

Novel Polyesters for Electrophotographic Toners

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Abstract

Many approaches to improve the properties of toner binders by coupling a styrene-acrylic resin with a polyester resin have been proposed. This paper describes a method to effectively form a linkage between a polyester resin component and a vinyl copolymer resin component by preparing the polyester in the presence of a styrene-acrylic copolymer containing hydroxyl groups. Syntheses and characterization of these resins and their use as binders in electrophotographic toners are described.

Introduction

Advanced techniques of electrophotography require the development of resins as toner binders that can withstand high speed copying operations and can provide copies of high quality. Thus, a toner resin must be capable, for example, of readily dispersing additives such as carbon black, ferrites, magnetite, Aerosil®, charge stabilizers and waxes. Another requirement is the good grindability in reverse-jet mills. Some resins give toners which require very long milling times before the desired particle size is obtained, preferably between 5 and 15 μm . Another frequent problem in milling with the reverse-jet mill is the production of fine dust, i.e. of particle sizes which are less than 5 μm .

The shelf life of the toner is also influenced by the toner resin. Caking of the toner powder may occur if a moisture-sensitive resin which is only slightly hygroscopic is used. In addition, resins which absorb moisture from the surrounding air lead to toners whose electrostatic properties are greatly dependent on the atmospheric humidity, leading to irregular blackening in solid areas on the copy.

A further problem is the increase in the fixing rate of an image transferred to the print medium by heat, i.e. the increase in the cycle time of the copier. The properties of the toner during fixing are greatly influenced by the melting behavior of the toner resin. A higher fixing rate is achieved by using a resin having a low softening point. However, this may result in a problem known as hot offset, i.e. some of the molten toner adheres to the hot fixing roller of the copier and is transferred to subsequent copies.

The electrostatic chargeability of toner resins is also important. The charge build-up can be controlled by means of charge stabilizers. Another important criterion is the stability of the charge. Many toners have a tendency to build up too much charge during the development process. The charge stabilizers keep the charge at a particular level, and a very uniform blackness of the copies is thus obtained. In

this context, the interaction between charge stabilizers and toner resin is the critical parameter.

Styrene-acrylic resins have been most widely used as toner binders. These resins are cheap and have excellent resistance to humidity as well as high resistance to blocking, but these resins have low mechanical strength and low rate of electrification.

It is known that polyester resins have excellent mechanical strengths and also possess a high rate of electrification, but have a low resistance to humidity that in turn leads to lowering of the electrifying properties when humidity is high.

In the present study we have synthesized a binder for dry toners that overcomes the above-mentioned problems. We have found that this goal is achieved by polyester resins based on hydroxyl-containing prepolymers of olefinic unsaturated monomers, and subsequent polycondensation of a mixture of this prepolymer with a dicarboxylic acid and a glycol.¹⁻⁷ Thus the properties of toner binders can be improved by coupling a styrene acrylic resin with a polyester resin.

Results and Discussion

Synthesis and Characterization of the Prepolymer

The prepolymer can be prepared by suspension, solution or block polymerization according to conventional methods. In the subsequent polycondensation, however, prepolymers prepared by solution polymerization are preferred. Polymerization and polycondensation can then be carried out in succession in one reaction vessel because isolation of a prepolymer can be dispensed with. Suitable solvents are inert organic solvents, e.g. toluene, xylene or cyclohexane. The polymerization is carried out as a free radical polymerization, employing free radical initiators such as benzoyl peroxide or tert-butyl peroctanoate. The polymerization temperature is the boiling temperature of the solvent, e.g. 110.6°C in the case of toluene.

The monomers for polymerization are styrene, acrylic esters and a hydroxyl-containing acrylic acid derivative, e.g. 4-hydroxybutyl acrylate or 2-hydroxyethyl acrylate.

The average molecular weight M_n of the prepolymer is 14,000 by GPC. The OH number is 7.8 mg KOH/g (calculated) and the glass transition point depends on the selection of the monomers. In the subsequent polycondensation this prepolymer acts as a polymeric crosslinking agent.

Preparation and Physical Properties of the Polyester Resin

A mixture of prepolymer described above (as a solution in toluene), dicarboxylic acid, e.g. dimethylterephthalate

and diol, e.g. neo-pentyl glycol are used in the polycondensation. The methanol formed during the reaction is distilled off directly from the resin melt along with toluene. The polycondensation is usually carried out in the presence of a catalyst, for example, dibutyltin oxide or titanium alcoholate. The condensation is completed towards the end of the reaction at 200°C.

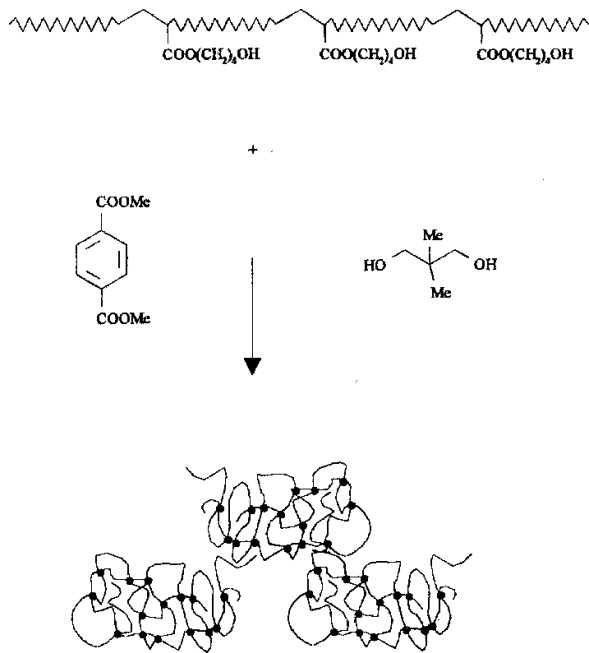


Figure 1. Preparation of a polyester using a polymeric crosslinker.

The resulting crosslinked polyester resins have glass transition temperatures in the range of 50°C to 80°C, a melt volume index of 10 ml/10 min and are completely soluble in tetrahydrofuran.

Another parameter that can be changed is the composition of the polymeric crosslinker. A higher degree of styrene increases the glass transition point of the polyester. Using a pure hydroxy functionalized polystyrene as prepolymer the polyester on the basis of dimethylterephthalate and ethoxylated Bisphenol A has a glass transition point T_g of 76°C (cf. Table 1, entry 1 versus entry 8). Under the microscope all resins showed two phases.

The novel polyesters can be prepared reproducibly and straightforwardly. In particular, the danger of uncontrollable crosslinking is substantially ruled out.

Rheology

As a typical example the rheological curves of polyester 9 from Table 1 are shown in Figure 2. The storage modulus G' , loss modulus G'' and complex viscosity η^* were measured as a function of shear rate $\dot{\omega} = 2\pi f$ (f = frequency). In another experiment the temperature ramp was determined.

Table 1. Chemical composition and physical properties of polyester resins

| Entry | Chemical composition ^a | MVI (ml/10 min) ^b | T_g (°C) ^c |
|-------|---|---------------------------------|-------------------------|
| 1 | dimethylterephthalate, ethoxylated bisphenol A | 32 | 59 |
| 2 | dimethylterephthalate, ethoxylated bisphenol A, ethylene glycol | 32 | 61 |
| 3 | dimethylterephthalate, ethoxylated bisphenol A, cyclo-hexane dimethanol | 95 | 57 |
| 4 | fumaric acid, ethoxylated bisphenol A | 17 | 76 |
| 5 | phthalic anhydride, ethoxylated bisphenol A | 49 | 76 |
| 6 | fumaric acid, dimethylterephthalate, ethoxylated bisphenol A | 35 | 72 |
| 7 | fumaric acid, neo-pentyl glycol | 7 | 77 |
| 8 | dimethylterephthalate, ethoxylated bisphenol A ^d | 17 | 76 |
| 9 | di methylterephthalate, neo-pentyl glycol | 10 | 57 |

a As prepolymer a hydroxy functionalized styrene copolymer was used (T_g 80°C).

b Melt volume indices were determined at 150°C and a mass of 2.16 kg.

c Midpoint, second run.

d As prepolymer a hydroxy functionalized polystyrene was used (T_g 97°C).

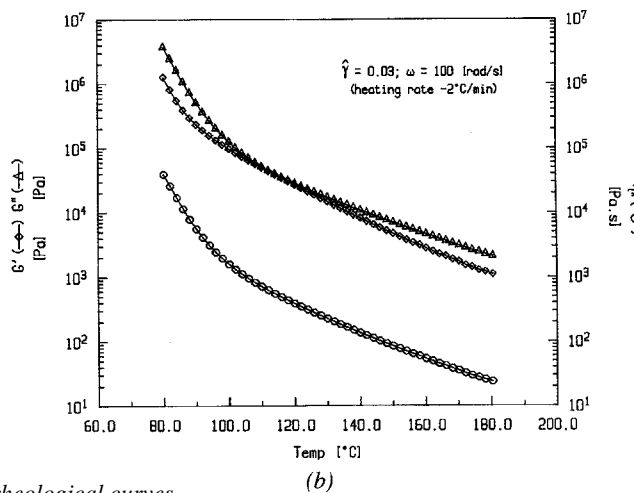
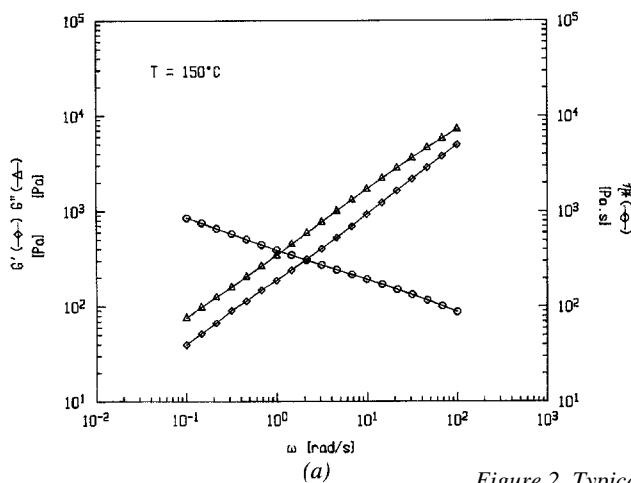


Figure 2. Typical rheological curves.

Gel Permeation Chromatography

GPC analyses of the polyesters showed a broad and bimodal molecular weight distribution. By comparison of the chromatograms with that of the polymeric crosslinker it was possible to assign the signals at higher molecular weights to the prepolymer.

Extraction of polyester samples with from 90 to 10% by weight of hexane in xylene gave different fractions that were wax-like or crystalline. GPC of all fractions showed identical bimodal molecular weight distribution with increased M_n for the more polar fractions, but in all cases the ratio of signals relative to one another remained identical. This confirms that there is a chemical linkage between polymeric crosslinker and polyester, and no mixture of either components.

Table 2. Properties of pseudotoners prepared with polyester resins

| Entry ^a | q/m ($\mu\text{c/g}$) ^b | Fixation window ($^{\circ}\text{C}$) ^c | Grindability (sec.) ^d |
|--------------------|--------------------------------------|---|----------------------------------|
| 1 | -7.0; -7.5; -8.0; -7.0 | 114-155 | 20 |
| 2 | -8.5; -9.5; -10.5; -9.5 | 110-140 | 18 |
| 3 | -11.3; -13.7; -15.1; -15.2 | 114-140 | 30 |
| 4 | -11.7; -9.1; -7.1; -5.6 | 114-140 | 24 |
| 5 | -12; -9.0; -7.0; -5.5 | 114-150 | 30 |
| 6 | -6.3; -4.9; -4.1; -3.7 | 90-140 | 86 |
| 7 | -2.6; -1.7; -1.4; -1.8 | 114-134 | 33 |
| 8 | -9.6; -12.1; -12.1; -13.2 | 114-140 | 23 |
| 9 | -9.7; -10.9; -13.0; -13.4 | 114-140 | 30 |

^a Polyesters from Table I were used.

^b The q/m values were determined as 3% by weight developers against spherical iron powder (Pometon TC 101) activated for 10, 30, 60 and 120 minutes on a roller trestle.

^c The fixation windows were determined on a Kofler bench type WME. The ground resin was put between two strips of a paper placed on the Kofler bench and weighted with a Teflon[®]-coated cover of ca. 2.8 kg mass for 1 minute. This measurement is only of interest to compare the fixation behavior of the resins relative to one another.

^d Grindabilities were determined in a Janke & Kunkel lab mill. The time in seconds was determined acoustically.

Preparation of Toners

Electrophotographic toners were prepared from the novel polyester resins by grinding the resin to a particle size of less than 1 mm and then mixing it with carbon black, a magnetic pigment or a colorant, wax, Aerosil[®] and a charge stabilizer. This mixture was kneaded to a uniform mass that

was then ground to a particle size of between 5 and 15 μm . Finally, it was coated with Aerosil[®] in a fluid mixer.

If the toner composition lacks certain additives required for their use in photocopiers the term pseudotoner is also used.

In all cases the particle size distribution of carbon black, as determined on thin films (ca. 1 μm) prepared on a Kofler bench, was excellent.

Toners obtained from the novel polyester resins have a long shelf life, are insensitive to moisture and exhibit good cold and hot offset properties in conjunction with a high fixing rate. Copies produced using a toner obtained from this resin have uniform blackness in the solid area and no background in unprinted areas. They also show no vinyl offset. Vinyl offset in this context means the detachment of toner particles from the copy by films, for example transparencies.

To test the incorporation characteristics of color pigments, Pigment Red 81: 1 (Fanal[®] Pink S 4830 by BASF) and others were finely dispersed in the polyester resins. Excellent dispersions were obtained.

Conclusions

The novel resins are crosslinked polyesters having a broad molecular weight distribution. This is partly responsible for their advantageous behavior. They have good dispersing properties for carbon black, colorants, ferrite Aerosil[®], charge stabilizers and waxes. They can be readily ground in a reverse-jet mill.

The novel polyesters have a substantially lower electrostatic chargeability compared with state-of-the-art media.⁸ This property considerably facilitates charge stabilization of the toners that can be prepared using the novel resins.⁹

References

1. U.S. Patent, 4 657 837.
2. U.S. Patent, 4 980 448.
3. European Patent, 195 604.
4. U.S. Patent, 5 241 019.
5. U.S. Patent, 5 227 460.
6. U.S. Patent, 4 981 939.
7. European Patent, 128 562.8.
8. Polyester resins usually show higher electrostatic chargeabilities, e.g. -23 $\mu\text{c/g}$ (Reference 3) or between -33.1 and -41.6 $\mu\text{c/g}$ (Reference 6).
9. The novel polyesters have also been described in Germany Patent Laid-Open 4 211 062.