Recent Progress in Polyester Resin Technology

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Abstract

Advantage of Polyester Resins

In past years, polyester resins have been mainly used for color toners. However in recent years, polyester resins have been finding more and more widespread applications in the production of all types of toners. The main advantage of polyester resin is the superior fusing performance at lower fixing temperature compared to with the conventional styrene-acrylate resins. This advantage is due in part to the inherent molecular structure of the polyester resins; in particular the roleplayed by functionalities such as carboxylic acid groups, hydroxyl groups, and ester bonds. This report will elaborate on the reasons why polyesters enjoy an advantage in lower temperature fusing.

Improvement of Disadvantage of Polyester Resins

On the other hand, polyester resins have some disadvantages such as an ambient dependency of the tribo charge, slower mill rates due to resin toughness, and increased cost due to higher specific gravity. However these disadvantages have been overcome in several ways, such as through the use of hybrid resins, (co-polymers with styrene acrylate), polymer blends, careful selection of the monomer, and so on. And also these problems can be improved by the modification of the other toner components, such as surface additives, and charge control agents.

This paper will elaborate on some of these approaches.

Introduction

In recent years, fusing at lower temperature has been required for energy saving. To meet the requirements, molecular weight of the polymer has to be reduced. Specifically, the low molecular weight portion has to be increased. (See Fig-1) But the reduction of molecular weight generally results in the formation of lower Tg value resins. In general, low Tg value resins give rise to poor storage properties. To achieve better fusing at lower temperature, it is important for resins to satisfy these contradictory properties simultaneously. (lower molecular weight and high Tg)

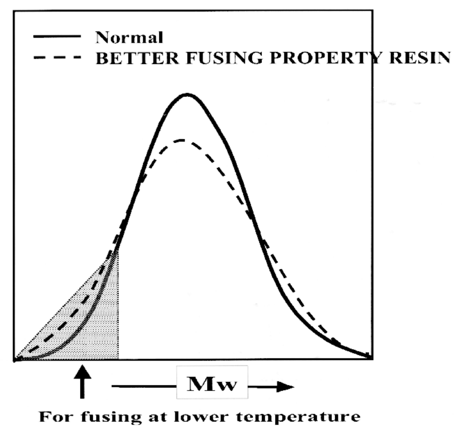

Figure 1. Schematic GPC pattern

In the market today, styrene-acrylic resins are still used for a majority of applications. But for fusing at lower temperatures, polyester resins are finding more and more widespread applications. This paper will elaborate on the reason why polyester resins enjoy an advantage in lower temperature fixing.

Advantage of Polyester Resins

Tg Value Comparison of Polyester vs Polystyrene Resins.

First, consider Tg values of polystyrene and polyester resins at differing molecular weights, especially lower molecular weight polymers. (Table-1 and 2)

Preparation of Polyester Resins

The monomer compositions of PES2, 3, 4, 5 are polyoxypropylene Bisphenol A and terephthalic acid. The degree of polymerization of PES-2, 3, 4, 5 is respectively changed by adjusting reaction time. Table-1 shows weight average molecular weight (Mw) and glass transition temperature (Tg) of these polyester resins.

Table 1. The Properties of Polyester Resins

Resin Name	Mw	Mw/Mn	Tg
			C
PES-2	767	1.25	11.73
PES-3	2309	1.87	43.53
PES-4	3512	2.10	56.17
PES-5	4779	2.28	62.01

The molecular weight was measured by ASTM 3536-91. The glass transition temperature was measured by a differential scanning calorimeter "DSC 200" manufactured by Seiko Instruments Inc., measuring condition: heating rate 10C/min

Preparation of Polystyrene Resins

Standard polystyrene resins were analyzed. Table-2 shows weight average molecular weight (Mw) and glass transition temperature of these polystyrene resins.

Table 2. The Properties of Polystyrene Resins

Resin Name	Mw	Mw/Mn	Tg
			C
A-300	448	1.13	-22.3
A-500	526	1.15	-17.2
A-1000	870	1.1	1.43
2000	1890	1.06	55.72
A-2500	2630	1.05	58.47
4000	4000	1.06	78.39
2012-8	7000	1.03	86.7
F-1	10300	1.02	92.2
F-4	43900	1.01	102.1

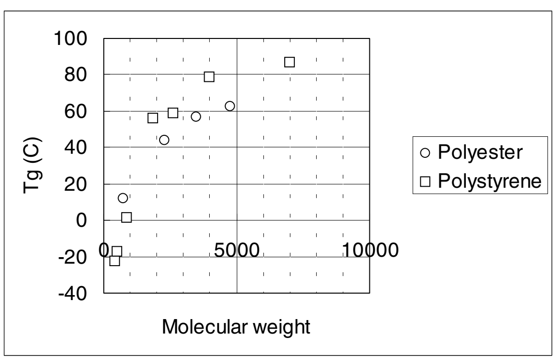

Figure 2. Molecular weight vs. Tg plot of polyester and polystyrene resins

Figure 2 shows the following results:

1. For both polyester and polystyrene resins, Tg is proportional to its molecular weight.
2. At lower molecular weight (less than 2000), Tg value of polyester is higher than polystyrene.
3. The degree of change of Tg for polystyrene resins is larger than that for polyester resins.

In general, styrene-acrylate resins are used for toner. Tg value of styrene-acrylate is lower than that of polystyrene. Thus Tg value of polyester is higher than that of conventional styrene-acrylate resins. Then lower molecular weight polyester resins can be used. It leads to be superior fusing at lower temperature,

Improvement of Disadvantage of Polyester Resins

Ambient Dependency of the Tribo Charge

Especially at high humidity conditions, polyester resins have a tendency to absorb moisture. This tendency is due to the hydrophilic functional groups ,such as carboxylic groups, hydroxyl groups and ester bonds inherent in the polymer chain.

Various compositions of polyester resins were analyzed for moisture absorption by loss of volatiles method.

Table 3. The monomer Components of Various Resins.

Resin Type	Acid Component	Alcohol Component	Comment
Non-bis	Terephthalic acid	Ethylene glycol	
High AV Resins		Bisphenol-A propylene oxide adduct	AV is 35
Low AV Resins			AV is 3.5
PES-DSA	TPA and DSA		
Hybrid 30			
Styrene-Acrylate	Styrene and 2-EHA		

2EHA:2-ethylhexyl acrylate, TPA: terephthalic acid
DSA: dodecenyl succinic anhydride

Table 4. Absorbed Water of Various Resins (%)

Resin Type	Water %				Comment
	Day				
	0	1	2	10	
Non-bis	0.55	0.83	0.79	0.96	
High AV Resin	0.15	0.25	0.40	0.40	AV is 35
Low AV Resin	0.15	0.2	0.22	0.23	AV is 3.5
PES-DSA	0.15	0.18	0.22	0.22	
Hybrid 30	0.15	0.2	0.22	0.20	
Styrene-acrylate	0.05	0.10	0.10	0.10	

Table 4 shows the following results

(1) Ester Bond Effect

In these polyester resins, especially, Non-bis containing ethylene glycol as the alcohol component tends to absorb moisture more than other polyester resins. Ethylene glycol is short-chain aliphatic alcohol, thus the ester bond % is higher than other polyesters containing polyoxypropylene Bisphenol A as the alcohol component. Ester bond tend to absorb moisture easily.

(2) Acid value effect

From the results listed in Table 4, low AV resins tends to absorb less moisture than high AV resins.

The use of Bisphenol-A type polyesters and the reduction of acid value of polyester resins are effective ways to circumvent the ambient dependence disadvantage

In addition, hydrophobic surface additives and charge control agent are effective against this disadvantage.

2. Slow mill rate (Crushability)

In recent years, smaller particle size of toners have been required because of the demand for high resolution images. Then more crushable resins have been required.

When the mill rate is compared between styrene-acrylate polymers and polyester resins of similar molecular weight, the mill rate of polyester resins is lower. This disadvantage is due to the inter-molecular interaction.Table 5 shows crushability (mill rate) of various polyester and styrene-acrylate polymers. Crushability can be deduced by means described in US Patent 5,607,805.

Table 5. Crushability (Mill rate) of several resins

Resin Type	Mw 10^4	Mn 10^3	Mill Rate	Comment
Low TMA	5.1	3.5	15	
High TMA	5.1	2.0	10	
Blended Polyester	5.1	2.0	12	
DSA PES	5.1	5.1	20	Reference PES(HB)
Hybrid 20	5.1	3.5	12	
Hybrid 30	5.1	3.0	7	
Styrene-Acrylate	5.0	3.5	6	

TMA: trimellitic acid (cross-linking agent)
Mn: number averaged molecular weight

Table 5 shows the following results:

(1) TMA cross-linking effect

From the results of crushability testing, it can be seen that high TMA resins can be crushed more easily than low TMA resins. By increasing the amount of cross-linking (more TMA), the length of polymer chain decreases (Mn) which leads to easier crushing.

(2) Blended resin

Blended resins with low molecular weight polyester are more crushable than non-blended resins, such as DSA PES. By adding low molecular weight PES, number averaged molecular weight (Mn) decreases and crushability increases.

(3)Hybrid resin (co-polymer with Styrene-acrylate)

Hybrid resins are prepared by the procedure described in US Patent 5,391,695. The ratio of polyester to polystyrene (Hybridizaition degree) was changed as follows: 100/0(reference resin: DSA PES), 80/20(Hybrid-20) and 70/30(Hybrid-30). It can be seen that crushability is proportional to the degree of hybridizaition.

The polymer blends with lower molecular weight polyester and hybrid resin (co-polymer with styrene-acrylate polymer) are effective against slow milling disadvantage

In addition to these chemical methods, pulverizing equipment for toner production has been improved.

Conversely, in recent years, high speed printer and PPC machines have been launched. Also non-magnetic monocomponent development systems have been developed. These systems require the resin to be more tough (slow mill rate). Tough polyester is suitable for these applications.[7)]

3. Higher Specific Gravity

This disadvantage is also due to the inter-molecular interaction mentioned above. Table-6 shows specific gravity of various polyester and styrene-acrylate polymer.

Table 6. The specific Gravity of Several Polymers

Resin Type	Specific Gravity g/ml
Non-bis	1.30
PES-4	1.20
PES-DSA	1.15
Hybrid 10	1.14
Hybrid 20	1.13
Hybrid 30	1.10
Styrene-acrylate	1.059

Table 6 shows the following results:

(1)Ester bond effect

From the result of specific gravity of Non-bis and other resins (Bisphenol-A type resins), Non-bis containing ethylene glycol as the alcohol component tends to have higher specific gravity than other polyesters. Ethylene glycol is a short-chain aliphatic alcohol, and the ester bond % is higher than other polyesters containing polyoxy-propylene Bisphenol A. Ester bonds are hydrophilic functional groups which can have lead to higher specific gravity.

In addition, Non-bis is similar composition with PET. These are typical types of crystalline polymers. TPA and ethylene glycol are symmetrical monomer. Thus, polymer structures whose monomer composition is symmetric are symmetric. So intermolecular interaction will occur easily.

From the two reasons mentioned above, specific gravity of Non-bis is higher than other polyesters.

On the other hand, Bisphenol-A type polyesters and hybrid resins (co-polymer with styrene-acrylate polymer) are effective against this disadvantage

Conclusion

Polyester resins have the advantage in fusing at lower fixing temperature than conventional styrene-acrylic resins. This advantage is due to the higher Tg at lower molecular weight. Higher Tg is due to the intermolecular interaction, such as hydrogen bond between acid groups and hydroxyl groups.

On the other hand polyester resins have some disadvantages as follows. These disadvantages are due to the hydrophilic functional groups and the intermolecular interaction mentioned above. However these disadvantages can be circumvented in following ways:

1. **Ambient dependency of the tribo charge**
   Lower acid value polyester resins, Bisphenol-A type polyester resins and the use of hydrophobic surface additives and charge control agents are effective against this disadvantage

2. **Slower mill rate**
   polymer blends with lower molecular weight polyesters and hybrid resins (co-polymer with styrene-acrylate polymers are effective against this disadvantage

3. **Higher specific gravity**
   Bisphenol-A type polyesters and hybrid resins (co-polymer with styrene-acrylate polymers) are effective against this disadvantage.

References

1. David E Stark, Polyester Resins Their Future for Color and Black Toners, 3rd Annual Imaging Chemical Conferences, Orlando, Florida, 2000, pg. 173.
2. Graham J Galliford, Market Update for Toner Raw Materials, 3rd Annual Imaging Chemical Conferences, Orlando, Florida, 2000, pg. 157.
3. Masayuki Maruta, The Material Design of the Polyester Color toners, IS&T, NIP12, San Antonio, pg. 488. (1996).
4. Koji Nakayama, New Polyester Resin for Toner Having Excellent Fixing Properties, IS&T, NIP14, Toronto Ontario, pg. 394. (1998).
5. USP 5607805
6. K. Tanaka, Proceedings of Symposium on Electrical Charging of Fine Particles and Electrophotographic Toner Technologies, pg. 37, (1995)
7. M. Maruta, 45 th Proceedings of Symposium on Electrophotogaraphy, pg. 117, (1998)

Biography

Yoshihiro Ueno received his B. S. and M. S. degree in Polymer Chemistry from the University of Kyoto at Kyoto, Japan in 1987. Since 1987 he has worked in the Wakayama Laboratory for Research and Technology at Kao Corporation in Wakayama, Japan. His work has primarily focused on the design of super-absorbent polymer, secondary on the design of polymerized toner and encapsulated toner, and tertiary on the design of polyester resins for toners.