Toner Binder Resins with Improved Fusing Properties

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Abstract

This study describes the latest progress in toner binder design to achieve low fusing temperatures as required for new energy regulations like the ZESM (Zero Energy Standby Mode).

Conventionally low temperature fusing is realized by reducing the molar mass of the binder polymer. In parallel with a reduced melt viscosity the glass transitions temperature Tg decreases resulting in a poor storage ability. This phenomenon is reviewed for typical toner binder resins like styrene acrylics and polyester and compared to cyclo-olefin-copolymers COC derived from ethylene and norbonene (trade name: Topas® of Ticona, Germany). For these new materials the glass transition temperature is easily adjusted by incorporating different amounts of the cyclic olefin into the polymer meaning that the Tg of COC can be controlled independently of molar mass. Thus an optimum balance between low melt viscosity necessary for low temperature fusing and excellent anti blocking properties is obtained.

In addition Topas® COC binder resins offer a unique combination of surface, electrical, mechanical and environmental friendly properties which is ideal for using these material as toner binder resins.

Introduction

New energy regulations like the ZESM (zero energy standby mode) sponsored by the International Energy Agency, ask for energy saving technologies. The ZESM provides user convenience with markedly improved power savings.

In the electrophotographic printing and copying process usually more than 60% of the power is consumed within the fusing process where toner is fixed onto the paper by using heated rolls or the like. Accordingly the energy consumption during the fusing step has to be improved by lowering the fusing temperatures for achieving ZESM. In addition such energy saving will result in higher printing speed because so far the fusing step is the slowest step within electrophotography.

This study describe the latest progress in toner design to fulfill these new energy regulations. Particular emphasis is given to cyclo-olefin copolymers, COC) derived from ethylene and norbornen.

These materials are available since 2001 under the tradename Topas® from Ticona, Germany.

Toner Design Criteria

Toner is a finely divided pigmented powder of dimensions between 5 an 9 μm and various shapes which serves a dry ink within electrophotography. A common toner consists of the following ingredients:[1]

External additives like fumed silica or titania in contents of up to 2.0% improve tone flow, decrease toner adhesion and improve charging characteristics.

Waxes basically based on polyolefins can be contained in amounts of up to 10% and act as substitutes for fuser release oils.

Chare Control Agents normally organic salts acids or metallo-compounds, are employed to control the charging sign, the charge level and the admix charging rate.

Pigments or dyes are necessary to make the image visible to the human eye and thus provide darkness or gamut. The are normally used in levels of up to 5%.

Toner polymers or binder resins, so far styrene-acrylics or polyesters, are normally used in amounts of 40 to 95% in a common toner formulation. It is necessary to transport the pigment through the electrophototgraphic process and to fuse the pigment onto the substrate.

Thus for energy saving during electrophotographic printing and consequently lower minimum fusing temperatures we have to concentrate on toner binder design. According to Reilly the following properties of toner polymer are appreciated:[2]

- Intermediate **surface tension** between 28 and 38 mN/m to facilitate cleaning and fusing.
- Constant **electrical** properties independent on humidity.
- **Brittle** materials for easy jetting but no degradation in xerographic process or during compounding.
- **Glass transition** temperature in the range of 60°C to prevent the toner powder from caking.
- Low **melt viscosity** at temperatures slightly above glass transition temperature.
- **Environmental** friendly material for safe use at home or in office.

Thermal Properties of Toner Polymers

For toner binder application amorphous materials are preferred over semicrystalline materials as lower amounts of energy are required for the transformation into the viscous melt state. Consequently amorphous materials are preferred for low energy fusing. Further advantages of such materials are that they are highly transparent thus delivering better print quality and that they are usually brittle and can be jetted easily.

It is normally believed that the glass transition temperature Tg of a given polymer is constant. A more detailed analysis on the effect of molecular weight reveals that for small chain lengths the glass transition temperature is no longer constant but decreases with decreasing chain length. This phenomena was studied for polystyrene by Kanig- Ueberrreiter.[3]

Their classic theory is based on the assumption that the glass transition occurs at a constant value of the free volume. By reducing the molecular weight the number of chain ends increase. Consequently the free volume increases. This means that a depression of the temperature is necessary to attain the constant free volume characteristic for the vitrification of the chains.

The following equation describes the influence of the number averaged molecular weight Mn on Tg of polystyrene even for low molar masses:

$$\frac{1}{T_g} = \frac{1}{T_{g\infty}} + \frac{A'}{M}$$

Tg∞ is the Tg value at infinite molecular weight and A' is a parameter. For polystyrene with narrow polydispersity of less than 1.1 A' = 0.734 shows best correlation with the experimental data if Tg is measured with a DSC at a heating rate of 20 K/min in the second heating run.

The impact of Mn on Tg for polystyrene is shown in figure 1.

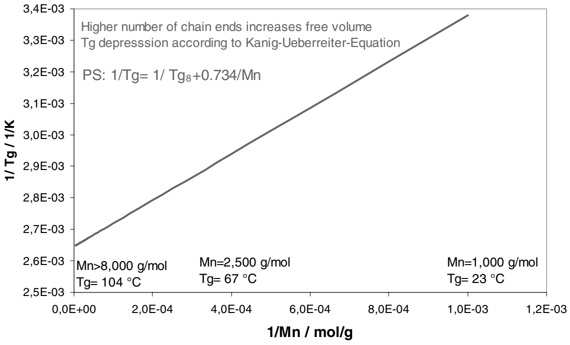

Figure 1. 1/Tg as a function of 1/Mn for polystyrene.

As concluded from figure 1 the Tg value is practically constant with a limiting Tg = 104°C for number average molecular weights of higher than 8,000 g/mol.

At lower molecular weights the Tg values decreases more and more significantly. For Mn = 2,500 g/mol a Tg of 67° is observed whereas the Tg drops to 23°C for Mn = 1,000 g/mol.

For toner applications styrene acrylic resins based on alkylmethacrylates preferably with 20 mol % butyl methacrylate or polyester resins preferably alternating copolymers based on polyoxypropylene bisphenol A and terepthalic acid are conventionally used as toner binder resins.[4]

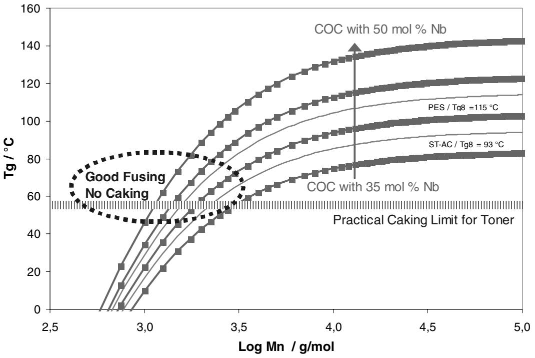

Figure 2. Tg as a function of Mn for typical toner binder resins.

In figure 2 the Tg of typical toner polymers measured by DSC are shown as a function of Mn. In order to ensure good storing properties of the toner powder a Tg of 55 - 60°C is regarded as the lower glass transition temperature limit of toner polymers.[5]

For commonly used styrene acrylics with a fixed limiting Tg of 93°C the critical value of 55°C is reached for Mn ≈ 2300 g/mol. In normal polyester resins derived from bisphenol A and terepthalic acid this temperature limit corresponds to a lower value of Mn ≈ 1500 g/mol. The molar mass can not fall below this Mn value without worsening the storage properties. But for low minimum fusing temperature low molar masses are required.

For COC based on the cyclic olefin norbornene Nb and the α-olefin ethylene Tg∞ depends on the molar ratio of the comonomers in the polymer chain according to the following equation:[6]

$$T_{g\infty} / °C = 4 * mol\%(norbornene) - 56$$

The glass transition temperature for COC as a function of molar mass Mn for different molar ratios of norbornene in the range from 35 to 50 mol % is as well shown in figure 4. It is assumed that the Tg dependence on Mn for COC is comparable to PS.

Thus by incorporating different amounts of the cyclic olefin into the polymer glass transition temperature and molecular weight are no longer coupled. Both values can be tailored independently. Consequently Topas® COC binder polymer deliver a completely new approach to toner binder resin design.

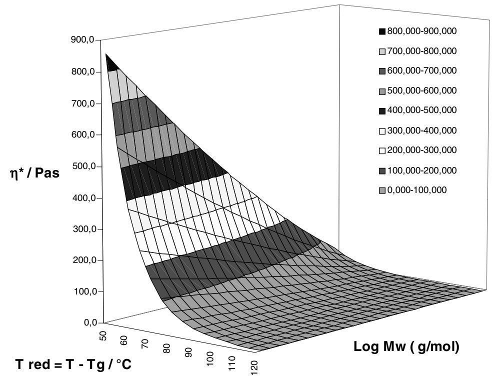

Figure 3. Melt Viscosity of COC toner binder resins.

Rheology of Toner Polymers

It is well know in polymer science that the zero shear viscosity ηo of polymers depends on the weight average molecular weight Mw. In general two different Mw-regimes are distinguished:[7]

- Above the critical molecular weight Mc corresponding to about twice the entanglement molecular weight Me ηo is proportional to $Mw^{3.5}$ meaning that slight changes in Mw lead to dramatic changes of ηo. Strong shear thinning as a function of frequency is observed. This chain entanglement is responsible for the typical prosperity combination of ordinary plastics. Please note that above the critical molar mass the glass transition temperature is no longer dependent on M.
- Below Mc ηo depends on Mw to a power of between 1 and 2.5. Such materials show Newtonian flow without shear thinning and the already described molecular weight dependence of Tg. Typical toner binder resins are located in this molecular weight range.

Topas® TM COC toner binder resins have shown to be Newtonian fluids meaning that the viscosity is not dependent on the applied frequency indicating that its molecular weight is well below Mc. Consequently the rheology is only studied as a function of temperature.

The thermo-rheological behavior of materials with identical molar mass but different Tg value can be superimposed by introducing a so called reduced temperature T_{red}. It describes the temperature difference between the measuring temperature T and the underlying Tg value. This means that the melt viscosity is no longer dependent on the three parameters Mw, Tg and T but only on two , i.e. Mw and T_{red}. By introducing such a reduced parameter the melt viscosity is described and modeled much easier.

Figure 3 describes how the melt viscosity of COC toner binder resins change as a function of weight average molecular weight Mw and T_{red}. The experimental inaccuracy of this model is less than 20%. Please note the broad viscosity range that is covered with by model.

An exponential scaling of the melt viscosity as a function of Mw and T_{red} is observed. As expected the melt viscosity increases as a function of Mw and decreases as a function of T_{red}. The model provides a unique tool to design fusing and anti blocking properties of toner binder materials. Furthermore it allows very accurate quality control of Topas® COC binder resins.

Properties of COC Polymers

Figure 4 shows the basic chemistry and the production process for COC binder polymers derived from ethylene and norbonene (trade name: Topas® of Ticona, Germany).

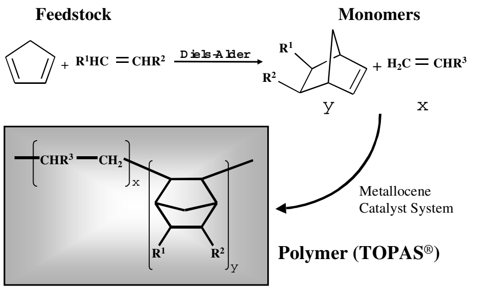

Figure 4. Production process and basic chemistry of COC.

The manufacturing process is a typical continuous process. First the cyclic olefin norbornene is obtained from DCPD, which is readily available from steam crackers, and ethylene.

Then a viscous polymer solution is generated by feeding norbornene, ethylene and the metallocene catalyst system at elevated temperature and pressure into the reactor. In order to obtain excellent optical quality the catalyst is separated. An additional fine filtration step can be applied as well. Solvents, including excess norbornene, are evaporated and TOPAS® is pelletized. Removed solvents are purified by distillation and recycled.

Finally an unpolar polyoefin with low amount of residual or volatile matter is obtained.

Figure 5 describes the physical properties which are already fixed by the basic chemistry of COC polymers.

Properties Given by Chemistry of Topas® COC

Property	Value	Effect
Surface	Polyolefin with intermediate surface energy	Good adhesion to paper but bad wetting of other surfaces
Electrical	Polyolefin with basically no water uptake	Stable Tribocharge level in different environments
Mechanical	Totally amorphous thus hard but brittle	Fast jetting with narrow PSD No degradation within xerographic process
Environment	Polyolefin with low TVOC	Environmental friendly matter No odor formation

Figure 5. Binder properties given by the chemistry of COC.

COC polymers show typical polyolefin surface tension as desired for toner applications. The binder material shows good adhesion to paper but bad wetting to other surfaces.

Due to the unpolar nature of Topas® COC polymers do not show significant water uptake. Consequently the tribocharge level remains constant in environments of different humidity.

Topas® COC polymers are completely amorphous. It is quite brittle especially at low molar mass so that fast jetting with narrow particle size distribution is achieved. On the other side COC binder do not degrade significantly during toner compounding or within the xerographic process.

Furthermore by the hydrocarbon nature and the production process of COC it is evident that the total volatile organic carbon content is low.

Conclusion

Due to the continuous production process and the polyolefin nature Topas® COC polymers offer a unique combination of surface, electrical, mechanical and environmental friendly properties.

The thermal properties of COC toner binder resins are adjusted independently on molecular weight by incorporating different amounts of the cyclic olefin into the polymer. Thus an optimum balance between low melt viscosity necessary for low temperature fusing and excellent anti blocking properties is obtained. A model describing the influence of Tg and Mw on the melt viscosity of Topas® TM materials was developed. Thus melt viscosity can be tailored to meet end use requirements.

This property combination is ideal for using these innovative materials as binder polymers in modern electrophotographic printers. Improved fusing characteristics with significantly lower energy consumption can be expected.

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Biography

Klaus Berger received his Ph.D. in Physical Chemistry from the university of Paderborn, Germany, in 1995. He then worked on biodegradable polymers at the Federal Institute for Cereal, Potato and Starch Research in Detmold, Germany and on the rheological properties of associating polymer solutions at the Laboratory for Ultrasounds and the Dynamics of Complex Fluids in Strasbourg, France. In 1997 he joined the research and development group of Topas® within Hoechst and later Celanese/Ticona. He is currently working on Topas® toner binder resins for high quality printing in a fully equipped state-of-the-art polymer and toner lab.