(1,6-hexylene adipate) showed rapid crystallization in the pure state, but when blended shows no tendency to crystallize even after several weeks.

Hydroxyl functional hyperbranched polymers were reacted with different levels of a crystalline aliphatic carboxylic acid monomer. Table 2 shows the effect that the number of crystalline end groups has on the physical properties of the CHBP.

Table 2. Physical Properties of CHBPs

CHBP [a]	**f** [b]	**T_m** [c] [°C]	**η** [d] [Pa-s]
H-85	35	48.2	2.4
H-75	31	47.5	2.9
H-65	26	47.1	5.9
H-55	22	46.0	12.8
H-45	18	45.2	32.3
H-35	14	44.6	134.0
H-25	10	44.3	1119

[a] Numeric designation refers to the percentage of hydroxyl groups reacted

[b] Average number of crystalline alkyl end groups per molecule (calculated)

[c] Melting point from DSC

[d] Melt viscosity at 55°C

Table 3. Crystallization of CHBPs in Resin Blends (10 wt % CHBP)

CHBP	**k_a** [sec^{-1}]	**n**	**X_c** [%]
H-85	0.0327	1.34	95.1
H-75	0.0259	1.56	92.9
H-65	0.0219	1.59	91.3
H-55	0.0215	1.41	81.5
H-45	0.0185	1.33	66.3
H-35	0.0237	1.05	66.3
H-25	0.0317	1.63	62.1

In blends with the primary toner resin, it was observed that lowering the average number of crystalline groups per molecule results in less CHBP regaining its crystalline structure during cooling (Table 3). The crystallization rate, for the portion that does crystallize, was similar for each of these polymers. This suggests that a critical level of crystalline functionality per molecule is required for intramolecular crystallization to occur. Despite the reduced crystallinity of some of the CHBPs, the T_g of the primary toner resin was not noticeably affected.

Conclusions

Blending CHBPs with polyester toner resins gave reduced viscosity at low temperature and increased storage modulus at high temperature. Crystallization of these polymers was rapid, even in the presence of a high level of amorphous resin. The T_g of the primary toner resin was not significantly reduced.

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Biographies

Alan Toman received his B.S. degree in Chemistry from the University of South Florida at Tampa in 1978. Since 1997 he has worked in the Reichhold, Inc. headquarters located in Research Triangle Park, NC. His work has primarily focused on the development of polyester resins for toners. He is a member of the IS&T and the American Chemical Society.

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