Polyester vs. Styrene: Binder Choice for Toners in Digital Printing

Dinesh Tyagi, Eastman Kodak Company, Rochester, NY 14653-4180, USA

Abstract

In electrophotography, the choice of polymer as toner binder is primarily limited to polyester or styrene–acrylate type vinyl copolymers. Each type of resin provides several unique advantages over the other. Although, the printer segment market once defined the choice of toner polymer, it is no longer the case now. Both types of polymers are now being used from low speed to very high-speed printers as toner binders. Similar trends are found in color and monochrome applications as well. An attempt was made to compare both types of toner resins across numerous performance criteria. Various toner samples were prepared using each type of binders and evaluated for different attributes. It was found that, at low molecular weights, higher Tg and toughness can be more easily achieved with polyesters resins based on bis-phenol A. These low MW resins are especially desirable in color toners where low melt viscosities are preferred for higher speed fusing and richer color reproduction. Although broad fusing latitude could be obtained with either type of polymer binder, the polyester based toner show better adhesion and fusing quality than vinyl counterparts. Styrenics, on the other hand, are less expensive and provide improved dispersion of waxes. Some differences in the tribocharging performance of the two resins were observed but comparable charges can be achieved with either resin by proper selection of toner formulation.

Many attempts have been made to reduce existing performance gap between the two polymers by either using a blend approach or by chemical bonding these two dissimilar and incompatible polymers. However, the desired results have been far from satisfactory. With the recently increasing trend in toner manufacturing towards chemically prepared toners, the choice of polymer has also become an issue. The choice of suitable toner binder is now restricted entirely by the manufacturing technique selected. Depending on the application, a case can be made for each polymer as the best choice for toner application.

Introduction

Digital printing has infused a new life to electrophotography by meeting new requirements from printed images with ease. There is an increased expectation from digital output in terms of increased image quality, cost per page and speed. As the market grows for digital printing, so does the burden on toner particles to meet these demands. Since polymer binder comprises the largest portion of the toner composition, the choice of binder plays a critical role in defining customer expectations, toner performance and manufacturing techniques. As digital printing embraces new applications, additional constraints are being continuously placed on toner binder.

The choice of polymer as toner binder is essentially limited to only a selected few as shown in Table I[4]. Also listed are the methods used for the polymerization of these binders. Among the toner polymers in use today, styrene-acrylate copolymer and polyester comprise the vast majority of the toner polymers employed.

TABLE I: Various polymers in use as toner binders

Toner Polymer	Polymerization Mthod
Vinyl polymers (Styrene-Acrylate, Styrene-butadiene)	Addition Polymerization - free radical initiated - Suspension - Emulsion - Solution - Bulk
Polyester	Step Growth/Condensation Polymerization - Catalyzed
Cyclic Olefinic Copolymers	Bulk or Solvent Polymerization - Ethylene-norbornene hydrocarbons - Metallocene catalyst
Polyether Polyols	Step Growth Polymerization

Many types of molecular architectures have been produced with these polymers depending on the application needs. These range from monomodal to bimodal and even cross-linked polymers for use in toner applications. Method of toner manufacturing, especially for chemically prepared toners, often dictated the choice of toner resin that can be employed.

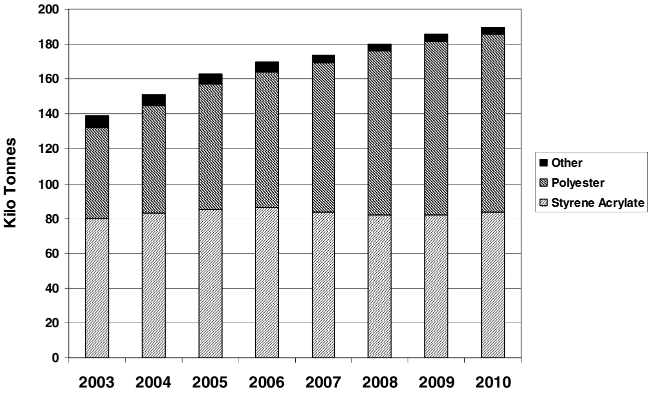

Figure 1*. Worldwide toner resin production for various polymer types[1].*

As shown in Figure 1, the polyester toner resin has now captured the lead from styrene-acrylate as the toner binder of choice [1]. The increase in polyester resin use is due because of its use in both black and color toners. Currently, about 88 percent of the toner market is captured by conventional Melt Pulverized Toners (MPT). Chemically Prepared Toners (CPT), in which volume of black toners produced is twice as much as that of color toners, fills the remaining toner demand.

Toner Binder Considerations

Several considerations go into a binder selection for any given toner. These requirements are often at odds with each other and include:

1. Brittleness for MPTs
2. Solubility for certain CPT processes
3. Toner rheology and viscoelastic behavior
4. Color and Transparency
5. Binder Cost
6. Adhesion to substrate
7. Fusing latitude and low temperature fusing
8. Tribocharging and charge stability
9. Environment sensitivity
10. Plasticizer resistance
11. Dispersion of toner additives (wax, CCA, pigment)

There are several features in styrene-acrylate copolymers that make them attractive as toner resin. Such resins are often more economical with a good balance of brittleness and toughness above 12,000 molecular weight. Dispersion of olefinic and aliphatic waxes is typically better with such vinyl copolymers, but the dispersion of pigments and charge control agents is often lacking in performance. Styrenic binders are quite easily attacked by plasticizers that are commonly used PVC but are more resistant to moisture. It is fairly simple to control the molecular weight and thermal properties of the styrene-acrylate copolymers and can cross-linked with the inclusion of a small quantity of additional comonomer such as divinylbenzene. Once there were more choices available as charge control agents for vinyl polymers, but that difference is not an issue any more.

Commonly used bisphenol A polyester binders provide an enormous toughness advantage at low molecular weight for toners. These toner binders can be fused at lower temperatures with good adhesion to wide range of substrates. Although, typical plasticizers cannot easily attack these binders, polyesters are affected by moisture after prolonged exposure to high humidity conditions. Good dispersion of charge control agents and pigments can be obtained with polyester resins. However, obtaining good dispersion of waxes is often more challenging. Typically polyester based toners exhibit faster charging rates and are relatively more negative tribocharging as shown in Table II.

Attempts have been repeatedly made to produce resins that can incorporate the advantages of both types of polymer resins by either melt blending or copolymerization techniques. In most cases, the results have been far from satisfactory and many disadvantages of both resins have also been carried over into such hybrid polymers.

Table II: Triboelectric series for various polymers

Polyamide	**Positive**
Polydimethylsiloxane	↑
Polymethyl methacrylate	
Styrene-Butadiene copolymers	
Styrene-butyl acrylate copolymer	
Polyethylene terephthalate	
Polyacrylonitrile	
Polycarbonate	
Polystyrene	
Bisphenol A polyesters	
Polyethylene	
Polypropylene	
Polyvinyl chloride	↓
Polytetrafluoroethyne	**Negative**

Melt Viscosity Behavior

A viscoelastic response of a styrene-acrylate copolymer is illustrated in Figure 2 along with the results obtained for a bisphenol A based polyester binder. The styrene equivalent molecular weight distribution for the two polymers is very similar. As shown, the viscosities of the two polymers are very similar and equal at about 125°C. However, the melt elasticity of the styrenic copolymer is an order of magnitude lower in the terminal region. It is likely that the higher critical molecular weight of SB copolymer curtails the chain entanglement causing decrease in melt elasticity.

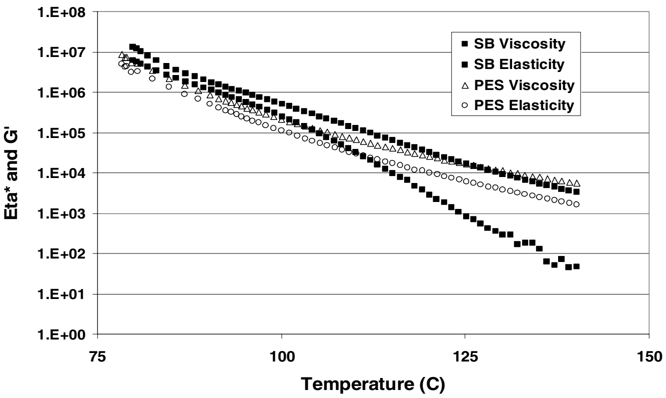

***Figure 2**. Viscoelastic response of styrene-acrylate and polyester binder*

For digital color applications where low melt fusing characteristics are desirable, low molecular weight polymer are often preferred. As mentioned previously, controlling the molecular weight can easily control the melt viscosity of styrene-acrylate copolymer. This is typically done with the aid of chain transfer agents along with the increased amount of initiator used during the free radical polymerization. A cross-linking agent can be incorporated if branched or gel structure is desired. For polyester binders, which are prepared by condensation polymerization, the monomer composition and reaction time are typically used to control molecular weight distribution.

Thermal Properties

As long as the polymer molecular weight is above their critical entanglement molecular weight, the glass transition temperature depends only on the polymer composition. For high molecular weight random copolymers, Tg is determined by the weighted average of the respective homopolymers as described by Gordon-Taylor equation[2]. But as the molecular weight is lowered, the glass transition temperature is reduced as expressed by the Flory-Fox equation[3]:

$$Tg = Tg_{\infty} - K/\langle Mn \rangle$$

Thermal properties were collected on styrene-butyl acrylate copolymers, all containing 75 weight percent styrene. The results are summarized in Figure 3. As the molecular weight falls below the critical molecular weight of 15,000, the Tg drops precipitously.

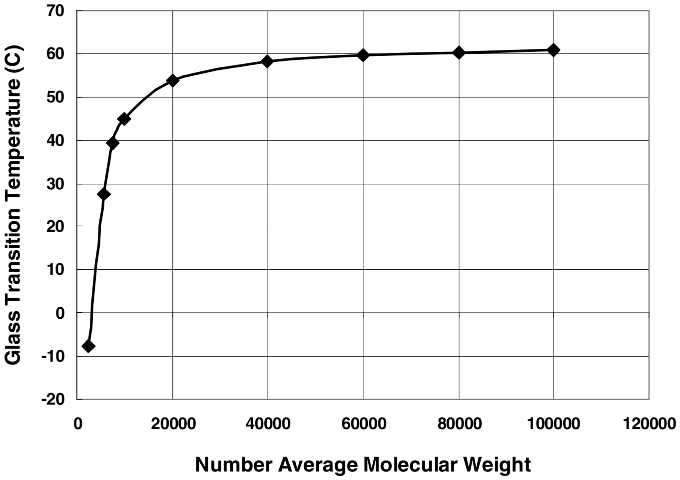

***Figure 3**. Relationship between glass transition temperature and molecular weight of a styrene-butyl acrylate copolymer (75/25).*

Changing the composition of the vinyl copolymer can compensate for such a drop in glass transition temperature. If the amount of butyl acrylate comonomer is reduced, then it would be possible to increase Tg. Figure 4 demonstrates DSC results from such an experiment where the amount of butyl acrylate monomer is reduced in order to obtain a copolymer with a constant Tg of 60°C. From these results it can be easily seen that when a low viscosity binder is required, the vinyl polymer would have to essentially consist of low molecular weight polystyrene. At these molecular weights, not only is Tg affected with any molecular weight variation between lots, but the binder is extremely brittle. Under these conditions resulting toners are not likely to withstand mechanical attrition during manufacturing, electrophotographic process or meeting print physical requirements.

Although polyesters exhibit similar behavior of lower Tg with the lower molecular weight. But the critical molecular weight of polyester is much lower. As a result, it is possible to produce tough toner binders that have low fusing performance necessary for digital color printing.

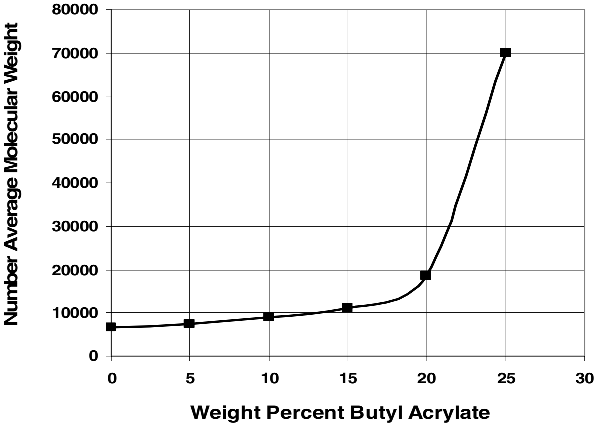

***Figure 4**. Molecular weight of copolymer and the butyl acrylate amount necessary to obtain a Styrene-Acrylate polymer with a Tg of 60°C*

Attempts have been to measure the mechanical properties of toner polymers. Since these polymer binders are typically very brittle, it is usually very difficult to good measurements on wide range of polymers. One method that works fairly well is measuring the surface area of particles created when these polymers are pulverized under the same grinding conditions. The results show that equivalent melt viscosities, bisphenol A based polyester have lower surface area than styrene-acrylate copolymers due to higher toughness.

Chemically Prepared Toners

In recent years, there has been a noticeable shift in the manufacture and use of toners manufactured by non-conventional methods. Although CPT term is used to describe toners other than melt pulverized toners, there are multitude of manufacturing processes that are used to make such toners. A list of various CPT manufacturing processes is listed in Table III along with the types of polymers used [4].

TABLE III: Various types of CPT processes and binder choice

CPT	Resin Pzn Method	Toner Binder
Suspension	Suspension	Styrene-acrylate
Emulsion Aggregation (EA)	Emulsion	Styrene-acrylate
Encapsulation	Suspension/Emulsion Step Growth	Styrene-acrylate, polyester
PxP	Step Growth	Polyester
Dispersion Pzn	Step Growth*	Polyester
Precipitation	Step Growth*	Polyester
Solvent Dispersion	Step Growth*	Polyester
Chemical Milling	Step Growth*	Polyester

*pre-formed polyester

The chemically prepared toners offer several advantages over the conventional MPT technology[5]. Some of the advantages with CPT include:

- Small particle size
- Narrow size distribution
- Various toner shapes with wide and controllable range of toner circularity surface roughness
- Good pigment dispersion
- High wax loading and uniform dispersion
- Uniformity of composition
- Core-shell technology possible
- Surface chemistry control

Toners prepared by chemicals means are typically more difficult to recycle and any residual surfactant/dispersants can adversely affect the toner charge and its environmental charge stability

Of the various types of chemically toners commercially available today, the emulsion aggregation and suspension polymerization types are most common. As a consequence, the CPT continues to be predominantly based on styrene-acrylate type of binder resins. Such toners have a much higher melt viscosity for a number of reasons as discussed earlier. In most cases, this is not a serious limitation because of the equipments such toners are selected for. Most such toners are used in relatively slow speed desktop color printers and monochrome applications.

For high-speed color printers, polyester would be much better suited than styrene-acrylate polymers because of their superior mechanical toughness at low molecular weights. It is possible to produce low melt viscosity toners without having to use very brittle polymer binder that can cause a negative impact on developer life and image permanence. Although polyesters can be cross-linked, there are limitations in how they can be used in some CPT processes. Since polyesters cannot be polymerized by addition polymerization methods, EA and suspension based polyester CPTs are not possible. Most CPT manufacturing techniques that can use polyesters involve the use of solvent or plasticizers. There is work being done to make polyesters dispersions by mechanical and/or chemical means to produce polyester based CPTs without using solvents.

Styrene-acrylate copolymers are generally less expensive than polyester resins, but the manufacturing cost of toners based on different CPT processes is still quite similar regardless of the binder polymer used. Advances are being continuously being made in CPT manufacturing processes and as a consequence, the price difference against MPT is slowly shrinking.

Environmental Issues

The eco-labeling programs have initiated a closer scrutiny of toxicological impact of all toner ingredients and polymer binders are no exception. There are potential issues with both styrene-acrylate and polyester binders that that has received considerable attention[4].

Vinyl polymers always have some amount of volatiles that remains with binder even after the polymerization. These volatiles consist of styrene and acrylate monomers, initiator fragments and certain other volatile organics. The total VOC limited is often surpassed with solution polymerized styrene-acrylate polymers. Polyesters, on the other hand, can contain some unreacted bisphenol A as well as catalyst fragments remaining from organic tin compounds used during the polymerization. New class of polyester is already in the market that does not require the use of any or heavy metal catalyst. The amount of unreacted bisphenol A is being also brought down below safe levels.

References

[1] Graham J. Galliford, Market Issues for Toner and Raw Materials in Emerging World Markets, Proc. 9th Annual Toner and Imaging Conference, St. Pete, FL (2006)

[2] M. Gordon and J. S. Taylor, J. Appl. Chem.,2,493 (1952).

[3] T. G. Fox and P. J. Flory, J. Appl. Phys., 21, 581 (1950).

[4] F. L Chupka and C. Johnson, Current and Future Polymer Trends, , Proc. 9th Annual Toner and Imaging Conference, St. Pete, FL (2006)

[5] D. Tyagi, Latest Developments in Toner Technology, Proc. International Conference on Digital Production Printing and Industrial Applications, Amsterdam, May 2005.

Author Biography

Dr. Dinesh Tyagi received his Ph.D. degree from Virginia Tech in 1985 from the Department of Chemical Engineering with a thesis entitled "Structure-Property Relationships in Segmented Polymers". After one year of post-doctoral position there, he joined Eastman Kodak Company as a Research Scientist where he started worked in the toner development area. He was promoted to Senior Research Scientist in 1989 and in 1993 he was appointed Research Associate. Following year he was inducted into Kodak's Distinguished Inventors Gallery. In 1999 he joined NexPress Solutions, which was later absorbed into Kodak. He has continued to work in the area of toners and electrophotography through most his professional career. Dr. Tyagi has over 70 patents worldwide.