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Control of the Morphology of Dispersed Crystalline Polyester in a Toner For Low-Energy Fusing

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Abstract. *In the electrophotographic printing market, a demand for printers with lower energy consumption has driven the need to design toners that are fusible at lower temperatures. It has been reported previously that the energy required for fusing a toner based on amorphous polyester (A-PES) can be reduced by including a crystalline polyester (C-PES) in the toner composition. The improved fusing ability of a C-PES-containing toner is attributed to the large drop in viscoelasticity of C-PES that occurs at its melting temperature. The fusing advantages provided by C-PES, however, can be accompanied by negative effects on the toner's storage stability and durability during printing. Thermal analysis of C-PES-containing toners reveals that the glass transition temperature (T_g) of a toner is dramatically reduced relative to the T_g of a similar toner without C-PES. The reduction in T_g caused by C-PES is linked to the loss in polymer crystallinity that occurs when C-PES is melt-mixed with A-PES during the toner kneading process. A key, therefore, to improving the storage stability and durability of a C-PES-containing toner is to achieve higher degrees of crystallinity in the toner. In this article, a thermal annealing process was investigated as a method to improve the storage stability and the durability of toner. The annealing treatment involved conditioning of the toner for controlled periods of time at temperatures between the T_g and the melting temperature of the toner. It was found that the annealing process promoted the recrystallization of C-PES in the toner, resulting in an increase in the T_g of the toner. It was revealed that the annealing process promoted the formation of nanometer-scale crystalline domains in the toner and that the crystalline domain size was dependent on the temperature at which the toner was annealed. Rheological evaluation of the annealed toners revealed that the melting temperature of C-PES-containing toner can be controlled by changing the temperature at which the toner is annealed. It was shown that the morphology of the C-PES domains in a toner can be controlled by annealing under the proper conditions to yield a toner that has good storage stability and durability simultaneously with low-energy fusing.* © 2011 Society for Imaging Science and Technology.
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INTRODUCTION

In today's electrophotographic printer market, there is a demand for printing devices that operate at higher print speeds and with lower energy consumption. These performance targets present a challenge in the design of fusing subsystems because higher print speeds and lower energy consumption make it more difficult for a fuser to supply the heat required to fuse the toner to each printed page. In response to these trends in printer design, it is desirable to have better fusing toners that can be fused well to paper with less heat input from the fuser. It has been reported previously that the fusing ability of a toner made of amorphous polyester (A-PES) can be greatly improved by using a crystalline polyester (C-PES) toner binder as a component in the toner.[1,2] Compared to amorphous polyesters, crystalline polyesters are known to undergo a very sharp phase transition from solid to melt, and the melting temperature of C-PES can be controlled through monomer selection.[3–5] The application of that technology to toner design allows the development of toners with lower-temperature fusing.[1,2] The improved low-temperature fusing of C-PES-containing toners is attributed to the sharp melting point of crystalline polymers and to the large drop in toner viscoelasticity that occurs when the toner is heated above the C-PES melting temperature.[5] Figure 1 reveals how the storage modulus G' of C-PES polymer drops sharply as the material is heated above its melting temperature. In contrast, the viscoelasticity of a typical amorphous polyester resin, also shown in Fig. 1, changes very gradually over a broad temperature range without any sharp drop in G'.

Although the low-temperature fusing ability of a toner can be greatly improved by including C-PES as a component in the toner, other performance attributes of the toner, including the storage stability and durability, can be affected adversely. Durability, in this sense, refers to a toner's resistance to mechanical stresses during printer operation that can cause failures such as carrier scumming and filming on the developer roll or doctor blade. These adverse features of C-PES are attributed to the reduction in the T_g of a toner which occurs during melt-mixing with amorphous polymer. The T_g depression occurs because the crystallinity of the C-PES is lost during melt-mixing with amorphous polymer, and recrystallization of the C-PES domains does not readily occur upon cooling of the toner. High miscibility between

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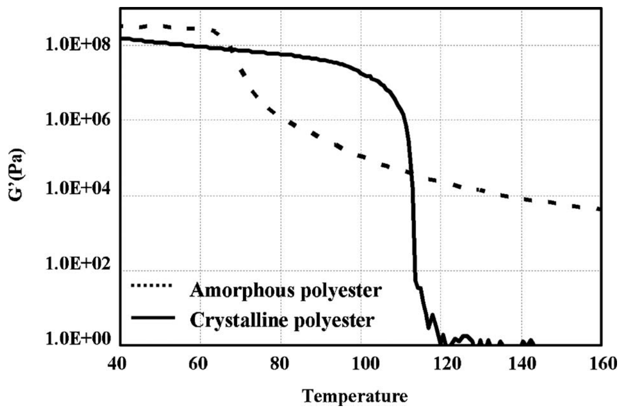

Figure 1. The relationship between temperature and viscoelasticity of amorphous polyester and crystalline polyester.

the C-PES and A-PES components is believed to inhibit recrystallization of C-PES in the toner.

In this article, methods to promote the recrystallization of C-PES in a melt-mixed toner were investigated as a means for improving the storage stability and durability. A known method for promoting polymer crystallization is the process of thermal annealing, which involves the slow heating and cooling of a polymeric material to allow the reorientation of polymer chains into an ordered configuration.[6–8] The degree of crystallinity and the T_g of the toner can be increased by thermal annealing, which can make it possible to obtain a toner that combines good storage stability, good durability, and good low-energy fusing.

In addition, this article investigated the mechanism of C-PES crystallization and the morphology of C-PES in annealed toner. It was found by AFM observations that crystals of C-PES in annealed toner were present in nanometer-sized crystalline domains (lamellae) in the amorphous polyester matrix. The size of the dispersed crystalline lamellae was dependent on the annealing temperature. Rheological analysis revealed that the temperature of the annealing process also can control the melting temperature of the crystalline domains within an annealed polymer blend. This investigation of the recrystallization of C-PES in toner suggests that thermal annealing can be used to optimize the performance of toner by controlling the morphology of crystalline polyester dispersed in the toner.

EXPERIMENTAL

Preparation of Amorphous Polyester Resin and Crystalline Polyester Resin

A-PES-1: A 10 l four-necked flask equipped with a nitrogen inlet tube, a dehydration tube, a stirrer, and a thermocouple was charged with bisphenol-A propylene oxide (BPA-PO) adduct, bisphenol-A ethylene oxide (BPA-EO) adduct, fumaric acid (FA), as monomer, dibutyltin oxide and hydroquinone as catalyst. The ingredients were reacted at 180°C for 1 h, the temperature was gradually raised to 210°C, reacted for an additional 5 h, and further reacted at 8.3 kPa for 1 h. Then trimellitic anhydride (TMA) was added as monomer, reacted for 1 h, and reacted at 8.3 kPa until the desired softening point was attained.

A-PES-2: BPA-PO, terephthalic acid (TPA), as monomer, and dibutyltin oxide as catalyst were charged into a 10 l four-necked flask. The ingredients were reacted at 230°C for 10 h. Thereafter ingredients were reacted at 8.3 kPa until the desired softening point was attained. The thermal properties of reacted A-PES products and chemical components are listed in Table I.

The monomer compositions of A-PES-1 and A-PES-2 were selected to provide physical properties that are typically suitable for electrophotographic toners, with A-PES-1 having a branched structure and high melt viscosity and A-PES-2 having a linear structure and lower viscosity.

C-PES: A 10 l four-necked flask equipped with a nitrogen inlet tube, a dehydration tube, a stirrer, and a thermocouple was charged with 1,6-hexanediol (1,6-HD), FA as monomer, dibutyltin oxide and hydroquinone as catalyst. The ingredients were reacted at 160°C and held for 5 h. Thereafter, the temperature was raised to 200°C, reacted for 1 h and further reacted at 8.3 kPa for 1 h. The thermal properties and chemical components of the crystalline polyester are also listed in Table I.

Table I. Properties and chemical components of the experimental amorphous polyester resins and crystalline polyester resin.

	Alcohol monomer (mol%)	Acid monomer (mol%)	Acid value[a] (mg KOH/g)	$T_{1/2}$ [b] (°C)	T_g [c] (°C)	Melting temperature[c] (°C)
A-PES-1	BPA-PO/BPA-E O (25/25)	FA/TMA (35/15)	23	140	61[d]	
A-PES-2	BPA-PO (50)	TPA (40)	12	100	63[d]	
C-PES	1,6-HD (50)	FA (50)	35	110		113[e]

[a] The acid value was measured according to ASTM D-1980–67.

[b] The softening point ($T_{1/2}$) was measured according to ASTM E-28–67.

[c] The glass transition temperature (T_g) or melting temperature was measured by a differential scanning calorimeter.

[d] T_g was calculated by the tangential method.

[e] Melting temperature was read by the peak top.

Table II. Resin composition of toner samples. The ratio of A-PES-1 to A-PES-2 in each toner is 50:30.

	A-PES-1	A-PES-2	C-PES
Toner-A	62.5	37.5	
Toner-B	50	30	20

Preparation of Polyester Resin Blend (Blend-A)

A-PES-1 and C-PES were premixed in a batch mixer at a ratio of 80 parts A-PES-1 to 20 parts C-PES. The mixture was kneaded at 100°C by a kneading device.

Preparation of Toner Samples

Toner samples were prepared comprising the polyester resins, a wax (polyethylene with a melting point of 80°C), a charge control agent (Fe azo-complex), and a carbon black. These materials were premixed in a batch mixer and kneaded at 100°C. Then they were pulverized and classified to obtain a toner having average size of about 8.5 μm. Each toner was blended with fumed silica to achieve good powder flow properties and charging ability for printer performance evaluation. The prepared toner samples are listed in Table II.

Measurement of Fusing Performance

Fusing performance was evaluated using an off-line, oil-less fuser that consisted of a variable-temperature heated roller and a pressure roll. The diameter of the heated roller was 30 mm, the width of the nip was 4 mm, and the nip pressure was 2 kg/cm^2. Using each toner sample, an image was developed and transferred to a sheet of paper to give a mass per unit area of 0.5 mg/cm^2. Then the paper was passed through the off-line fuser at a line speed of 250 mm/s.

The upper limit of the fusing temperature was defined as the highest fuser temperature at which hot-offsetting was not observed. The lower limit of the fusing temperature was defined as the lowest fuser temperature at which cold-offsetting was not observed and the fusing ratio of the toner exceeded 70%. The fusing ratio of the toner was measured by a tape-peel test and was calculated as the percent drop in optical density of a fused solid area image measured with a densitometer before and after subjecting the fused image to Scotch tape stripping. The fusing latitude of each toner sample was defined as the difference between the upper and lower limits of fusing temperature.

Measurement of the Storage Stability

The storage stability of each toner was tested by conditioning the toner at a temperature of 50°C for a period of 48 h (after completing the pulverization and surface treatment of the toner). After the heat treatment, the powder cohesiveness of the toner was measured with a Hosokawa Micron powder tester. The cohesiveness is a measure of the toner's resistance to powder flow. Lower cohesiveness values are indicative of better storage stability. Before heat treatment, the cohesiveness of the finished toner is near zero.

Measurement of the Toner Durability

The toner durability of was evaluated by using a toner cartridge of a typical color laser printer. A 30 g sample of toner was charged into a cartridge, and the developer roll of the cartridge was rotated continuously at 70 rpm without developing the toner to the photoconductive drum. During rotation, the cartridge was monitored for signs of stress-induced toner failure, such as filming of toner material on the doctor blade and the formation of streaks on the developer roll. The cartridge was periodically placed in a fully functioning printer to monitor any changes in print quality that occurred during the stress test. The durability of the toner was defined as the period of time of continuous rotation until toner failure occurs due to doctor blade filming or developer roll streaking.

Annealing Treatment

The C-PES-containing materials used in this article (blend-A and toner-B) were subjected to an annealing treatment that involved conditioning the materials in a temperature-controlled chamber for a period of 48 h at a temperature of either 50°C or 90°C. The annealing treatment was applied to the materials after melt-mixing and coarse crushing, but before jet-milling. Toner-A, which did not contain C-PES, was not annealed.

Analysis by Wide-Angle X-Ray Diffractometry (WAXD)

WAXD analysis of C-PES and C-PES-containing toners was performed with an x-ray diffractometer (RIGAKU RINT2000) with monochromatic Cu Kα radiation ($\lambda = 0.154\,06$ nm) operated at 40 KV and 120 mA. The data were corrected in the range of $5° < 2\theta < 60°$ with an interval of 0.01° and a scan speed of 5° min^{-1}.

Analysis by Differential Scanning Calorimetry (DSC)

Thermal properties of the toners were measured with a Q100 differential scanning calorimeter (TA instruments). A temperature sweep was conducted from 0 to 150°C using a heating ramp of 10°C/min.

Analysis by Atomic Force Microscopy (AFM)

A flat cross section of blend-A was made using an ultra microtome (Leica Ultracut EM UPR) for AFM measurements. AFM images of the cross section of blend-A were obtained using a Nanoscope IIIa Multi Mode AFM (Veeco Instruments, Santa Barbara, CA) with a JV-Scanner. Tapping mode imaging was used to obtain topographic and phase images of the cross section of Blend-A. Phase imaging by tapping mode revealed differences between the mechanical properties of crystalline and amorphous domains within the polymer blend. The nominal spring constants of the cantilevers are reported by the manufacturer to be 20–100 N/m. All images presented in this work were obtained reproducibly over at least five locations on the sample surfaces. The images were acquired with a scan rate of either 0.5 or 1.0 Hz and were flattened with a first-order polynomial prior to analysis.

Rheological Analysis

An ARES parallel-plate rotational rheometer (TA Instruments) was used to measure the viscoelastic properties of the polymers and polymer blend. Three grams of sample were applied to a parallel plate with a diameter of 8 mm. A tem-

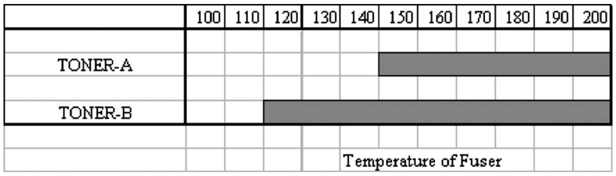

Figure 2. The effect of C-PES addition on the fusing latitude of a toner. The range of fuser temperature that provides acceptable fusing is widened in toner-B containing 20% C-PES.

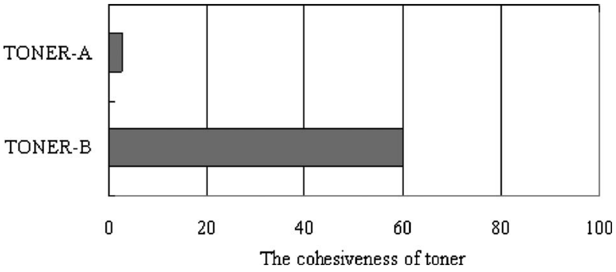

Figure 3. Higher cohesiveness in C-PES-containing toner indicates a reduction in storage stability.

perature sweep was performed from 40 to 180°C using an oscillation frequency of 6.28 rad/s and a strain of 0.05%. With the A-PES and C-PES resin samples, the temperature sweep was applied at a heating rate of 5°C/min. To measure the rheology of an annealed polymer blend, a sample of blend-A was annealed between the parallel plates of the ARES rheometer for a period of 12 h at either 50 or 90°C. After annealing, the sample was cooled to 40°C and a temperature sweep from 40 to 180°C was conducted at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Effect of CPES on Toner Performance

To understand the effect of C-PES on the performance properties of toner, including fusibility, storage stability, and durability, a C-PES-containing toner (toner-B) was compared with a control toner (toner-A) that contained no C-PES. The fusing latitudes of the two toners are shown in Figure 2. The presence of 20% C-PES in toner-B significantly widened the fusing latitude by reducing the lower limit for the fuser temperature by 30°C without reducing the upper limit. Considering the rheological behavior shown in Fig. 1, it is believed that the C-PES component may melt sharply as a first step when the toner passes through the heat roller, while the other amorphous material may melt more gradually resulting in effective low temperature fusing without reducing upper limit.

Figure 3 shows the results of an accelerated aging test used to compare the storage stability of toner-A and toner-B. The cohesiveness of the toner is a measure of the resistance to powder flow. Higher cohesiveness values in an aged toner are indicative of particle agglomeration that occurs with aging, and this condition can lead to problems with the movement of toner particles in the electrophotographic process. As shown in Fig. 3, the presence of 20% C-PES in toner-B caused a large increase in the cohesiveness of the aged toner, which indicates a significant drop in the storage stability of the toner.

Table III. The performance of toner-A and toner-B.

	Lower fuse temperature (°C)	Upper fuse temperature (°C)	Cohesiveness	Time at which filming occurred (h)
Toner-A	150	200	5	6
Toner-B	120	200	60	2

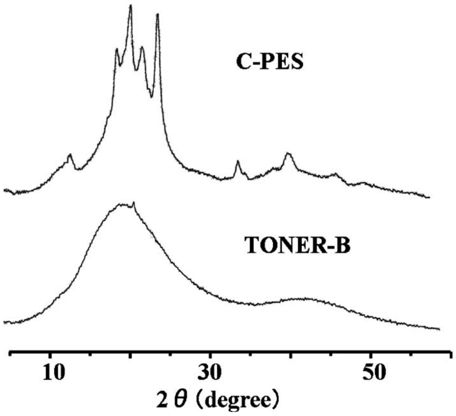

Figure 4. The WAXD analysis of C-PES and a C-PES-containing toner (toner-B).

The effect of C-PES on the durability of a toner was evaluated by comparing toner-A and toner-B in a stress test using a color laser printer. With toner-A, the time of failure due to doctor blade filming was 6 h of continuous rotation in the printer cartridge. But with the C-PES-containing toner, doctor blade filming occurred after only 2 h of continuous rotation.

The performance evaluation indicated that while the addition of C-PES provided great improvement to the low-energy fusibility of toner-A, there was an adverse effect on other performance aspects of the toner including its storage stability and durability. The performance of each toner is listed in Table III.

Crystallinity and Thermal Behavior of a C-PES-Containing Toner

In order to understand why the performance properties of a toner are affected adversely by the addition of C-PES, the test toners were analyzed for crystallinity using wide-angle x-ray diffractometry (WAXD). The diffraction scan of a C-PES-containing toner (toner-B) is compared with that of pure C-PES in Figure 4. The diffraction scan of pure C-PES revealed several sharp peaks at certain angles of diffraction that are characteristic of the diffractive nature of the polycrystalline material. In toner-B, however, the characteristic diffraction pattern of C-PES was not observed, which indicates that the C-PES polymer was no longer in a crystalline state. It is assumed that the crystallinity of the C-PES was lost during the melt-mixing stage of toner processing and

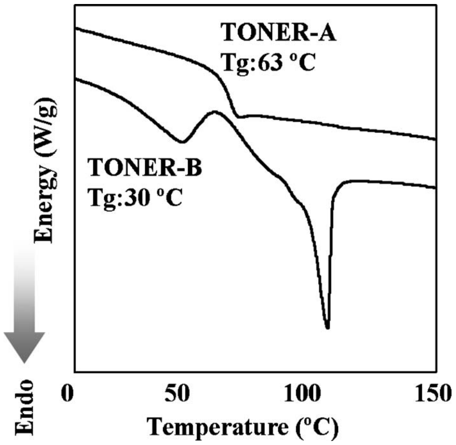

Figure 5. DSC analysis of toner without C-PES (toner-A) and with C-PES (toner-B).

that the good miscibility of A-PES and C-PES polymer melts prevented the recrystallization of C-PES polymer within the toner.

The thermal behavior of the test toners was evaluated using differential scanning calorimetry (DSC) to understand how the glass transition is affected by the addition of C-PES. The DSC curves of toners with and without C-PES are shown in Figure 5. The thermal analysis revealed that the addition of C-PES caused the T_g of the toner to decrease from 63 to 30°C. The large drop in T_g was attributed to the miscibility between the A-PES and C-PES materials causing the plasticization of A-PES when melt-mixed with C-PES. This plasticization results in a toner with a T_g that is significantly lower than any of the pure components of the toner. The lower T_g of toner-B contributes to the improved fusing at low temperature as shown in Fig. 2. However, the loss of crystallinity and the subsequent reduction in T_g in C-PES-containing toner is the root cause for the problems with storage stability and durability; therefore maintaining higher levels of crystallinity is a key to achieving better toner performance. The process of polymer annealing was investigated as a way to achieving higher crystallinity by promoting recrystallization in the toner.

Furthermore, in the thermal analysis of toner-B, exothermal behavior occurred at about 50–90°C indicating that recrystallization of C-PES occurs in this temperature range. Endothermal behavior was observed at about 100°C indicating that that C-PES melting occurs in toner-B at this temperature. This thermal analysis suggests that thermal annealing of C-PES-containing toner in the temperature range of 50–90°C could be suitable for promoting the recrystallization of C-PES.

Recrystallization of C-PES by Toner Annealing

The process of thermal annealing was applied to the C-PES-containing toner after melt-mixing to promote the recrystallization of C-PES. The annealing process involved conditioning samples of toner-B (before pulverizing) for an extended period of time at a temperature above the T_g and below the melting point. For this article, annealing temperatures of 50°C and 90°C were tested. Samples of toner-B were removed from the annealing chamber after different periods of time and analyzed by DSC to determine the effect of annealing time on T_g, as shown in Figure 6. At annealing temperatures of both 50 and 90°C, the T_g of toner-B increased substantially from the low value of about 30°C to a much improved value of about 50°C. The rate at which the T_g changed was dependent on the annealing temperature. The T_g changed much faster at the higher annealing temperature of 90°C presumably due to faster recyrstallization of C-PES, and the maximum T_g was reached in less than 2 h. At the lower annealing temperature of 50°C, the maximum T_g was reached after about 24 h.

WAXD analysis was used to confirm the presence of recrystallized domains of C-PES in the annealed toner. WAXD scans are shown in Figure 7. The sharp peaks which are characteristic of C-PES polymer in its crystalline state were observed in the toner samples annealed at both 50 and

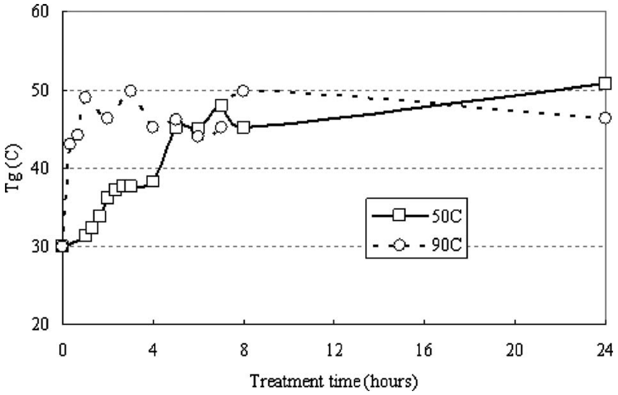

Figure 6. The effect of annealing on the T_g of a C-PES-containing toner at different annealing temperatures.

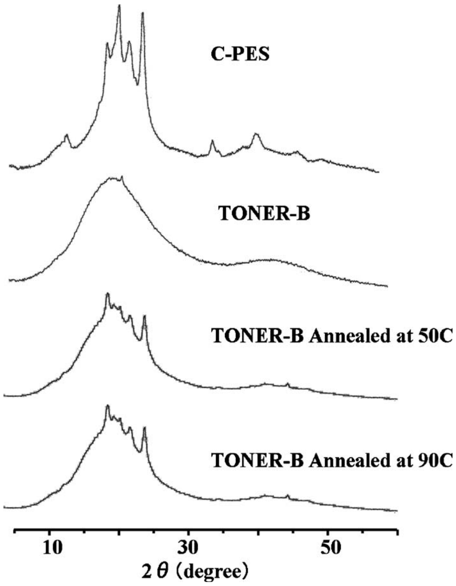

Figure 7. WAXD analysis of the C-PES-containing toner with and without annealing treatment.

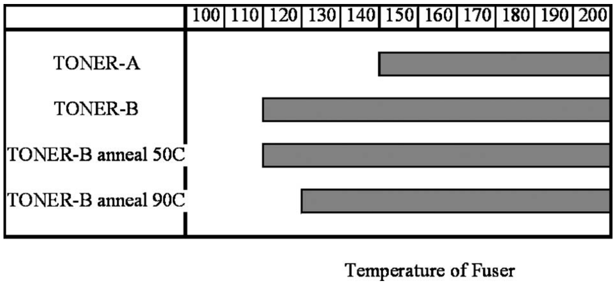

Figure 8. The wide fusing latitude of C-PES-containing toner (toner-B) is maintained after annealing at 50 or 90°C.

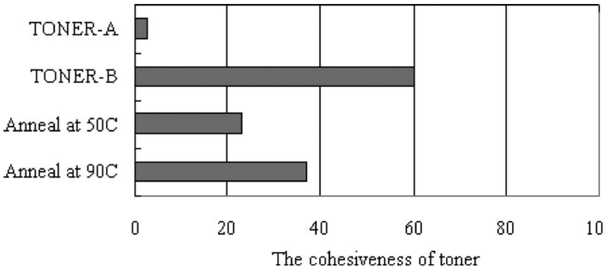

Figure 9. The storage stability of toner-A and toner-B annealed at 50 and 90°C.

90°C confirming that the annealing process promoted the growth of crystalline domains of C-PES in the toner.

Effect of Annealing on the Performance of C-PES-Containing Toner

The WAXD and DSC analyses of C-PES-containing toner revealed that the polymer annealing process promoted the recrystallization of C-PES within a period of about 24 h and reversed the T_g reduction that occurred during melt-mixing. The effect of annealing on the performance of the toner was determined by evaluating the fusing behavior, storage stability, and durability of C-PES-containing toner that was annealed for a period of 48 h. Samples of toner-B annealed at 50 or 90°C were found to maintain the wide fusing latitude that was observed in toner-B prior to annealing, as shown in Figure 8. Thus the annealed toner maintained the good fusing behavior that was achieved by the addition of C-PES to toner-A. It was seen that the fusing latitude of toner-B annealed at 90°C was slightly narrower than toner-B annealed at 50°C. Possible reasons for this difference are discussed later in this article.

Figure 9 shows the results of the storage stability testing of the C-PES-containing toners after annealing. The annealed samples of toner-B were found to have lower cohesiveness values than nonannealed toner-B in the storage stability test, i.e., the annealed toners retained better powder flow characteristics after annealing. This finding indicates that the recyrstallization of C-PES promoted by toner annealing results directly in improvements in the storage stability of the toner. The storage stability of the toner annealed at 50°C was better than that of the same toner annealed at 90°C, which is consistent with the slightly higher T_g of toner annealed at 50°C, as shown in Fig. 6.

Table IV. The durability of toner-A, toner-B, and annealed toner-B.

	Time at which filming occurred (h)
Toner-A	6
Toner-B	2
Toner-B anneal at 50°C	6
Toner-B anneal at 90°C	3

The durability of thermally annealed toners was evaluated in a stress test using a color laser printer. The results are shown in Table IV. As compared to the nonannealed, C-PES-containing toner (toner-B), the duration of printing without failure due to doctor blade filming was extended significantly with the annealed toners. The improvement in durability was especially noticeable with toner annealed at 50°C, which could endure 6 h of the continuous-rotation stress test without doctor blade filming, matching the durability performance of the toner containing no C-PES. The reasons for the inferior durability of the toner annealed at the higher temperature are discussed later.

Effect of Annealing on the Polymer Morphology of C-PES Dispersed in A-PES

Performance testing of the annealed toners revealed that the storage stability and durability of C-PES-containing toner could be greatly improved using the thermal annealing process while retaining the advantages that C-PES provides in low-energy fusing. The performance enhancements of annealing were linked to the increase in C-PES crystallinity that occurs with thermal annealing. In order to better understand the mechanism of C-PES recrystallization and its influence on the toner performance, the polymer morphology of C-PES dispersed in amorphous polyester was analyzed by phase imaging AFM, which has become an established research tool for visualizing the crystalline structure of polymers.[7–14] Phase imaging AFM can be used to generate images of the nanoscale structures in semicrystalline polymers by detecting differences between the surface modulus of amorphous and crystalline polymers. In this article, a melt-mixed blend of A-PES-1 and C-PES (blend-A) was analyzed rather than a complete toner to simplify the detection of crystalline domains in the amorphous matrix. Microtomed sections of blend-A were analyzed by phase imaging AFM before and after thermal annealing. Micrographs of the imaged surfaces are shown in Figure 10. Phase images of blend-A without thermal annealing showed a mostly flat surface without high contrast features caused by regions of higher modulus, which indicates that the C-PES was not in distinct crystalline domains in the polymer blend. It is reasoned that the crystalline domains of C-PES lost their regularly packed morphology during melt mixing with A-PES-1 due to the miscibility between the two polymers, and the crystalline structure could not be regained during rapid cooling.

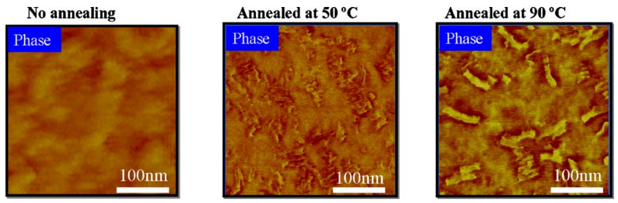

Figure 10. AFM phase images of a polymer blend of A-PES and C-PES before and after thermal annealing.

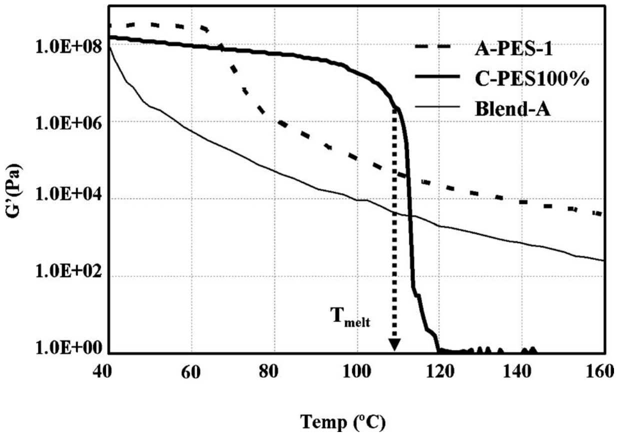

Figure 11. Temperature dependence of the storage modulus G' of A-PES-1, C-PES 100%, and blend-A.

Phase images of blend-A after annealing at either 50 or 90°C revealed many nanometer-sized domains of higher-modulus material presumed to be lamellar crystalline structures dispersed throughout the polymer blend. The crystalline lamellae were fairly uniform in size, but the size varied according to the temperature at which the polymer blend was annealed. When annealed at 50°C, the crystalline lamellae were about 10–20 nm in length; but when annealed at 90°C, the crystalline lamellae grew larger, up to about 100 nm in length. Thus the thermal annealing process promoted the formation of crystalline domains whose size could be controlled by the temperature of annealing.

The evaluation of C-PES-containing annealed toner by AFM phase imaging was complicated by the presence of various dispersed materials in the toner, including colorant, wax, and CCA, which obscured the detection of crystalline lamellae. It is assumed, however, that in toner the same recrystallization behavior occurs as in a binary blend of C-PES and A-PES.

Effect of Annealing on the Rheology of a Blend Of Amorphous and Crystalline Polyester

To understand the effect of thermal annealing on the rheology of a blend of amorphous and crystalline polyester, blends of C-PES and A-PES-1 (blend-A) were analyzed by rotational rheometry before and after annealing and were compared with pure C-PES and A-PES-1 polymers. Figures 11 and 12 show the temperature dependence of the storage modulus G' of each polymer system. To better understand the mechanism of crystallization, blend-A was used instead of toner. The rheological behavior of the C-PES polymer, shown in Fig. 11, was characteristic of a semicrystalline thermoplastic, having a relatively small drop in G' with increasing temperature in the low-temperature region, followed by a very large, sudden drop in G' at about 110°C near the temperature where the polymer crystallites undergo a phase transition to the liquid state. The temperature at which the material shows the sharp drop in G' is termed the melting temperature (T_{melt}) of the material. In contrast, the unannealed sample of blend-A showed a steady gradual drop in G' throughout the full temperature sweep, and no T_{melt} value could be observed even though the blend contained 20% C-PES. The absence of any T_{melt} with blend-A is attributed to the absence of polymer crystallites in the copolymer blend.

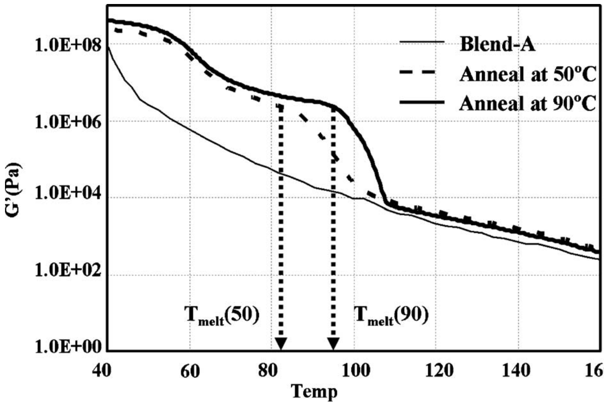

Figure 12. Temperature dependence of the storage modulus G' of blend-A with no annealing, annealed at 50°C, and annealed at 90°C.

As shown in Fig. 12, the rheological behavior of blend-A after thermal annealing was found to have a more complicated temperature dependence, including a steady gradual decline in G' and a sharp drop in G' corresponding to the T_{melt} of the crystalline material in the annealed polymer blend. It is noted, however, that the T_{melt} values in the annealed blends varied depending on the temperature at which the blend was annealed. For the blend annealed at 90°C, $T_{\mathrm{melt}}(90)$ was about 95°C. But for the blend annealed at 50°C, which was shown by AFM to have smaller crystalline lamellae, $T_{\mathrm{melt}}(50)$ was only about 85°C. This difference in T_{melt} suggests that the temperature at which crystal melting occurs in the annealed polymer blend depends on the size of the crystalline lamellae in the blend. It is proposed that the melting of smaller crystalline lamellae is affected to a greater extent by crystal lattice disruption at the interface with the surrounding amorphous polymer, and this crystal lattice disruption shifts the melting point of the polymer blend downward relative to the pure C-PES polymer.

Discussion of the Mechanism of Crystallization by Annealing and Its Effect on Toner Performance

When the rheological results of the thermally annealed polymer blends are viewed together with the AFM observations of crystalline size, the dependence of melting temperature on crystalline domain size is clearly seen. As the crystalline lamellar structures in the annealed blend become larger, the melting point increases, approaching the melting point of the pure C-PES polymer. It was found that the size of the crystalline domains could be controlled by the temperature at which the polymer blend was annealed. As discussed previously, the fusing latitude of toner-B annealed at 50°C was slightly wider than that of toner-B annealed at 90°C (see Fig. 8). The better low-energy fusing of the toner annealed at 50°C can be attributed to the smaller crystalline domains which melt at a lower temperature. This relationship between lamellae size and melting temperature could be utilized in the design of a toner for low-energy fusing by controlling the crystalline domain size to fine-tune the melting temperature of the toner.

The AFM observations of the C-PES crystalline domains also suggest some reasons for differences observed in the durability of toners annealed at different temperatures. As presented above in Table IV, the durability of toner-B annealed at 50°C was much better than that of the same toner annealed at 90°C. This difference is attributed to the smaller crystalline domains of the toner annealed at 50°C. It is suggested that the smaller C-PES crystals remain well embedded in the interior of the toner particles, so the C-PES is not present at a high surface concentration on the toner particles. In contrast, the toner annealed at 90°C contained much larger crystalline domains which could more easily protrude from or bleed to the surfaces of the toner particles. This condition could lead to more rapid filming during printing as the doctor blade and developer roll surfaces are exposed to C-PES through contact with toner particles. Thus it is believed that careful control of crystalline domain size by thermal annealing of C-PES-containing toner is a key technology for designing toners with wide fusing latitude, good storage stability, and high durability.

CONCLUSIONS

This study of the thermal annealing of toners containing crystalline polyester has led to the following conclusions:

(1) Thermal annealing promoted the recrystallization of C-PES in melt-mixed toner and in blends with amorphous polyester.
(2) The domain size of C-PES recrystallized by thermal annealing was on the order of 10–100 nm, and the size of the crystalline domains depended on the temperature of annealing.
(3) Thermal and rheological properties of a C-PES-containing toner were adjusted by controlling the size of dispersed crystalline domains.
(4) Thermal annealing of a C-PES-containing toner can be used to optimize toner performance for excellent low-energy fusing, good storage stability, and high durability.

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