Fusing Quality of Toner with Tunable Thermal Properties

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Abstract

In electrophotogrphy, print image is obtained by fusing toner developed on latent image and transferred onto printing medium. In fusing process, heat and pressure are applied to toner when a developed image passes through a fusing nip formed between fusing roller and pressure roller. During a short dwell time in fusing nip, there occur several rheological phenomena, such as sintering toner particles, adhesion of toner onto paper, spreading of toner particles and release of molten toner from fuser. Fusing process is complex and fusing performance is determined by a wide variety of factors such as rheological properties of toner, paper characteristics, and a fuser design and fusing parameters such as temperature, speed and pressure.

This study reports the relationship between the rheological properties of toner and fusing quality. Toner is prepared from a mixture of 2 different binder resins and it has tunable thermal properties, which can be controlled by the dynamic viscoelastic properties of each resin and the ratio of resins in toner. The prepared toner has a wide range of thermal properties, such as glass transition temperature (T_g), $T_{1/2}$, storage modulus, loss modulus depending on molecular weight of toner controlled by ratio of binder resins. Prepared toner is transferred onto paper in a modified color laser printer and the un-fused image is fused through a fusing apparatus. Fusing quality, such as fusing efficiency and gloss, and image quality, such as image density, are analyzed and their dependency on the rheological properties of toner is studied. This study can be useful in not only understanding the underlying principles in fusing process, but also designing toner with better fusing properties for better print quality.

Introduction

In electrophotogrphy, print image is obtained by fusing toner layer, which is developed on latent image and then transferred onto printing medium. Fusing is one of the most important processes in determining print quality. An error in fusing process results in image defects, such as hot offset and cold offset, or poorly fused image that cannot last long. Many fusing methods have been developed, such as cold pressure method, solvent method, flash method, radiant method and heat roll method [1,2]. Cold pressure method consumes less energy and fusing can be instant, but it requires high pressure above 1,000 psi and normally results in poor fusing quality. A radiant method has a simple process and a long machine life, but it consumes a lot of energy and a very high level of temperature control is required. Among many fusing methods, heat roll fusing is the most commonly used fusing method [2]. Heat roll fusing method adopts a pair of roller, one soft roller and one hard roller. One of the rollers functions as a fusing roller and the other roller functions as a pressure roller. Hard Fusing roller and Soft Pressure roller (NFPR) combination and Soft Fusing roller and Hard Pressure roller (NFFR) are mainly used [3].

In heat roll fusing process, toner melts are fused onto printing medium under the influence of heat and pressure. The heat and pressure are exerted to toner at fusing nip, which is formed between a heating roller and a pressure roller. There are many fusing performances, such as minimum fusing temperature, hot offset temperature, cold offset temperature, releasability from fuser surface, which all depend on the thermal and rheological properties of toner. During a short time in fusing process, there occur several rheological phenomena, such as sintering toner particles, adhesion of toner onto papers and spreading of toner particle and release of molten toner from fuser [4,5]. The rheological change in toner is one of the most critical factors in determining fusing quality and it needs to be optimized for a fusing method and fuser design [6].

The level of toner fusing can be measured by various methods, such as scratch, gouge, abrasion, crease, peel-off [2,3]. Hot offset, cold offset, fusing efficiency, dot gain and gloss are a measure of fusing performances. Hot offset and cold offset are explained by the relative strength of adhesion between toner and paper, cohesion among toner, adhesion between toner and fusing roller. When the cohesion among toners becomes smaller than the adhesion between toner and roller, the molten toner sticks to fusing roller and hot offset will occur. When the adhesion between toner and paper becomes smaller than the adhesion between toner and roller, toner particle sticks to roller and cold offset will occur. The fusing process needs to be such as the adhesion between toners and roller should be smaller than the cohesion among toner and adhesion between toner and paper to prevent hot offset and cold offset. High gloss can be obtained by flat toner layer and reflects incident light regularly and is preferred for color print, especially photo like printing.

Toner fusing is mainly determined by thermal properties of toner, which includes T_g, $T_{1/2}$, Tm and rheological properties such as storage modulus, loss modulus, tangent delta, and complex viscosity. Also fusing parameters such as fusing speed, dwell time, and fusing pressure play a key role in determining fusing quality. The structure and molecular weight of binder resin are key factors in determining such thermal properties. The molecular weight of toner can be determined by binder resin molecular weight and it can be easily controlled by using a mixture of two or more different types of binder resin. The properties of each binder resin and the ratio of each binder resin in resin mixture are controlled to obtain different molecular weight and thermal properties of toner. This study reports the relationship between the thermal and rheological properties of toner, which is made from a mixture of two different binder resins, and fusing performance.

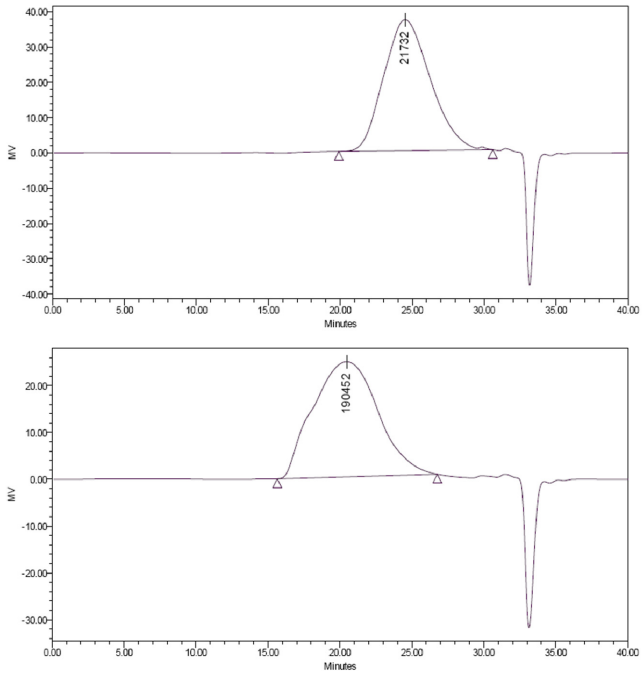

Figure 1. GPC measurement of binder resin molecular weight. Toner has a molecular weight of 83,000 g/mol (top) and 22,500 g/mol (bottom). Binder resins are prepared by mixing different types of resins and the properties of binder resin is controlled by the ratio of a mixture.

Experiments

Chemically prepared toner (CPT) was used in this study. Toner was prepared from a mixture of two different binder resins with different characteristics. Two resins differed in average molecular weight but they shared common monomer unit and functionality. One binder resin had a low molecular weight and the other had a high molecular weight, which was 15 times higher than that of low molecular weight. Other characteristics such as glass transition temperature, latex dispersion particle size were same. The CPT was prepared by the synthesis procedure, which was already published [7,8]. The thermal properties of prepared toner were controlled by the ratio of two binder resins. The molecular weight of a binder resin mixture was measured by Gel Permeation Chromatography using Waters 1515 isocratic pump, Waters 2414 RI detector, and Waters 2707 auto-sampler. The size and the size distribution of 5 toner samples were measured using Multsizer 4 Coulter counter and listed in Table 1. The average diameter of toner with different molecular weight ranged from 6.79 μm to 7.25 μm, and the size distribution, GSPp and GSPv, were in range of 1.205 ~ 1.209 and 1.217~1.251 and it showed a very narrow size distribution. The size and distribution of five samples were similar regardless of the molecular weight of binder resin. Depending on the ratio, the molecular weight varied from 22,500 g/mol to 83,000 g/mol as shown in Table 1. Figure 1 showed the GPC measurement of two samples, whose molecular weight was 83,000 and 37,600. The prepared toners had same sizes and size distributions, and the effects from toner size were controlled in fusing test. The characteristics of prepared toners were listed in

Table 1. The characteristics of tested toner

Toner	Mw	D50 (μ m)	GSPv	GSDp
1	22500	6.89	1.223	1.209
2	37600	7.25	1.251	1.206
3	52800	6.79	1.224	1.209
4	57900	6.87	1.217	1.203
5	83000	6.92	1.217	1.205

table 1. The toner was prepared for fusing test by blending 200g of bare toner with 4 different external additives in a power mixer. The additive blending was done at 8000 rpm for 6 minutes. The tribocharge of toners were measured by blow off method using Epping Q/M meter. The toner was mixed with ferrite carrier for 10 minutes and the resulting charge level ranged from -51.85 μC/g to -61.31 μC/g as shown in Table 2. The thermal and rheological properties of toner were measured using capillary rheometer, rheometer, and differential scanning calorimeter.

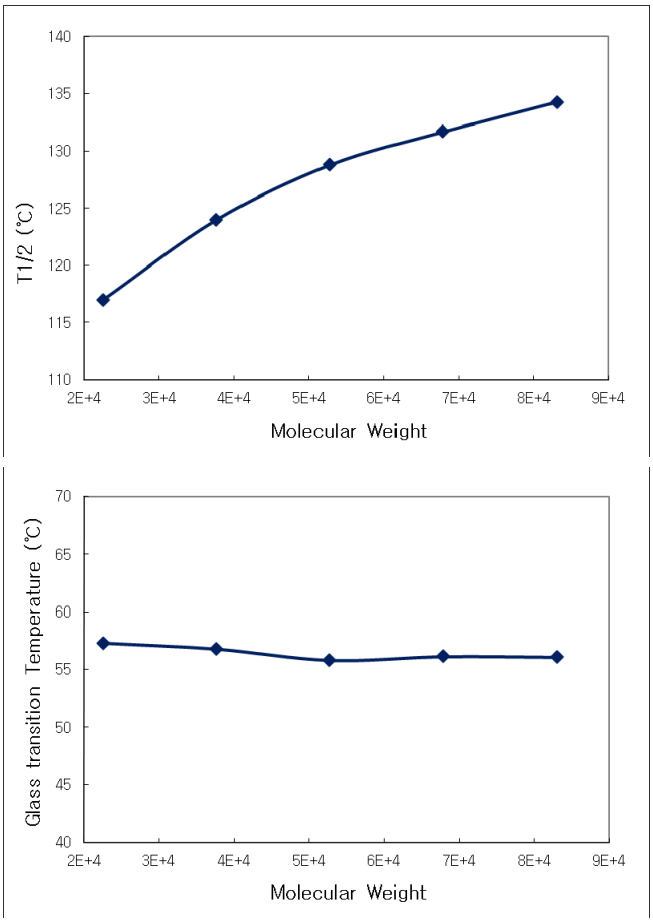

Figure 2. The thermal properties of toners with various molecular weight of binder resin. $T_{1/2}$ increases from 117 ℃ to 135℃ as the molecular weight increases from 22,500 to 83,000 (top). T_g does not change and is in the range of 55.81 ℃ to 57.3 ℃ (bottom).

Table 2. Tribocharge of tested toner

Toner	1	2	3	4	5
Tribocharge (μ C/g)	-61.31	-60.39	-61.07	-57.89	-51.85

$T_{1/2}$ (half effusion temperature) was measured using Shimadzu capillary rheometer and T_g (glass transition temperature) was measured using TA Q2000 DSC. Storage modulus, loss modulus, tangent delta and complex viscosity were measured using TA ARES-G2.

The prepared toner was loaded into a toner cartridge. A color laser printer was modified, so that each step in electrophotography processes could be separately conducted. For fusing quality test, printing process stopped between 2nd transfer and fusing process and the un-fused images, which was toner transferred on paper, were obtained. The amount of toner per unit area was controlled by process parameters and the same amount of toner was transferred on paper in each fusing test. The un-fused image passed through a fusing apparatus, in which fusing temperature, speed, and pressure could be individually controlled. The fusing roller speed was varied from 75 rpm to 140 rpm. The pressure of pressure roller was varied from 100 kPa to 500 kPa. The fusing temperature was varied from 120 ℃ to 190 ℃. After each fusing test, a fusing roller was cleaned to remove any residual toner. The qualities of fused image including fusing efficiency, gloss and image density were characterized on solid image. Hot offset and cold offset were visually checked. Fusing efficiency was measured by peel-off method. An original image density of solid image was measured with densitometer by GretagMcbeth. 3M tape was put on the solid image and was rubbed by a test jig, where a load of 50g was rubbing 3M tape automatically, and then 3M tape was peeled off gently not to damage original image. Finally, image density was measured after peel-off. The ratio of image densities before and after peel-off was obtained as fusing efficiency. The gloss of fused image was measured with gloss meter by BYK Gardner. The surface of fused toner layer was observed with SEM to observe the fusing state. The rheological properties such as the storage modulus, loss modulus and tangent delta were measured as temperature increased from 65 ℃ to 200 ℃ at the increment rate of 2 ℃/min. The oscillatory frequency was set at 6.28 rad/s.

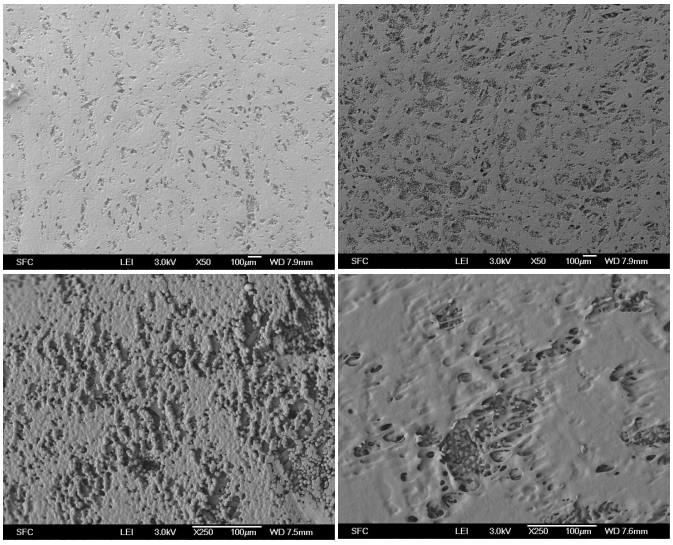

Figure 3. SEM images of fused toner layer surface. (a) The surface of fused toner with low molecular weight. The toner surface is smooth and it shows higher gloss (top left). (b) The surface of fused toner with high molecular weight. The surface is rough and it shows lower gloss (top right). (c) The surface of cold offset image. Toner particles are not fully melt and are missing at some areas (bottom left). (d) The surface of hot offset image.

Results and Discussion

Figure 2 shows $T_{1/2}$ and T_g of toners with different molecular weight. $T_{1/2}$ increases from 117 ℃ to 134.3 ℃ as the molecular weight increases from 22,500 to 83,000. T_g stays in the range of 55.81 ℃ to 57.3 ℃ and does not change with molecular weight. T_g of two different binder resins was designed to have same value, so T_g of the mixture stays same regardless of the ratio of each binder resin. Figure 3 shows the SEM image of fused toner layer. The toner layer surface is smooth for well-fused image with high gloss. Figure 3(a) and (b) shows the surface of toner layers of molecular weight of 37,600 and 57,900, which are fused at same temperature, speed and pressure. The toner with lower molecular weight shows more flat surface than the toner with higher molecular weight. The surface became rough with the increased molecular weight as seen in Figure 3(b). The surface of cold offset image is shown in Figure 3(c) and the toner particles, which are not fully melt yet, are observed. Also areas, where toner particles are missing, are observed in toner layer. The missing toner sticks to fusing roller and cause cold offset. Figure 3(d) shows the toner surface of hot offset image. The toner particles are fully melt, but the surface becomes rough since toner melt has lower viscosity than needed and stick to the fusing roller. The temperature, where hot offset starts to occur, increases with the molecular weight and toner with highest molecular weight do not show any hot offset, while toner with low molecular weight shows hot offset in the tested temperature range.

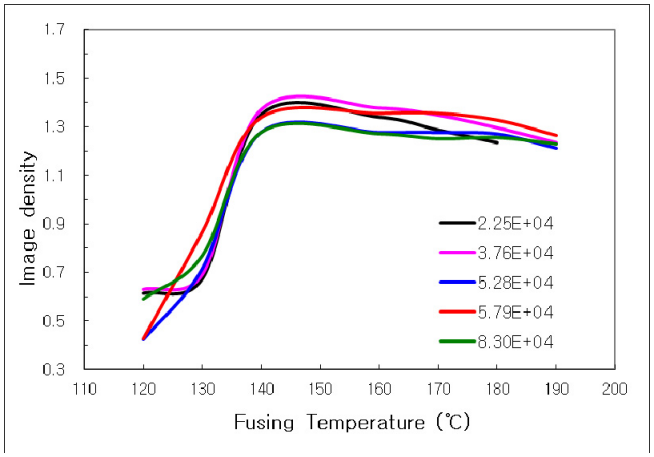

Figure 4. Image densities of solid pattern of toner, with different molecular weight. The difference between samples is less than 0.2 and can be neglected. The image densities are low below 140 ℃ due to cold offset and reaches the maximum at 140 ℃.

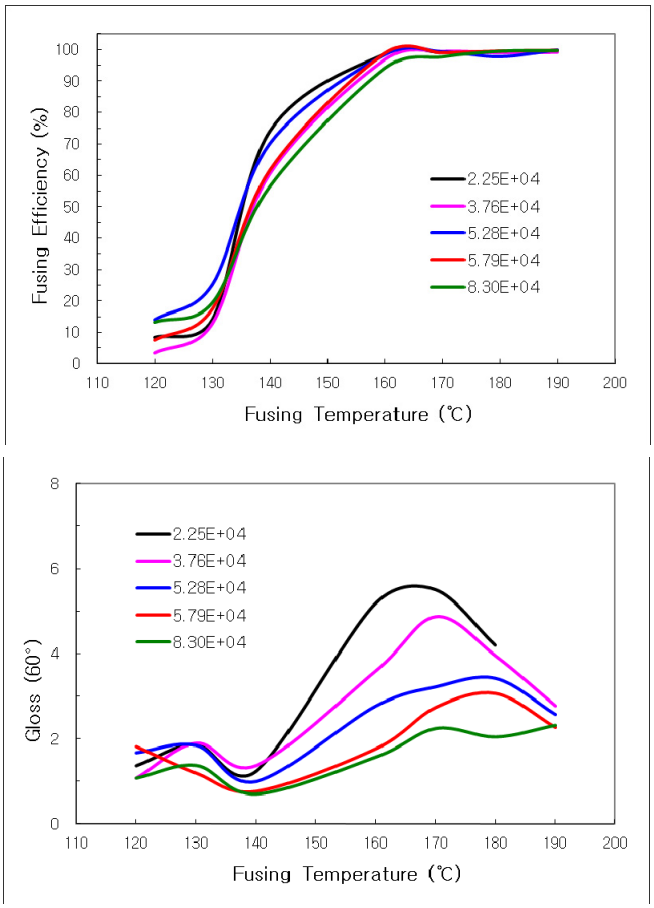

Figure 5. (a) Fusing efficiencies of toner samples with different molecular weight. Fusing efficiencies rapidly increases from 130℃ and reached maximum values at 160 ℃. (b) Gloss changes at each fusing temperature. Toner with lower molecular weight exhibits higher gloss at the same fusing conditions. Gloss increases and reached maximum value as temperature increase, but decrease as temperature increases further. The temperature, at which gloss reaches its maximum, increases with molecular weight.

The image densities of each toner fused at different temperature are plotted in Figure 4. The image densities do not change much with molecular weight but rather with fusing temperature. The image density is low below 140 ℃ due to cold offset. The image density decreases with temperature above 140 ℃. However the hot offset does not have much effect on image density, where image densities are similar regardless of hot offset. The toner with different molecular weight shows different tribocharge level, even after additive-blended same way, as in Table 2. It is suspected that the mechanical hardness of toner changes and it affects the additive dispersion conditions on toner surface. The dynamic mechanical properties of individual toner particle are analyzed with nanoDMA and it varied with molecular weight as seen in Figure 8. With higher molecular weight, individual toner particle has smaller tanδ, and tends to be more elastic. We observed the additive dispersion state on toner surface becomes non-uniform as molecular weight increases and it may affect the tribocharge level of toner. The relationship between additive dispersion and the toner particles properties needs extensive study

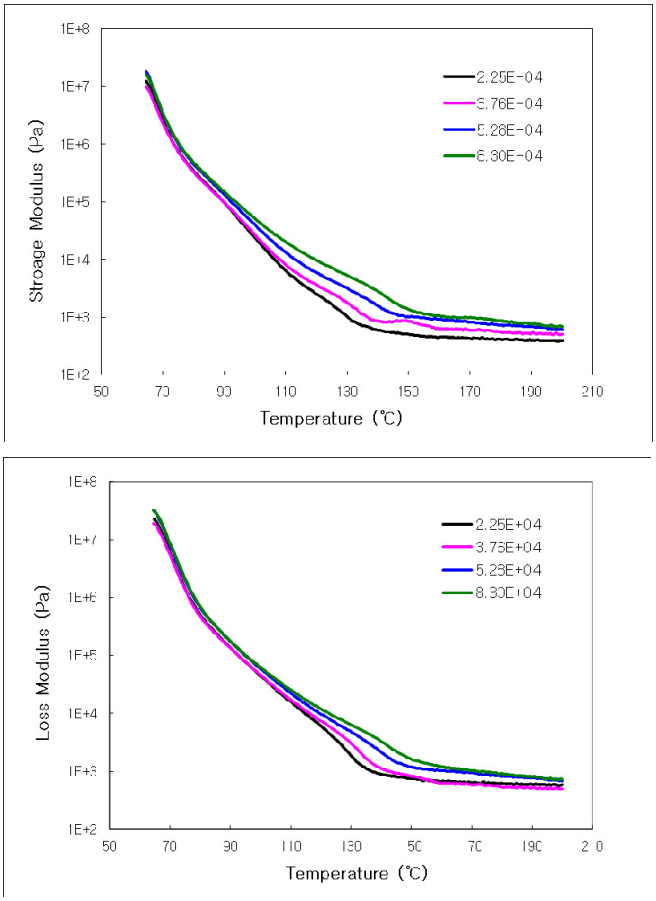

Figure 6. (a) Storage modulus of toners. Toner with low molecular weight exhibits low storage modulus value and storage modulus increases with the molecular weight. Storage modulus for all samples are similar below 80℃. (b) Loss modulus exhibits similar trends as storage modulus. It decreases with temperature and toner with lower molecular weight has lower loss modulus value. Loss modulus for all samples is same below 90℃ and above 80℃. The storage modulus and loss modulus intersection is not observed in tested temperature, since T_g is not in the tested range.

and it will be useful for who design the toner and additive blending process. However it is beyond the scope of this study and left for future work.

The fusing efficiency and gloss at each fusing temperature are plotted in Figure 5. Fusing efficiency increases with temperature below 160 ℃. After reaching maximum fusing efficiency at 160 ℃, fusing efficiency stays at the maximum value, almost 100%. Toner
1 with the lowest molecular weight shows higher fusing efficiency between 130 ℃ and 160 ℃ and Toner 5 with the highest molecular weight shows lowest fusing efficiency. The 60° gloss is plotted in Figure 5(b). Gloss increases with temperature and reached maximum value and then decreases with fusing temperature. The temperature, where gloss reaches its maximum, increases with molecular weight. The toner with molecular weight of 22,500 reaches the maximum value at 165 ℃ and the toner with

molecular weight of 57,900 reaches the maximum gloss at 180 ℃. The dependency of gloss on the molecular weight is much clearer than that of fusing efficiency. The toner with higher molecular

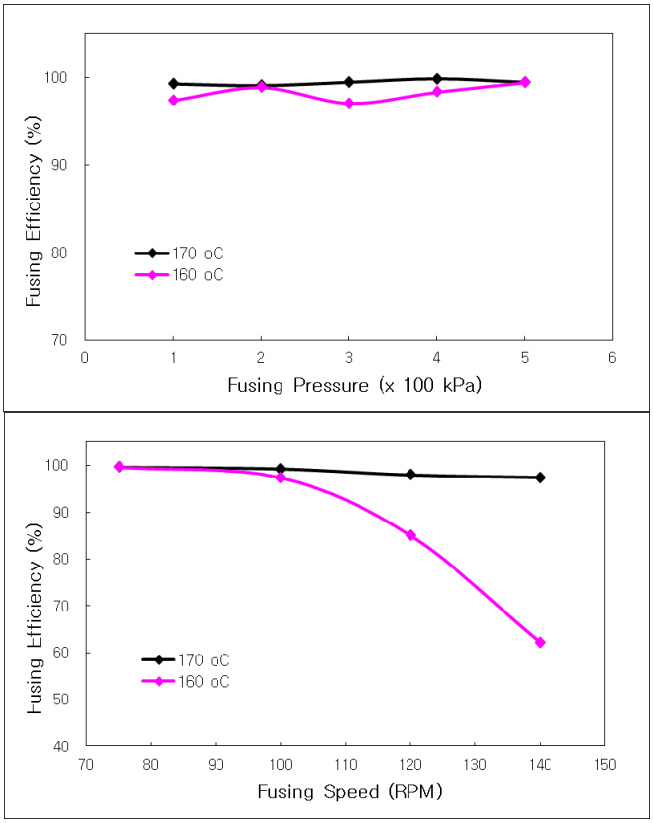

Figure 7. The fusing efficiency and gloss of printed images fused at different fusing speed and pressure. The fusing efficiency does not change with fusing pressure. It drops rapidly with fusing speed when fused at 160 ℃, but stays same when fused at 170℃.

weight exhibits lower gloss due to the surface state of fused toner layer.

It is known that as molecular weight increases, the storage modulus increases and thus tanδ decreases. When this occurs, the elastic behavior of toner becomes strong and gloss decreases. Also when the molecular weight increases, the complex viscosity shifts into the higher temperature regions and the temperature, at which the toner has viscosity level of being fused, increases [9]. This phenomenon is confirmed by rheology measurement as seen in Figure 6. The storage modulus monotonically decreases with temperature. All five toner samples have similar values below 80 ℃, and the storage modulus differentiate, but toner with higher molecular weight has higher storage modulus at all temperature range including plateau region. Toner 1, with the lowest molecular weight, has lowest storage modulus and Toner 5, with the highest molecular weight, has highest modulus. Storage modulus drops below 1,000 Pa at high temperature ranges in all five samples. The loss modulus exhibits similar behavior, but the discrepancies is smaller than in storage modulus. The loss modulus below 100 ℃ shows similar values for all samples and they become similar again in plateau region above 170 ℃. The dependency of loss modulus on temperature is same as that of storage modulus. In tested temperature range, the storage modulus and loss modulus intersection is not observed and it is suspected that it will occur below 60℃ as Tg of all 5 samples is below 60℃.

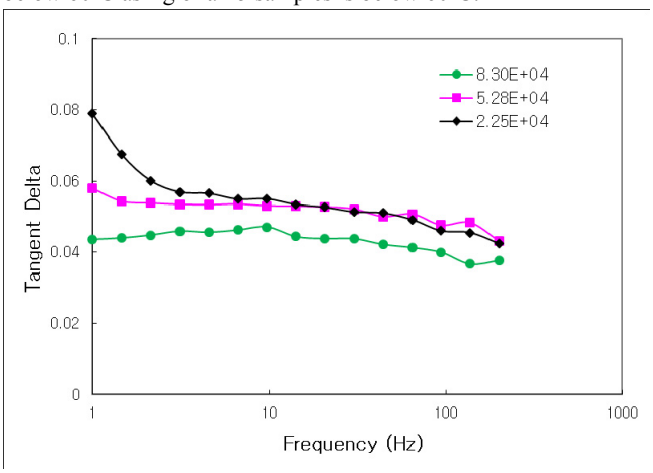

Figure 8. The dynamic mechanical measurement of individual toner particles. The measurement is done by nano DMA and 20 particles are measured to obtain statistic values. The average tangent delta decreases with molecular weight.

It cannot be neglected that fusing quality is determined by fusing apparatus design and fusing conditions as well. The two fusing parameters, fusing speed and fusing pressure are tested in Figure 7. The pressure of pressure roller in fusing apparatus varies from 100 kPa to 500 kPa and it does not have any effects at fusing temperature of 160 ℃ and 170 ℃. However the fusing speed has a noticeable effect on fusing efficiency. As fusing speed increases from 75 rpm, which is equivalent to the processing speed of 72.5 mm/s, to 140 rpm, which is equivalent to the processing speed of 135.3 mm/s, the fusing efficiency drops from 100% to 60%, when fused at 160 ℃. This corresponds to the dwell time at nip of 56.5 ms and 30.3 ms. As dwell time at nip decreases, the heat transfer to toner is not enough to fuse toner and thus fusing efficiency decreases. However, the fusing efficiency does not change with fusing speed, when fused at 170 ℃. Since the higher fusing temperature induces more heat transfer to toner during the same dwell time and for 170. It is reported that dwell time increases, the toner-paper interface temperature decreases due to the heat transfer during dwell time [10]. Thus minimum fusing temperature as well as fusing quality is strongly affected by fusing speed and fuser design. Also this phenomena is explained by τ_w, the weight average relaxation time, which is defined as

$$\tau_w = A_G/\eta_0$$

where A_G is the infinite frequency limiting value of storage modulus and η_0 is zero-shear viscosity. When dwell time at nip is longer than τ_w, the binder resin is in terminal zone and all the entanglement of polymer chains may be undone. When this occurs, high gloss is obtained [11]. When dwell time at nip is shorter than τ_w, the resin behavior is not in terminal zone and entanglement may partially remain in polymer chain. When this occurs, fused image has low gloss [6].

So far we have studied the fusing quality, which is mainly determined by thermal and rheological properties of toner and its dependency on toner molecular weight. However the molecular weight of toner not only determines the thermal properties of toner, but also other properties, including mechanical properties. The dynamic mechanical properties of individual toner particle are measured with nanoDMA and shown in Figure 8. To get rid of possible thermal effect, which may occur during sample preparation for DMA tests, the mechanical property of individual toner particle is measured. Since we measure individual particles, we expect variation from toner particle size and shape and measure 20 particles for each sample. Tangent delta of toner particle decreases with molecular weight. The discrepancy becomes larger as frequency decreases and the average tanδ becomes double, as molecular weight decreases from 507,000 to 184,000. Table 3 shows the statistic value of tanδ at 3.11 Hz and the standard deviation is less than 10% of average value and the particle to particle variation can be tolerated to use average value.

Table 3. NanoDMA measurement

Mw	83,000	52,800	22,500
Average Tanδ	4.59×10^{-2}	5.34×10^{-2}	5.69×10^{-2}
Standard deviation	2.6×10^{-3}	5.0×10^{-3}	8.5×10^{-3}

Conclusion

The fusing quality of toner samples made from a mixture of binder resin with different molecular weight has been studied. The fusing efficiency and gloss are measured and their dependency on toner molecular weight, fusing temperature, fusing speed and fusing pressure are tested. The fusing quality depends on many factors, from toner material to fusing apparatus, and the more detailed relation between fusing quality and those factors needs to be studied to discover fundamental phenomena in fusing are studied following this empirical study. Also, the mechanical properties of individual toner particle are measured and the effect of molecular weight on them is observed. To related both properties more clearly, the mechanical and rheological properties need to be studied in more detail.

References

[1] John Doe, Recent Progress in Digital Halftoning II (IS&T, Springfield, VA, 1999) pg. 173.

[2] D. Thomson, Fusing Technologies and toner material relationships, tutorial 14, NIP24 (2008)

[3] M. Smith, "Digital Imaging," Jour. Imaging. Sci. and Technol., 42, 112 (1998).

[4] X.E. Jones, An Inexpensive Micro-Goniophotometry You Can Build, Proc. PICS, pg. 179. (1998).

[5] M. Tse, A fusing apparatus for toner development and quality control, NIP 13 (1997)

[6] M. Nakamura, The effect of toner rheological properties on fusing performance, Recent progress in toner technology, pg 404

[7] KR patent 0119786 (pending)

[8] KR patent 0118536 (pending)

[9] S. Inoue, A new EA-Eco toner for B/W printer and its gloss control, Imaging conference Japan 2012

[10] S. Hasebe, A consideration of the mechanism about fusing quality based on toner deformation, Imaging conference Japan 2012

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