The Effects of Branching agent for Toner Binder Resins

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Abstract

In recent years, from the viewpoint of saving energy, it is requested that the toner can be fused at lower energy. And the speed of machine system is increasing year by year. So, high durability toner is requested as well. However, it is very difficult to satisfy high durability and excellent fusing ability at the same time. Conventionally low temperature fusing is realized by reducing the molecular weight of the binder resin. However the binder resins having narrow molecular weight distribution, low melt viscosity, low glass transition temperature, low durability. In order to solve the problem, we have synthesized several branched polyester, by controlling the kinds of branching agent and amounts of branching agent, various kinds of branched polyester are prepared. And the effects of branching agents and amounts for the physical properties of toner were investigated.

Introduction

Recently, as color toner printers have become to be widely used, the requirements of the improvements for the color printer toner have been also increasing.

Generally, the binder resin having low and narrow molecular weight distribution is used to achieve the good transparency. However such binder resin cannot give the wide non-offset range in fusing because the elasticity of the toner melted by heat roller is low. To avoid offset phenomenon, a technique of broad the molecular weight distribution of binder resin has been proposed. To achieve the polyester resin have broad molecular weight distribution, a technique of using a branching agents have been employed. However there are many problems, for example, by increasing the molecular weight, the pulverazibility of polyester should be worse and increased gel contents result in increased melt viscosity and impaired fixability although it is effective in improving the offset phenomenon. Another important weak point is that the glass transition temperature of the resin should be lowered. The lowered glass transition temperature influences the storage stability of the toner and the high gel content has a detrimental effect on the dispersion of the additives (wax, colorant, CCA).

In this paper, by controlling the kinds and amounts of branching agent, various kinds of branched polyester are prepared. And the effects of kinds and amounts of branching agent for the physical properties of toner were investigated. Using a branching agent such as trimellitic anhydride, glycerol, trimethyolpropane, trimethyolethane, and pentaerythritol that works as a branching agent can not only expand the molecular weight distribution but also increase the molecular weight of polymer.

Experimental

Preparation of branched polyester resins

Bisphenol A derivatives, ethylene glycol, terephthalic acid and each branching agents (TMP, TME, PER, TMA, glycerol) were allowed to react for condensation polymerization at 230℃, period of 3 hours with small amount of titanium butoxide, zinc acetate in a 1L flask, which was equipped with a thermocouple, a stainless steel stirrer, torque meter, a reflux condenser. And then the temperature of the reaction mixture was increased stepwise to 240℃. Over a period 3 hours, and the components were reacted under a reduced pressure of 0.1mmHg until the reaction mixture reached a desired softening point, to give a polyester resin. Monomer composition of branched polyester resins are listed in Table 1, 2. The structures of monomer used are given in Table 3.

Table 1. Monomer composition of polyester resins

Entry	Alcohol monomer	Acid monomer	Branching Agent (20mol%)
Resin 1	BPA-PO, BPA-EO, EG	TPA	TMP
Resin 2	BPA-PO, BPA-EO, EG	TPA	TMA
Resin 3	BPA-PO, BPA-EO, EG	TPA	TME
Resin 4	BPA-PO, BPA-EO, EG	TPA	PER
Resin 5	BPA-PO, BPA-EO, EG	TPA	Glycerol

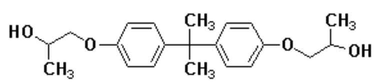
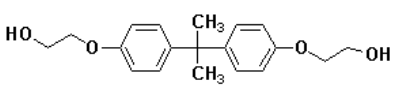
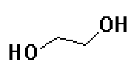
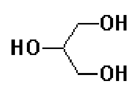
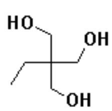
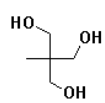
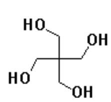
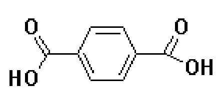
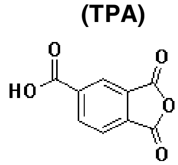
Softening point ($T_{1/2}$)

Softening point refers to a temperature corresponding to 1/2 of the height(h) of the S-shape curve showing the relationship between the downward movement of a plunger (flow length) and temperature, namely, a temperature at which a half of the resin flow out, when measured by using a flow tester (CFT-500D) in which a 1.5g sample is extruded through a nozzle having a die pore size of 1mm and length of 1mm, while heating the sample so as to raise the temperature at a rate 6℃/min and applying a load of 20Kg thereto with the plunger.

Table 2. Monomer composition of polyester resins

Entry	Alcohol monomer	Acid monomer	Branching agent
Resin 6	BPA-PO, BPA-EO, EG	TPA	TMP 10 mol%
Resin 7	BPA-PO, BPA-EO, EG	TPA	TMP 15mol%
Resin 8	BPA-PO, BPA-EO, EG	TPA	TMP 20mol%
Resin 9	BPA-PO, BPA-EO, EG	TPA	TMP 25mol%
Resin 10	BPA-PO, BPA-EO, EG	TPA	TMP 30mol%

Table 3. The structures of monomer used

Alcohol monomers	 **BPA-PO**  **BPA-EO**  **EG**  **Glycerol**  **(TMP)**  **(TME)**  **(PER)**
Acid monomers	 **(TPA)**  **(TMA)**

Glass transition temperature (Tg)

The glass transition temperature is measured by DSC. The Tg was designated to be the temperature at the middle point through the second scan.

Gel permeation chromatograohy(GPC)

The molecular weight of resin was measured by GPC.
Mn : number average molecular weight
Mw: weight average molecular weight
Mp: peak top molecular weight
MWD: molecular weight distribution (Mw/Mn)

Gel content

Insoluble parts in THF (%)

Rheology

Polyester rheological properties were measured by ARES. A temperature sweep was conducted 100℃~180℃ at frequency of 6.28 rad/sec.

Specific volume

The specific volume of resin was measured by PVT tester (Toyoseki). The test was carried out to be measured the isothermal mode at 180℃, 3MPa ~ 20MPa.

Preparation of toners

97 wt% of resin, 4 wt% of carbon black, 3wt% of a polyester wax, 1wt% of charge control agent(CCA) were added, and they were compounded by twin extruder, pulverized and classified to 9 µm in volume median diameter. All toners for test were treated with 0.3wt% of hydrophobic silica.

Result and Discussion

The properties of the polyester resins

The results of polymerization are given in Table 4.

Table 4. Physical properties of polyester resins

Entry	$T_{1/2}$ (℃)	Tg (℃)	Mn	MWD	Gel %
Resin 1	131	62	5387	22	10.0
Resin 2	130	65	5731	15	6.0
Resin 3	131	61	3339	30	15.0
Resin 4	131	50	1626	35	22.1
Resin 5	130	68	6238	9	2.0
Resin 6	131	66	6288	12	5.1
Resin 7	129	64	5554	19	8.2
Resin 8	131	62	5387	22	10.0
Resin 9	131	60	4854	20	22.2
Resin 10	131	58	4597	27	30.0

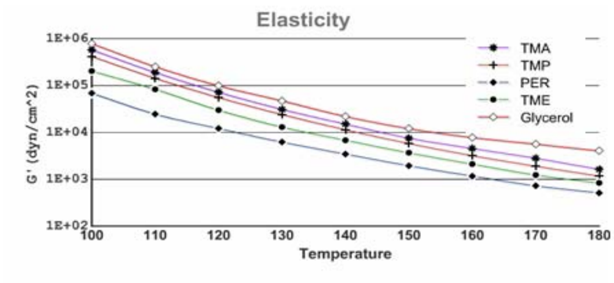


Figure 1. Elasticities of branched polyester resin against the kinds of branching agent

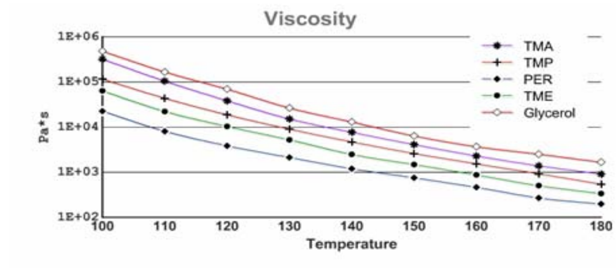


Figure 2. Melt viscosities of branched polyester resin against the kinds of branching agent

Relation between Glass transition temperature (Tg) and branching agents

Relation between glass transition temperature (Tg) and amount of branching agent is shown in Table 4. This result indicates the more the amount of branching agent is contained in the branched polyester resin, the lower the glass transition temperature of the polyester resin becomes.

Glass transition temperature of branched polyester resins against kinds of branching agent was affected kinds of branching agent and gel content. By increasing the amount of gel content, the length of polymer chain decreases which leads to low glass transition temperature. The Resin 4 is contained in the PER, the lowest glass temperature and the highest gel content.

Comparison of rheological properties of polyester resin against kinds of branching agent

The large number of branches leads to a compact shape of the molecule, which contrast with the highly flexible linear polyester resin. This compact shape has important implications for the rheological behavior of branched polyester resin. Due to reduced intermolecular interactions compared to linear polyester resin. Both melt viscosities and elasticities of branched polyester resins are generally low. Figure 1, 2 shows that comparison of elasticity (G'), melt viscosity of branched polyester resin against kinds of branching agent. As shown in figure1, 2, the elasticity, melt viscosity of Resin 4 is the lowest. The elasticity, melt viscosity of branched polyester resin was obviously depended on kinds of branching agent. In other words, the rheological properties are no longer dependent on the kinds of branching agent but molecular weight, gel content.

Comparison of rheological properties of polyester resin against amounts of branching agent

Figure 3, 4 shows that comparison of elasticities (G'), melt viscosities of branched polyester resin against amounts of branching agent (TMP). The elasticity of branched polyester resin was obviously depended on amounts of branching agent. By increasing the amounts of branching agent, the branching density of polyester increases which leads to high gel polyester resin.

By increasing the amount of gel content, the elasticity, melt viscosity of polyester decreased which leads to low molecular weight (Mn) and broad molecular weight distribution. As shown figure 3, 4 the rheological properties of Resin 10 is the lowest.

It seems that dominant factors for the rheological properties are molecular weight (Mn) and gel content.

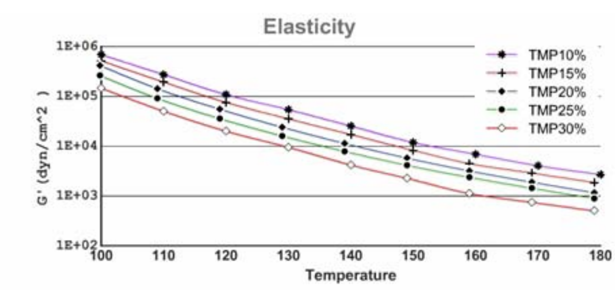


Figure 3. Elasticities of branched polyester resin against the amounts of branching agent

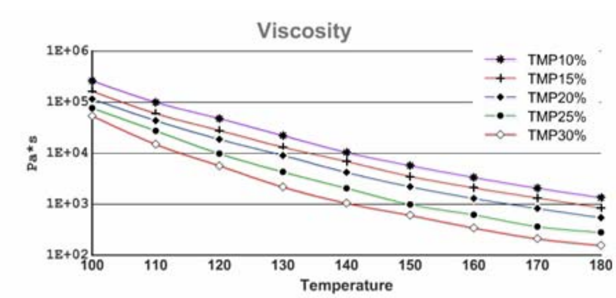


Figure 4. Melt viscosities of branched polyester resin against the kinds of branching agent

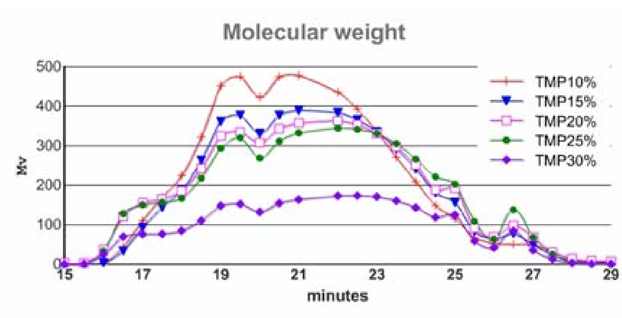


Figure 5. Molecular weight and molecular weight distribution of branched polyester resin against the amounts of branching agent.

Relation between molecular weight and amount of branching agent

Relation between molecular weight (Mn) and amount of branching agent is shown in Figure 5. This result indicates the more the amount of branching agent is contained in the binder resin, the lower the molecular weight (Mn) of the polyester resin becomes but the broader molecular weight distribution of the polyester resin becomes.

Also the higher gel content of the polyester resin becomes. By increasing the amount of cross-linking, the length of polymer chain decreases which leads to low molecular weight and broad molecular weight.

Relation between molecular weight and branching agent

On the branched polyester resin, the number of active sites (hydroxyl group or carboxyl group) in the branching agent will affect on the molecular weight distribution and molecular peak top molecular weight, the branched polyester resin contained PER having four active sites showed more broad molecular weight distribution and lower peak top molecular(Mp) than the others with branching agent having three active sites.

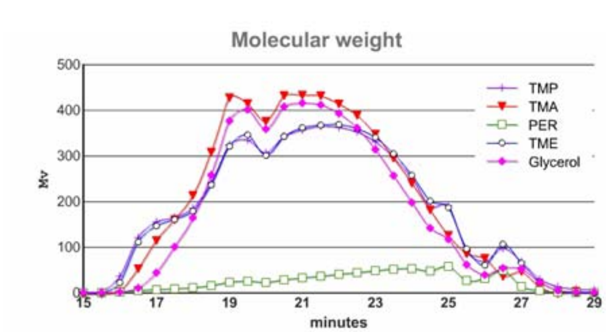


Figure 6. Molecular weight and molecular weight distribution of branched polyester resin against the amounts of branching agent.

As shown figure 6, the molecular weight distribution and molecular weight of branched polyester resins was obviously depended on kinds of branching agent. The result showed different amount of gel content and molecular weight for the respective branched polyester resin.

Consequently, by decreasing the amount of gel content, the soluble parts of polymer increases which leads to high molecular weight and narrow molecular weight distribution.

Relation between specific volume and branching agent

Generally 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 bond inherent in the polymer chain. This disadvantage is due to the intermolecular interaction. Figure 7 showed that comparison of specific volume of branched polyester resin against kinds of branching agent and amounts of branching agent. Specific volume is the volume occupied by a unit of mass of a material. It is equal to the inverse of density.

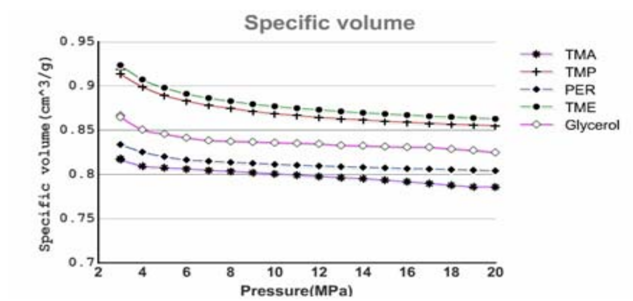


Figure 7. Specific volume of branched polyester resin against the kinds of branching agent

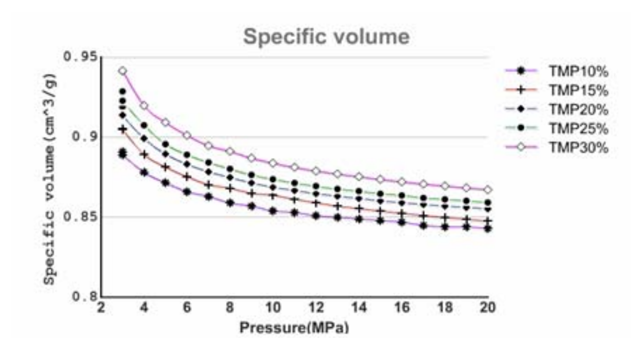


Figure 7. Specific volume of branched polyester resin against the amounts of branching agent

Conclusion

The influences of the branching agent of the branched polyester resin can be summarized as follows

1. By increasing the amount of branching agent, the molecular weight (Mn), glass transition temperature, elasticity, melt viscosity of branched polyester resins decreased. On the other hands, the molecular weight distribution, gel content of branched polyester resins increased. Also, the specific volume was increased.

2. The specific volume of the branched polyester resins were affected by the kinds of branching agent. This result is due to the hydrophilic functional groups and the intermolecular interaction.

3. In order to obtain the broad molecular weight distribution and high gel content, it is preferable to select polyol components having more than four active sites as a branching agent. But the rheological properties, glass transition temperature will be decreased.

References

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Author Biography

Joung ui gab received his B.S. and M.S. in organic chemistry from the Ajou University in 2003 and 2005 respectively. Since then he has worked in the Samyang corporation R&D center and has been engaged in research and development of engineering plastics. His work has focused on the development of binder resin for toner.