

CHAPTER V

CONCLUSIONS AND SUGGESTIONS

Preparation of the micrometer-sized polymerized toner by suspension polymerization for electrophotographic printers was investigated in *in-situ* polymerization of carbon black and other additives. Based on this technique, syntheses of the polymerized toner particles with desired properties in water medium using PVA and BPO as a dispersant and an initiator, respectively, were accomplished. Mechanical homogenizer was used for the suspension polymerization to generate small, uniform, and well controlled droplets of less than 10 μm . The resulting particles were in the range of 4-10 μm with a narrower size distribution with a CV of 20-30%.

To achieve the polymerized toner with desired properties, the influence of different reaction parameters on particle sizes, size distribution, molecular weight, molecular weight distribution, glass transition temperature, and other important properties necessary for the formation of the polymerized toner were investigated. We can therefore conclude the finding as follows:

Control of the polymer particle size and its size distribution is one of the most important points in this research. The particle size decreased rapidly with an increase of the mechanical homogenizing speed. However, above a rate of 10000 rpm, any increase in mechanical force did not contribute to a much reduction in the particle size, but an increase in a broader particle size distribution was observed. For this reason, it is suggested that the mixing or shearing force to disperse all ingredients for

the suspension polymerization in producing the polymeric particles with a narrower size distribution be limited to a critical value.

It was noted that the polymerization carried out in the stirred glass reaction at different agitation rates resulted in different particle sizes. The particle size decreased slightly with an increase of the agitation rate and then their distribution was shifted towards the small particle size. It could be described that an increase in agitation rate led to an increase in shearing force, which could disperse the oil phase to form the small droplets sizes. However, when the rate of agitation was increased up to 240 rpm, a large number of secondary particles were obtained. It can be explained that the stirred glass reactor with a high agitation rate might not be efficient in producing the uniform particles.

The dispersant is a decisive factor, affecting the dispersion of monomer in water, particle formation and the stability of the polymer suspension. The particle size generally decreased with increasing the dispersant concentration. An increase in the dispersant concentration produced an increase in the viscosity of the reaction medium and the rate of adsorption on the particle surface. The stability of polymer particles in the suspension system was also increased. The increase in stability followed the formation of an efficient protective layer on the particle surface and thus reduced the particle size of the resulting polymer. Insufficient or excess amount of dispersant caused the particle coalescence and the secondary stabilization of new particles. The highly recommended dispersant concentration of the dispersant was thus between 3-5 wt%.

The reaction temperature is one of the important parameters to control the formation of particles. The particle size slightly increased with an increase of the

reaction temperature. The critical chain length of precipitated oligomer chains was increased, because an increase in the solubility of oligomer chains in the continuous phase at the higher reaction temperature led to an increase in their aggregates and the resulting larger polymeric particles were obtained. However, above a reaction time of 75°C, a large number of secondary particles with a broader size distribution was observed.

Control of glass transition temperature of the copolymer is one of the most important in this research. The resulting copolymer particles with a T_g in the range of 65-79°C could be achieved by adjusting the suitable ratio of styrene and normal butyl acrylate in the monomer feed. The single glass transition temperature indicated that the two monomers were miscible and formed one-phase droplets during suspension polymerization. The high composition of nBA yielded the particles with a lower T_g . Furthermore, the feed composition also affected the size of the final particles. Since an increase in the amount of nBA was similar to increasing the polarity of the reaction medium, thus the large particles were obtained in this case.

The limited amount of crosslinking agent (DVB) was incorporated to develop the network within the particles. The crosslinking agent with less than 6 wt% produced the polymeric particles of spherical shape. When the concentration of DVB increased beyond this level, the deviation from sphericity became more apparent. The reason for this phenomenon lies in the effect of destabilization of PVA and the phase separation occurred during the copolymerization, especially at the beginning of the reaction.

The effect of initiator concentration (BPO) on particle size and size distribution were investigated. The result indicated that the particle sizes slightly

increased with increasing initiator concentrations. The conversion also increased due to more initiating radicals formed in the initiation step. The polymer formation of larger particle sizes increased with increasing initiator concentrations as follows: (1) initiation of more polymer chains, (2) the rate at which the stabilizer molecules adsorbed on the particles, and (3) a higher rate of polymer chain aggregation. However, the higher initiator concentrations gave more polymer chains with the lower molecular weight.

The length of reaction time for suspension copolymerization influences the particle growth in terms of the average particle size. Increasing polymerization times, the conversion slightly increased because the more monomers were increasingly converted to the polymer. The average particle size also increased with increasing polymerization times. The increased particle size at higher polymerization times because the microspheres were aggregated to form the larger particles.

The amount of carbon black used as a coloring agent incorporated to the polymerization mixture was limited. With further increases in carbon black feed level from 1 wt% to 5 wt%, the particle size slightly increased. Moreover, a tar-like product with an irregular shape was often formed at the bottom of the reactor. The carbon black feed level also had a strong effect on the final yield of polymer beads. With further increases in carbon black feed level, the final yield tended to decrease. This results can be explained that the carbon black has a strong inhibitory effect on the radical polymerization, therefore, increases in carbon black feed levels decreased the rate of polymerization. The free-radical process was inhibited because both a low radical concentration with a low polymer content were obtained. The non-radical monomer particles were subject to coalescence because of their mutual collision and

led to the formation of larger particle, the size of which depended on the effect of coagulation. The resulting copolymer particles in the presence of carbon black with a T_g in the range of 66-70°C could be achieved by adjusting the proper mole ratio of the comonomer between styrene and nBA.

The amount of charge control agent was added into a polymerized toner to give an adequate charge level or rate of charging. The result indicated that the q/m values slightly increased followed by an increase of the charge control agent concentration from 1 wt% to 4 wt%. The resulting polymerized toner with a q/m values in the range of 7-20 $\mu\text{m g}^{-1}$ were obtained. It could be described that increase the concentration of charge control agent was to increase the stronger effective charging sites of the toner, which should result in a reduction in the charging time for a saturated charge to develop and increase the values of q/m.

Analyses of the print quality with respect to the q/m values were studied, which showed the higher background fog, low maximum density, and a little of the image raggedness. In most cases of the experimental results, an inverse correlation between particle size and molecular weights was obtained. As the particle size decreased, the average molecular weight increased. This rationale depended mainly on the locus of the polymerization, which involved both solution and monomer-swollen particle phases. The molecular weights of particle-phase polymerization were usually higher than those in solution polymerization, because the termination rate was reduced due to the gel effect. For small particles, a higher proportion of the polymerization occurred in the particle phase, because the oligomeric radicals initiated in solution were captured more efficiently by the smaller particles due to their greater surface areas. In contrast, the large particles could grow by capturing

dead polymer molecules already in the solution, thus exhibited the low molecular weight.

In conclusion, this work found the operating parameters for the preparation of the micrometer-sized polymerized toners by suspension polymerization for electrophotographic printers, their charging properties, image qualities, and other important properties necessary for polymerized toner were included.

Suggestion for Future Work

1. In order to try to achieve some control over the degree of dispersion of carbon black within the copolymer, various dispersion agents were also examined.
2. Incorporation of various monomers used as shell layer onto the surface of the copolymer as core binder resin to improve the blocking resistivity of the core-shell polymerized toner.
3. Copolymerization with other pigments different in color to achieve various colored particles expected for use in color dry polymerized toner application in a single step of polymerization.
4. Use charge control agents are a boro-diphenyl complex but high its electronic configuration and reactivity to polarization and ionization to improve high charge transfer ability.
5. Use carbon black has more hydrophobicity to improve the degree of dispersion of carbon black within the copolymer beads.
6. Use fumed silicas as flow aids to improve flow ability and control the charging characteristics of toners