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Characterization of Electrophotographic Printing Toner: Thermomechanical Point of View

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ABSTRACT

Digital printing is affected by several parameters therefore, Process changes aimed at improving printer engine performance must take into consideration not only the process variables, but also the melt rheological variables. The thermo-mechanical properties of Konica Minolta BizHub C350 toners (in four colors) have been investigated with TGA, DSC and rheometer, as well as the physical and optical properties that have been evaluated using optical microscope, laser scattering particle size analyzer and spectrophotometer. The thermo-rheological evolution of the electrophotographic printing toners in the fusing stage of the image development has been investigated thoroughly. It was found that by increasing the temperature, the toner particles undergo initial surface fusing at around 70 °C which is followed by reduction in viscosity. However, the melting of the particles takes place at 155-172 °C which is resulted in completely merged particles. The melting temperature of the fur colors are occurred at a specific order that matches the standard printing sequence of four-color printing. Prog. Color Colorants Coat. 17 (2024), 175-183© Institute for Color Science and Technology.

1. Introduction

The flow properties of fine powders at very low consolidation levels are relevant to small scale industrial application of powder flow, such as in small process hoppers or in everyday applications such as toner flow in cartridges [1]. Toners are fine powders (particles typically lie in the size interval from a few µm to 12 µm) that are used in modern laser printers and photocopiers [2]. They are in fact complicated mixtures that consist of a thermoplastic base material within which the colorant (organic or inorganic pigment nanoparticles and/or dyes) and different ingredients such as a charge control agent (CCA), flowing agents, pigments, UV-stabilizers and other additives have been mixed [3].

The electrophotography process can be divided into 6 steps: Charging, Exposing, Developing, Transferring, Fusing, And Cleaning. These different steps are well explained in other reviews [4, 5].

The transferred toner is then permanently fixed on the paper by fusing in the fifth step. This involves application of heat, e.g. radiantly with an infrared source, to induce toner flow, often together with applied pressure, e.g. in the nip between heated rolls. Fusing is complex process and tuning it requires an understanding of: mechanical engineering–chemistry/ organic chemistry, heat transfer, paper handling, temperature control systems, colorimetry/light transmission through toners, toner rheology/ viscoelasticity, toner flow, conformable roller coating technologies, fluid coating/ fluid splitting, mechanics of

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conformable nips and high performance elastomers (high temperature, stress) [5].

Fusing is the final process in electrophotographic printing. If the toner has not melted enough, the adhesion on paper is very poor. The optimal fusing temperature of the toner can be estimated from the viscosity and the viscoelastic transition of the toners. Digital printing quality is affected by several parameters including printer, paper and toner which determine the final printing quality. For investigation those effects in the series of previous studies, the authors studied the production of black [6], ceramic [7], fluoresce [8], color [9], food grade [10] and textile toner [11] toner with eco-friendly emulsion aggregation (EA) and polymerization [12, 13] method. It has been extensively established that achieving optimal printing quality relies on the careful optimization of toner's thermal properties. The toner must strike a balance between softness for effective fuser binding and sufficient hardness to prevent fusion in the photoreceptor during development. Therefore, the rheological properties of the toner play a crucial role in facilitating coalescence, spreading, and successful penetration into the paper, ultimately leading to the best printing results [14]. To meet these stringent requirements, it is essential to carefully tune the physical and mechanical properties of the toner, as well as ensure the appropriate particle size and shape.

In continuation of our works, the aim of this study is to investigate the rheological behavior of four most common used color toner as well as their physical characteristics. In this work authors combined the thermomechanical measurement with other analysis to better understand the toner properties.

2. Experimental

2.1. Material

Konica Minolta BizHub C350 toner in four colors (cyan 350, magenta 350, yellow 350 and black 350) are used.

2.2. Characterization

Reflectance measurement of the printed toner was performed in the range of 380-780 nm with 10 nm intervals using a GretagMacbeth Color Eye 7000A spectrophotometer (USA), an instrument with 8/d geometry in a specular component including (SCI) mode. Then it transformed into CIELAB colorimetric coordinates (L*, a*, b*) by using CIE standard illuminant D65 and a CIE 1964 standard colorimetric observer [15]. An increase in L* indicates lightening of the sample. A positive Δa* signifies a color shift toward red; a negative Δa* signifies a color shift toward green. Similarly, a positive Δb* signifies a color shift toward yellow; a negative Δb* signifies a color shift toward blue [3].

The measurements of particle size and particle size distribution done by using particle size analyzer (PSA, Malvern Rasterizer 2000, England) in the range of 0.02-2000 μm. Evaluation of the particle size distribution (PSD) is normally achieved through the span parameter, as follows (Eq. 1):

$$\text{Span}= \frac{(D_{90}\text{-}D_{10})}{D_{50}} \tag{1}$$

where D50 denotes diameter (μm) at which half of the particles have the size below this value. Similarly, D90 and 10 were defined.

Thermal behavior of the toner was conducted on a differential scanning calorimeter (DSC, PerkinElmer USA). Approximately 5 mg of each sample was loaded onto a pan and sealed with a covering lid. The measurements were taken over a temperature range of 0-150 °C at a heating rate of 10 °C/min in an atmosphere of nitrogen. Thermogravimetric analysis (TGA) was carried out, in order to determine the thermal stability of the samples (TGA, PerkinElmer USA). The samples were heated from 25 to 500 °C with a heating rate of 10 ºC/min under nitrogen atmosphere.

Amplitude sweep testing was performed for each sample, prior to the intended rheological measurement to ensure that the experiment carries out in the linear viscoelastic (LVE) regime of the sample (Figure 1) [16].

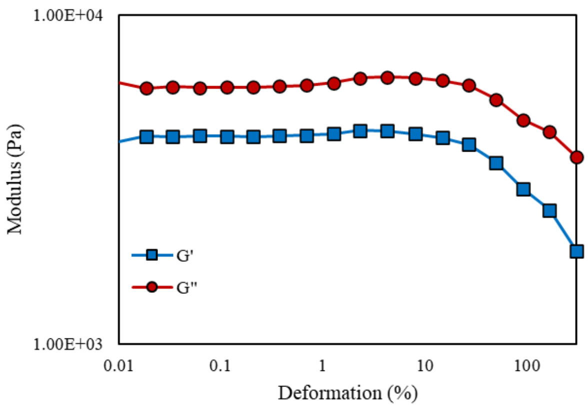

Figure 1: Storage and loss moduli of the Black 350 as a function of deformation in order to find the LVE region of its behavior.

Viscosities of bulk molten toner of the four process colors have been measured at different temperatures using an Anton paar MCR300 rheometer with cone-plate set-up in controlled shear stress mode. In each case the shear rate was increased from 0.01 to 10 Hz and reversed back down to 0.01 Hz, with 7 measurements distributed on a logarithmic scale for both increasing and decreasing shear rates.

The morphology of the toners was observed using polarized optical microscopy (KYKY-EM3200, China), and the circularity of the toners were determined utilizing Image J software.

3. Result and Discussion

3.1. Thermal and microstructural analysis of toner

The measurements of the particle size and the particle size distribution of all toners with the Malvern PS analyzer show that toners have appropriate particle size and, mean particle size distribution (~1) for printing (Table 1).

The thermal characteristics of the toners, namely T_g (glass transition temperature), are important. This importance is due to having a direct effect on the fixing properties of toners onto the paper substrate. A moderate T_g value is generally required for the toner to have appropriate fixing properties. A too high T_g results in large-scale energy consumption during the printing process [17], and a too low T_g causes the toner to stick to the printer cartridge. Adjusting the T_g of the toner and subsequently its transfer temperature is critically important since it is desirable to reduce the fusing temperature according to environmental concerns and various methods have been proposed to reduce it such as incorporating small amount of crystalline resins [18] or using thermal insulating paper coatings [19]. For an industrial toner, to have suitable fixing properties for energy-efficient laser printing, T_g should normally be in the range of 50 to 70 °C [20]. The amorphous polyester resins that are typically utilized in toner production also have the Tg in this range [17]. Figure 2 shows the results of DSC analysis of commercial industrial toner. The slight shift of the base line is recognizable that can be attributed to the Tg. It is noteworthy that, in all the curves, the Tg is coincided with enthalpy relaxation peak and initial melting stages, which has been reported in other researches [20]. So, the exact temperature of glass transition cannot be stated but it is clear that it is resides around 70 °C which is in good correlation with other researchers' findings [21, 22].

Figure 3 shows the TGA diagram of commercial toner. Toners has followed a one main decomposition step around 300 to 400 °C. After the thermal decomposition of organic constituents at high temperatures, the residual weight percentage of the sample can be considered as the inorganic content which was consisted of carbon black and inorganic toner additives (≈ 20 %) [18, 20]. Surprisingly, in other samples, as well as the black sample, 14-22 % of the initial weight was remained. Since the inorganic pigments generally do not provide enough color strength to be utilized in printing toners, it can be interpreted as the presence of thermally stable organic and organometallic pigments such as copper phthalocyanine in addition to inorganic fillers and additives in these samples [23].

Table 1: Results of colorimetric and particle size analysis of the toners.

Toner properties	Cyan	Magenta	Yellow	Black
Color	L* = 52.07 a* = -14.86 b* = -30.8	L* = 51.31 a* = 45.75 b* = 6.64	L* = 85.79 a* = 3.46 b* = 78.38	L* = 37.65 a* = 0 b* = -.52
Particle size (μm)	10.84	9.84	10.173	9.496
Mean particle size distribution	0.787	1.191	0.822	0.741

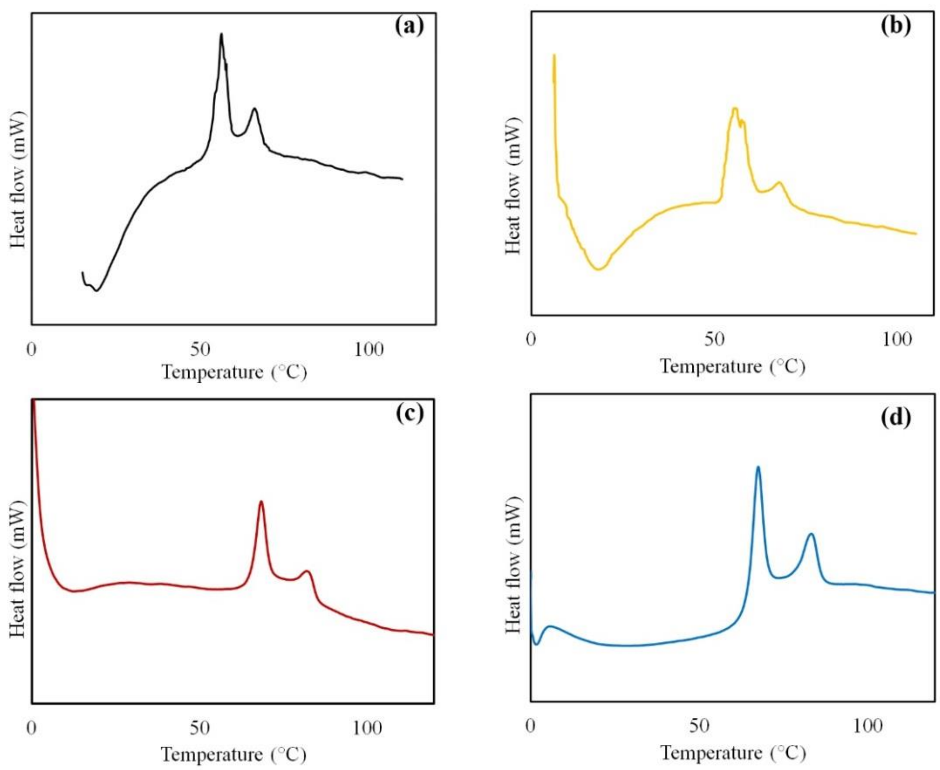

Figure 2: DSC diagrams of the sample (a) Black 350, (b) Yellow 350, (c) Magenta 350, and (d) Cyan 350. In all the curves, endo peak is up.

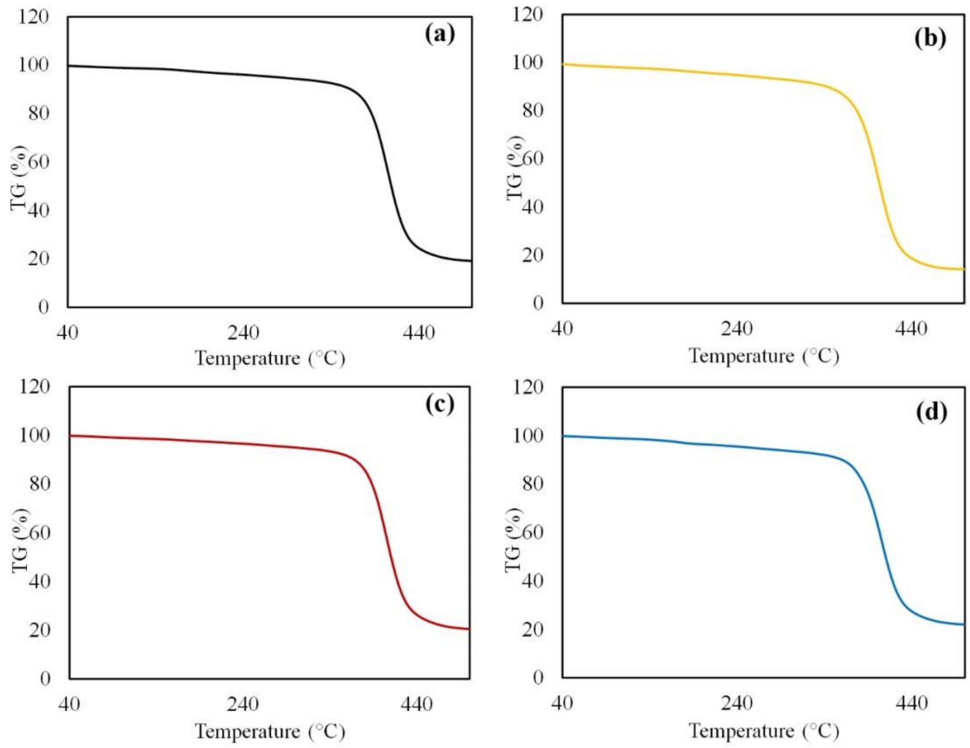

Figure 3: TGA diagrams of the sample (a) Black 350, (b) Yellow 350, (c) Magenta 350, and (d) Cyan 350.

3.2. Rheological behavior of toner

Viscoelastic properties of the toner and its evolution during melting process affects its transfer and printability. Accordingly, the effect of compositional aspects of the toner on its rheological properties has been the subject of several researches [24, 25]. Thermal changes in the toner during the fusing process can be divided into three stages (Figure 4):

1. Warming: Increase in temperature of toner particles and paper.

2. Softening: Melting of the toner starts from the surface of particles and toner particles start to cohere and adhere to each other.

3. Melting: Partly melted toner Adheres to the paper [21].

At stage 1, the temperature rises from room temperature to about 70 °C, but no melting occurs in this range. In stage 2, the toner starts to melt on the surface (from about 70 to 85 °C). When the toner is heated for the first time, the softening (glass transition) temperature is higher than when it is heated for the second time, when the toner is already Glass-like [26]. Toner particles first cohere, and in stage 3, the toner starts to melt and adhere to the paper, too. In this stage, which is also accompanied with complete emergence of the separate particles with each other, the adhesion on paper is almost complete. The toner continues to penetrate and spread as the temperature increases [27].

The melting stages of the toner can be followed by scrutinizing the rheological properties of the samples. As it can be seen in Figures 5 and 6, in all the samples, complex viscosity as well as storage modulus and loss modulus are reduced expectedly by elevating the temperature. It is attributed to the higher mobility of the polymer chains at increased temperatures.

Figure 4: Schematic illustration of the fusing stages of toner in electrophotographic printing.

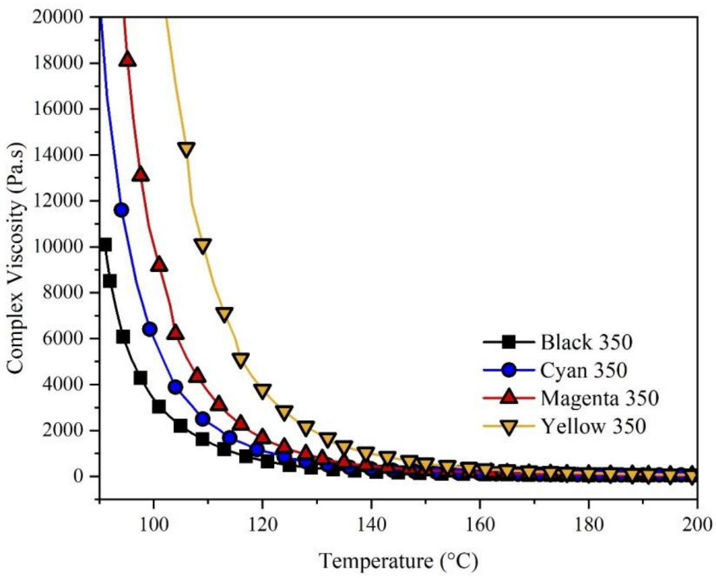

Figure 5: The evolution of Complex Viscosity of color toners as a function of temperature at constant frequency.

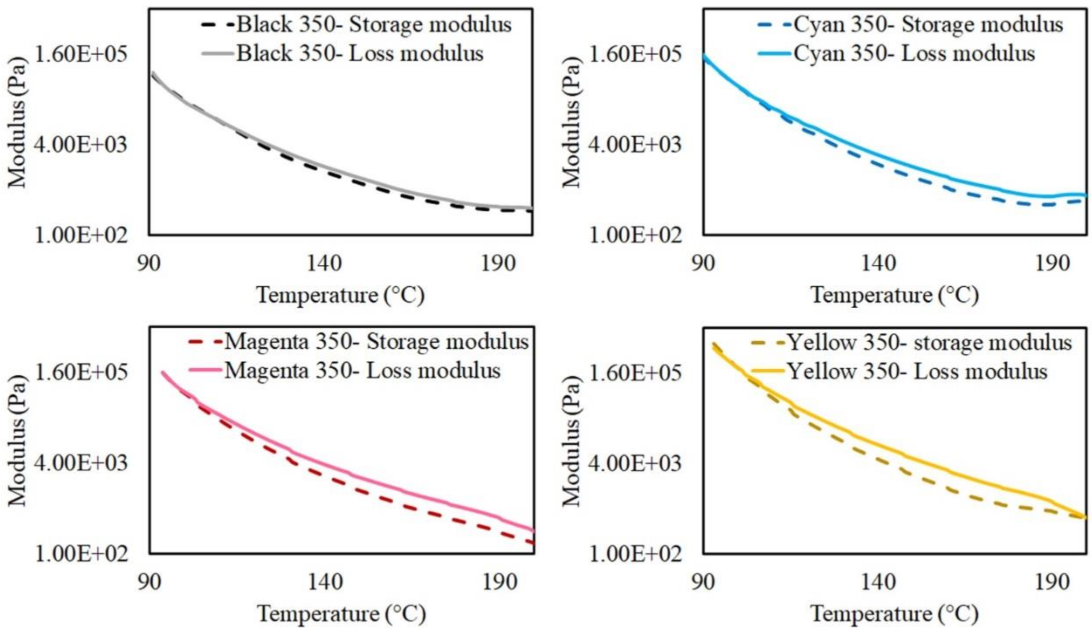

Figure 6: Viscosity components of the toners, as a function of temperature.

Damping factor however, gives further insight into the thermo-mechanical evolution of the toners under the implementation of heating. Damping factor is the proportion of loss modulus to storage modulus and clearly shows the transition points that involve energy loss owing to the segment rearrangement and internal friction and reaches its maximum at such points [28]. Furthermore, dampening factor closely relates to the relaxation time of the toner since both describe the response of a viscoelastic system to the motion [29] and the adhesion of the toner to the substrate as well as its transfer to the paper are strongly dependent on the relaxation time of the toner [30]. As it is clearly depicted in Figure 7, damping factor of all the samples reach a maximum at temperatures between 155-172 °C which is stated in Table 2. It can be attributed to the melting; the final stage of the fusing process (Figure 4), since at this stage, the previously surface fused particles, undergo thorough melting and merge into each other which causes the interparticle friction and polymer entanglement to be significantly grow up. It is also noteworthy that the black toner has the lowest melting temperature of 155 °C which is followed by the melting temperature of cyan toner that occurs at 162 °C. The yellow and magenta toners undergo melting at higher temperatures of 166 and 172 °C, respectively. Therefore, the black toner is the first toner that melts down and penetrates into the porous structure of the paper while the cyan is the next color which is followed by magenta and yellow toners. It corresponds with the standard printing sequence of KCMY which brings optimum printing quality and color gamut. Elsewhere, it has been found that the printing sequences that print either black or cyan as the last color, are more prone to the formation of moiré-like patterns [31]. Therefore, it can be interpreted that the final stage fusing temperature sequence of the toners, arranged in order to provide better printing quality.

Table 2: Temperature of maximum damping factor of the toners.

Toner sample	Maximum tanδ temperature (°C)
Black 350	155
Cyan 350	162
Yellow 350	166
Magenta 350	172

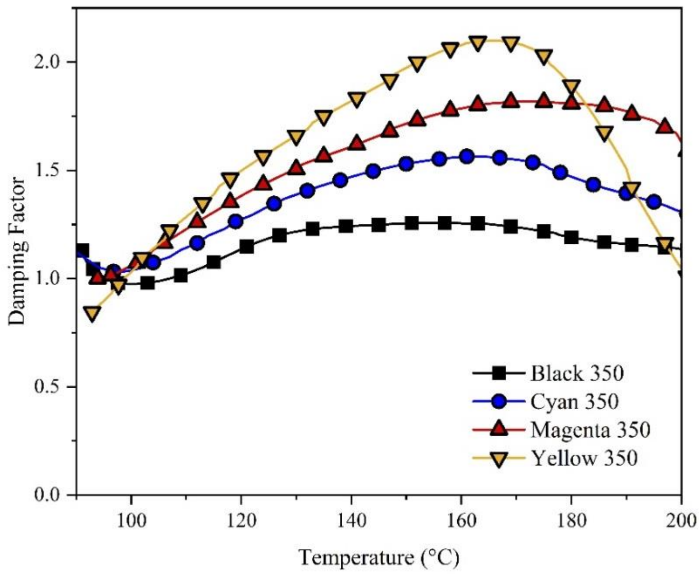

Figure 7: Damping factor of the toners as a function of temperature.

3.3. Morphology of the toners

Figure 8 shows toner surfaces as depicted by polarized micrographs. A powder toner particle is ~ 9–10 microns in diameter as confirmed by results for particle size. Circularity values of the toner particles prepared with the various pigments were calculated using image J software. Results determine that variation in a pigment's physicochemical and solid-state parameters do not affect the circularity of a color toner, and all colored toners have a semi-spherical or a potato shape (circularity ~0.8).

Polarized optical microscopy images of color toner particles show that particles had a rough surface. This phenomenon can be attributed to the particular surface tensions of the toner's constituents that resulted in migration of the pigment from the inner part of the particle to its surface.

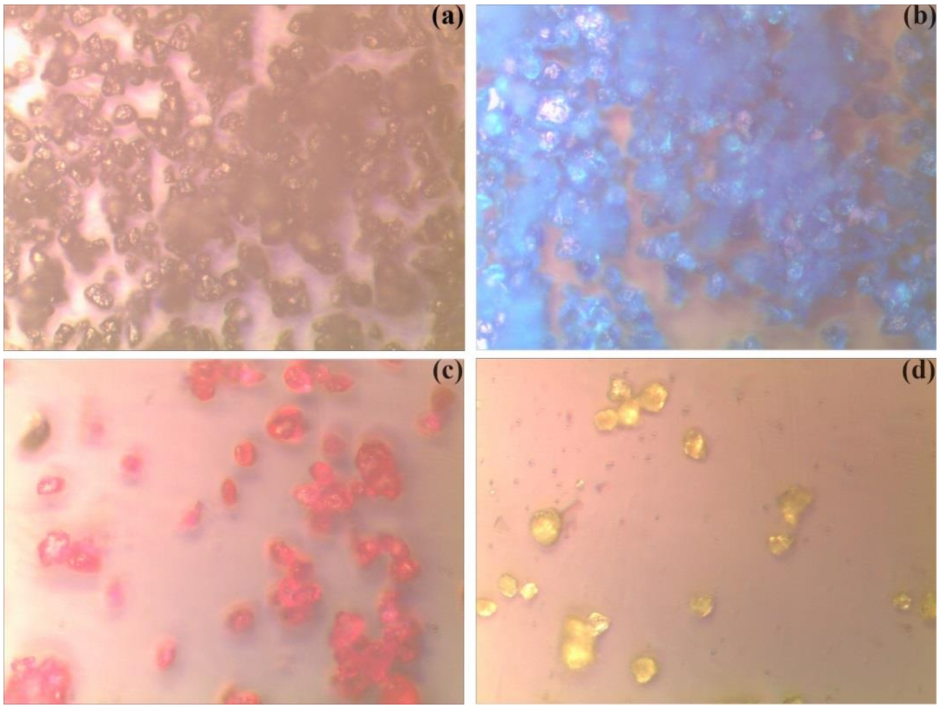

Figure 8: Polarized optical micrographs of (a) Black 350, (b) Cyan 350, (c) Magenta and (d) Yellow 350 toner.

4. Conclusion

There are several parameters that influence characteristics of the final printing quality in electrophotographic printing. This study discussed the melt rheological behavior. Rheometer along with DSC and TGA analysis are used to investigate the thermo-rheological behavior of Konica Minolta BizHub C350 toner in four colors (cyan, magenta, yellow and black). Fusing as a critical step in development process in electrophotographic printers is monitored through Rheological investigation. The order of ultimate fusing temperature of the toners is found to be in good correlation with standard printing sequence of four-color printing, where the black color prints first and cyan prints afterward which is finally followed by yellow and magenta. However, the effect of aging and the time scale of fusing has to be further investigated in the following researches. It is important since the chargeability of the printing toners are getting worse under tribological charging [32]. Maybe the rheological properties of the toners can be changed upon aging. Also, the findings suggested that the toner has a particle size of about 10μm for the provision of a printing resolution around 600 dpi. The toner particles were found to be irregularly shaped due to their fabrication via a pulverization method. Finally, the toner exhibited appropriate thermal properties ($T_g \approx$ 60 °C) for printing purposes and showed just one main decomposition step at 400 °C.

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