Tailoring Resin Properties of In-situ Suspension Polymerized Toner

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Abstract

Tailoring resin property of polymerized toner by varying monomer ratio, temperature, initiator, pigments and cross-linking agent is being experimentally studied in this paper. The resin properties of polymerized toner and commercial melt-mixing toner were evaluated with the glass transition temperature, molecular weight distribution, softening point and melt index. Research results indicate that added pigment has a heavy influence on the resin's property.

1. Introduction

In previous paper, an in-situ suspension polymerization method was used to prepare chemical spherical toner.[1] However, the rheological property has not been analyzed thoroughly. Although the parameters of hot roll unit are important to fixing behavior, the resin property is also crucial for fixing performance. Generally speaking, qualified toner should have a low fixing temperature and wide molecular distribution.[2] However, unlike melt mixing toner where the specified resin has already prepared to meet the requirements of toner, the resin property of polymerized toner must be synthesized and tailored to meet the toner's requirement. In this paper, glass transition temperature, softening temperature and melt index are used to evaluate the property of toner.

2. Experiment

Preparation of polymerized toner can be referred to in Ref. [1]. Glass transition temperature of polymerized toner was detected by DSC (TA). SHIMADZU FLOWTESTER (Japan) was used to determine the toner's softening temperature and melt index.[3] Molecular weight distribution was measured by GPC (Waters) with pure polystyrene used as standard sample. TGA (PERKIN ELMER) was used to determine the grafting ratio of pigment.

3. Results and Discussions

3.1 Monomer Ingredients

FOX equation is frequently used to calculate the glass transition temperature (T_g) of pure copolymer.

$$\frac{1}{T_g} = \sum \frac{C_i}{T_{gi}}$$

The equation indicates the T_g of polymerized toner can be adjusted by varying ratio of monomers (C_i). Experiment results of polymerized toner with IB as pigment are plotted in figure 1, where the toner's glass transition temperature against the monomer ratio is shown. It illustrated that T_g is linear decreasing with increasing the amount of n-butyl acrylate. However, calculated T_g of toner is lower than the experimental results with 6 to 11 degrees, which is also true when carbon black was used as pigment. The reason is attributed to the existence of fine pigments particles inside of toner. These filled fine particles obstacle the random Brownian movement of polymer chain and result in a higher T_g.

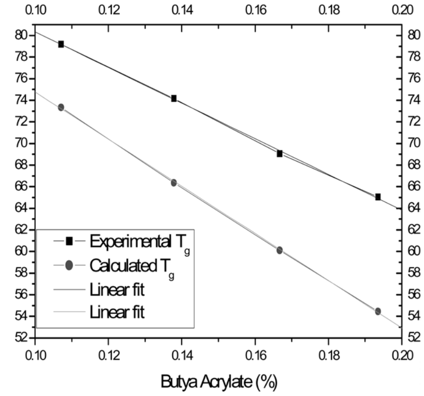

Figure 1. Relationship of T_g with Contents of n-Butyl

Another interesting thing is the DSC shape of polymerized toner is totally different with commonly homopolymer. As shown in figure 2, the DSC line demonstrated a deep peak rather than a stage when the sample was firstly scanned. However, the peak can be eliminated by annealing treatment. But the T_g value of annealed sample is a little lower than the peak value of unannealed sample (from 69.11 to 65.05). Since there is no evidence to show that the polymer is crystallized, it seems that it was the inner stress that responsible for the peak's formation. Since annealing eliminates the inner stress and quenching localizes the free volume of toner, the glass transition of polymerized toner becomes more evident when the sample was secondly scanned.

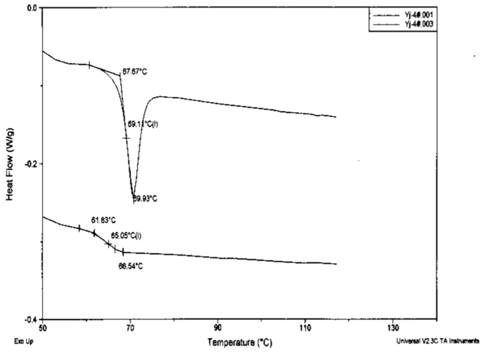

Figure 2. Shape of DSC before and after annealing higher T_g.

3.2 Effect of Temperature

The principle of free-radical copolymerization indicates that the increasing of reaction temperature will result in lowering molecular weight of resin. Experiment results are shown in figure 3 where the molecular weight distribution against reaction temperature was plotted. The average molecular weight of the toner prepared under 65°C, 85°C and 95°C are 31568, 46473 and 34636 respectively. Although the molecular weight of 85°C is higher than 95°C as expected, the molecular weight of 65°C is lowest. However, the curve of 65°C toner has two peaks with molecular weights of 700 and 54864 respectively. It seems the lower peak was caused by the inefficient conversion of the monomer. Corresponded experiment indicates that increasing reaction temperature is favor of reducing softening temperature and increasing melt index as well.

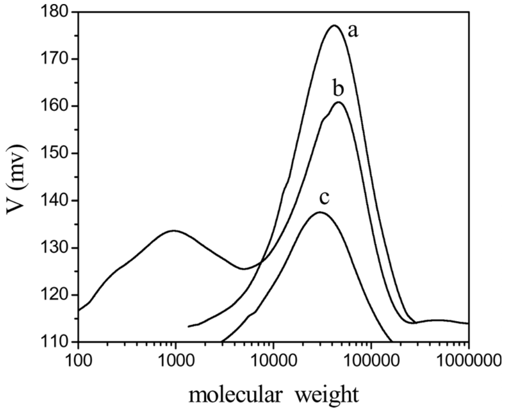

Figure 3. Effect of reaction temperature on Mw (a) 85°C, (b) 65°C, (c) 95°C.

3.3 Effect of Initiator

The increasing of initiator will also decrease the molecular weight of resin. As shown in figure 4, when the initiator amount reducing from 5.0g to 0.5g, the molecular weight increasing from 19153 to 54498, but it has no obviously effect on molecular distribution. In addition, lower amount of initiator will result in reduction of reaction's speed and monomer's conversion.

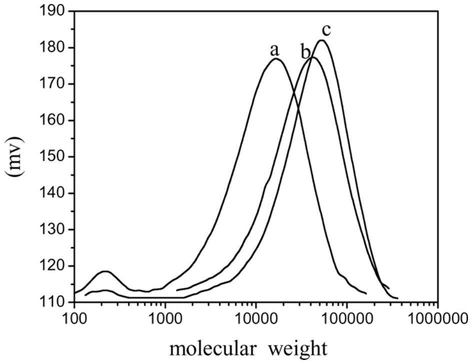

Figure 4. Effect of initiator amount on Mw. (a) 5.0g; (b) 1.0g ; (c) 0.5g

3.4 Effect of Pigment

The addition of carbon black and iron black has a different effect on the molecular distribution. As shown in figure 5, the addition of carbon black decreases the molecular weight from 25072 to 9719. However, the existence of iron black increases the molecular weight from 46473 to 76147. The difference between them was attributed to the surface property. On the surface of carbon black, there are a lot of reactive group, which may capture the free radicals and result in grafting reaction. DTA analysis indicates the grafting ratio is 26.46%. It seems this effect consumes a large amount of reactive radicals and result in insufficient conversion of monomer, which corresponded to the lower molecular weight. But for iron black, since there is no chemical reactive group on its surface, it has no effect on reducing the concentration of free radicals. However, these dispersed pigments isolated the free radicals in different area and reduced the possibility of the coupling termination of radicals, which may result in high molecular weight as shown in figure 6. Although different pigments have different effect on molecular weight, they are all capable of widening molecular weight distribution. In addition, iron black enables to increase the toner's softening temperature about 30°C and decrease its melt index to 30 times as well. As it has been discussed above, the filled pigments not only obstacle the Brownian movement of polymer chain, they also occupy the holes between the polymer chain when resin is heated above its viscosity temperature. Thus, the flowing of polymer chain is suppressed and results in a higher softening temperature.

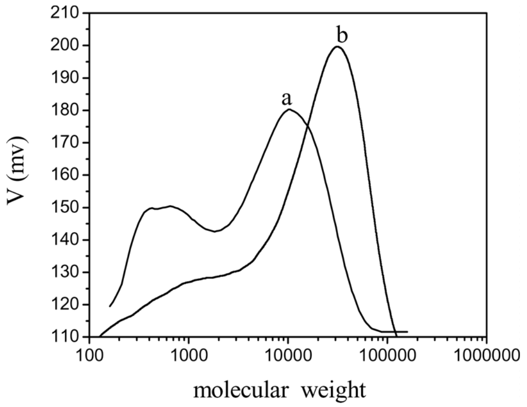

Figure 5. Effect of carbon black on Mw (a) with carbon black, (b) without carbon black.

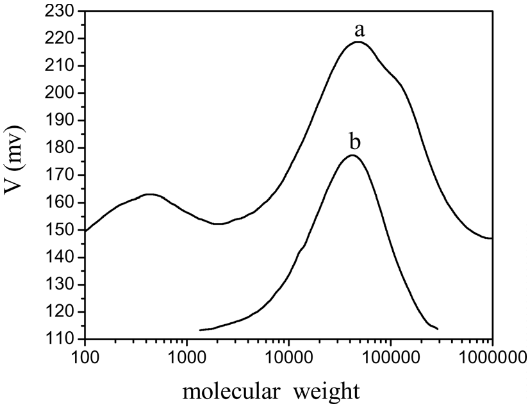

Figure 6. Effect of iron black on Mw (a) with iron black, (b) without iron black.

Table 1. The influence of cross-linking agent on toner's molecular weight, softening temperature and melt index

CA(g)	Mw	D	ST (°C)	MT (ml/s)
0	46473	2.11	101.0	1.615
1.0	26564	13.02	>150	0.009
4.0	27835	9.21	>150	hard

CA: cross-linking agent; Mw: molecular weight; D: polydispersity, ST: softening temperature; MT: melt index.

3.5 Effect of Cross-Linking Agent

The effect of cross-linking agent on molecular weight distribution and melt index was listed in table 1. Surprisingly, the addition of cross-linking agent, diethyl benzene, didn't increase the molecular weight of polymer but even decreasing its molecular weight from 46473 to 26564 (or 27835). Although their molecular weight curves also show that they have two peaks there, the higher peaks are still no more than 46473. The reason for this is not clearly understand yet. However, the softening temperature of polymerized toner was significantly increased from 101°C to more than 150°C and the melt index was sharply reduced with more than 100 times, which may be attributed to the formation of insoluble steric structure in the toner molecular.

3.6 Comparison to Melt Mixing Toner

The comparison of polymerized toner and melt mixing toner is listed in table 2.

Table 2. Resin properties of polymerized toner and melt mixing toner.

Toner	Mw	D	ST(°C)	MI (ml/s)
Polymerized	67848	22.4	132	0.0522
Polymerized	76147	13.7	134.5	0.04568
Melt mixing	73873	2.44	136.2	0.02836
Melt Mixing	38218	6.26	142.1	0.01532

The results reveal that the molecular weight distribution, softening temperature and melt index of polymerized toner is very close to the commercial melt mixing toner and can be used as a replacement for it.

4 Conclusions

Research results indicate that: (1) The glass transition temperature of toner is decided by monomer ratio; (2) Increasing the reaction temperature or the initiator amount result in decrease of molecular weight, decrease of softening temperature and increase of melt index, but it has less effect on the molecular weight distribution. (3) The addition of carbon black results in the decrease of molecular weight, however the addition of iron black results in higher molecular weight and broader distribution. At the same time, the softening temperature increases, the melt index decreases. (4) Cross-linking agent increases the toner's softening temperature and decreases its melt index. (5) The resin properties of polymerized toner are similar to commercialized melt mixing toner.

Reference

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2. Jun Yang et al, Preparation and Characterization of polymerized toner, *Journal of Information Recording Materials*, 2000, Vol. **1** No.1-2, P12-16.
3. G.Forgo et al, Styrene-acrylate copolymers as toner resin: correlations between molecular structure, viscoelastic behavior and fusing properties, *Journal of Imaging Science and Technology*, **37**(2): 176-186 (1993).

Biography

Jun YANG, Male, 1971, graduated as a Ph.D. from University of Science and Technology Beijing in 1999 and major in Chemical Engineering. From Jan 1999 to Dec 2000, be a postdoctoral research fellow in Tsinghua University and did research in the field of powder technology. Currently is a research associate in New Jersey Center for Engineered Particulates at NJIT and doing research in synthesize, mixing and characterization of nano-structured materials and engineered particulate.