

Polymer Grafted Carbon Black with High Dispersibility and Stability for Ink Jet Printers

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Abstract

An attempt is being made to apply a pigment type ink using a pigment like carbon black as a coloring agent component in the place of dye type ink for ink jet printers. Since the carbon black is insoluble in the liquid of ink, however, a highly advanced technique is required for finely dispersing the carbon black in the liquid medium of ink and usual difficulty is involved in imparting exalted stability to the dispersion. Based on a polymer grafting carbon black, it is possible to synthesize of the ink which has high dispersibility and stability of carbon black. In this study, a polymer grafted carbon black was synthesized in ethanol and its dispersibility and stability were examined. Reactive polymer is organized stylen and isopropenyl oxazoline which react to carbon black and ethylene glycol macromer which is soluble in ethanol. A reactive polymer, carbon black and ethanol were placed and dispersed. Further zirconi a beads were placed, and they were stirred and heated at 78°C to effect a grafting reaction. The polymer grafted carbon black with high dispersibility and stability can be synthesized. The polymer grafted carbon black keeps a state of high dispersibility in ethanol at room temperature, and low temperature, too. An ink of good quality could be formed from the polymer grafted carbon black. The ink was stable and gave good printing performance under any environmental conditions.

Introduction

Recently an attempt is being made to apply a pigment type ink using a pigment like a carbon black as a coloring agent component in the place of the dye type ink for the ink jet printers. Already there are some inks which are using carbon black, but there are still some issues. In commercial ink jet printers, liquid medium of ink is exchanging organic solvents for alcohol or water for safety, and few inks based on alcohol or water use carbon black. The carbon black generally has particle diameters in the range of several nm to some hundred nm.

Since the carbon black produces large cohesive strength between the individual fine particles, aggregated particles having diameters of not less than several microns are usually formed. Since the cohesive force is markedly large as compared with the affinity of the

carbon black for the other media, it is extremely difficult for the carbon black to be dispersed on the order of submicrons in the medium. It has been also known to the art to adopt a procedure of adding a suitable dispersion stabilizer to the dispersion medium and physically stirring the resultant mixture for effecting necessary dispersion for the purpose of producing a dispersion of the carbon black. But there are some problem in which the carbon black in liquid medium has no stability under high or low temperature and adding other agent gives wrong influence on the dispersibility. One of solutions of this problem is grafting a polymer to surface of the carbon black.¹⁻³ A polymer grafted carbon black keeps stability, because the polymer functions as like a surfactant and never separate from carbon black. There are some way of synthesis of the polymer grafted carbon black.

In this study, we obtained the polymer grafted carbon black by the reaction of the polymer containing a reactive groups in the molecular unit and examined its dispersibility and stability in ethanol.⁴ First, we describe synthesis procedure for the reactive polymer and the polymer grafted carbon black. Then experimental results of dispersibility and stability of the polymer grafted carbon black are given.

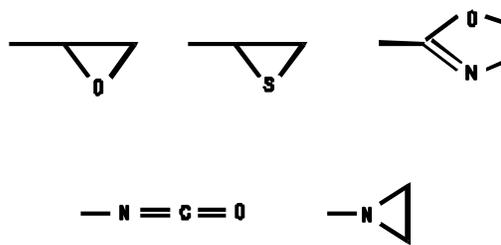


Figure 1. Pendants which react with carboxyl groups.

Experimental

In this study, we applied a carbon black which has many carboxyl groups on its surface, because the carboxyl groups react the reactive polymer which has pendants. We obtained the polymer grafted carbon black by reaction of carboxyl groups on the carbon black surface and pendants of the reaction polymer. In this study, we applied oxazoline groups as pendants of reactive polymer. The reactive polymer was organized with segment A which has pendants and affinity for carbon black and segment B which has affinity for ethanol. Concretely, the segment A was organized with a styrene (St) and isopropenyl oxazoline (IPO) and B was organized with an

ethylene glycol (EG) macromer. The IPO is a monomer which contain an oxazoline group. The pendants which are possible to react with carboxyl groups are shown in Figure 1.

Synthesis of the reaction polymer

A polymerizable monomer composition was obtained by dissolving ethanol, EG macromer, St, IPO and 2,2'-Azobis(2,4-dimethylvarelonitrile) as an initiator in ethanol. In a separable flask provided with a stirrer, a thermometer, a condenser, a dropping funnel, and a N₂ inlet, ethanol was placed and heated to 78°C. The polymerizable monomer composition mentioned above was placed in the dropping funnel and dropped to the hot ethanol over a period of three hours, and polymerized at 78°C. Further, it was left standing at this temperature for four hours to terminate the polymerization, to obtain a reactive polymer. The structure of the obtained reactive polymer is shown in Figure 2.

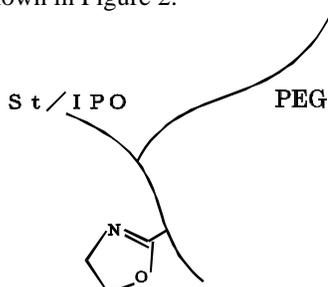


Figure 2. Chemical structure of a reactive polymer.

Synthesis of the polymer grafted carbon black

Synthesis of the polymer grafted carbon black is a reaction of carboxyl groups on the carbon black surface and pendants of the reactive polymer, mentioned above. Therefore the carbon black which has many carboxyl groups, in other words, low pH is more effective in the reaction. In a separable flask provided with a thermometer, stirring vanes, and a condenser, the obtained reaction polymer solution, carbon black (Mitsubishi Chemical Industries, Ltd.: MA-100R), and ethanol were placed and dispersed. Then the zirconia beads were placed, and they were stirred and heated at 78°C for two hours to effect a grafting reaction. Then, the reaction mixture and zirconia beads were separated to obtain a dispersion containing a polymer grafted carbon black.

The structure of the polymer grafted carbon black is shown in Figure 3. For comparison, a polymer which was organized with St and EG macromer and without IPO, and carbon black were dispersed in ethanol with the same equipment. The structure of dispersed non-grafted carbon black is shown in Figure 4.

Results and Discussions

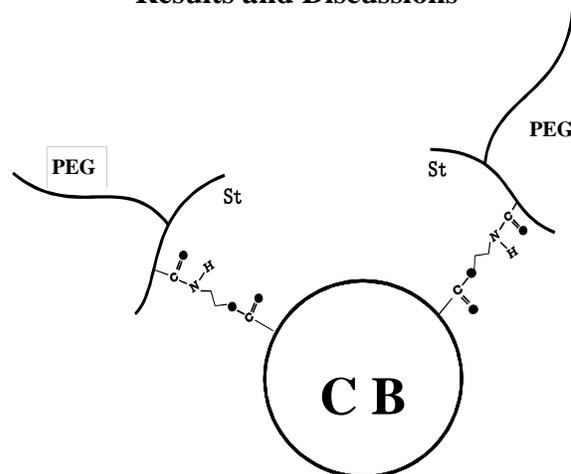


Figure 3. Chemical structure of a carbon black particle with polymer.

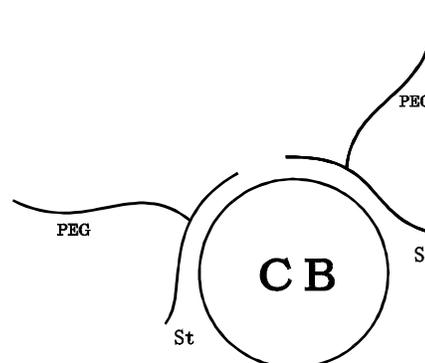


Figure 4. Chemical structure of a dispersion system of carbon black particle and polymer without grafting.

Dispersibility of the polymer grafted carbon black and non-grafted carbon black.

The dispersibility of solutions was investigated for the polymer grafted and non-grafted carbon blacks. We measured carbon black particle size by light scattering method. The particle size distributions of carbon black with the polymer grafting was almost the same as that without grafting just after the synthesis. A typical particle size distribution of carbon black is shown in Figure 5. The mean particle size and the distribution width of the result in Figure 5 are smaller than those of conventional carbon blacks. Just after the synthesis steps, the polymer grafted carbon black has high dispersibility because of bonding the carbon black and the polymer, and the non-grafted carbon black has also high dispersibility because of adsorption of the polymer onto the carbon black. This fact means the high dispersibility of both the carbon blacks with and without the polymer grafting prepared in this study. Actually the high dispersibility of the polymer grafted carbon black was confirmed by observation of carbon black dispersed films prepared by casting method.

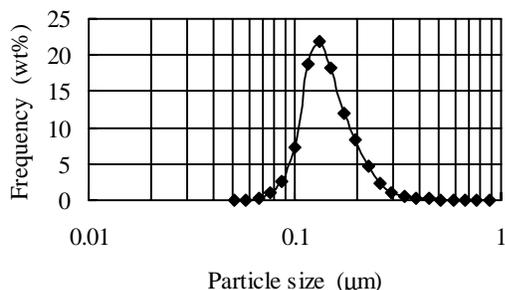


Figure 5. Typical particle size distribution of polymer grafted carbon black.

Stability of the polymer grafted carbon black and non-grafted at room temperature

The stability of solutions was investigated for the polymer grafted and non-grafted carbon blacks. We placed both dispersed solutions stationary for 5 and 10 days and measured the change of the carbon black particle size distributions.

The particle size distributions of carbon black with polymer grafting and non-grafting were not changed 5 or 10 days after the synthesis. The polymer grafted carbon black has high dispersion stability because of bonding the carbon black and the polymer. The non-grafted carbon black has high dispersion stability because of adsorption of the polymer onto the carbon black, too. It is not necessarily to graft the carbon black with a polymer for high dispersion stability of solution at room temperature. It is possible to obtain high stability of solution at room temperature by adsorption of a polymer onto the carbon black in the case of non-grafting.

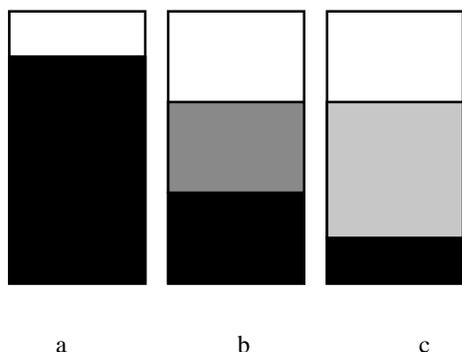


Figure 6. Change of polymer non-grafted carbon black dispersion with time at -5°C.

- (a) just after the synthesis process,
- (b) 2 h after the synthesis process,
- (c) 24 h after the synthesis process.

Stability of the polymer grafted and non-grafted carbon blacks at low temperature

Then, the stability of solutions was investigated for the polymer grafted and non-grafted carbon black at -5°C. We placed both dispersed solutions stationary for 2 and 24 hours after the synthesis and measured the change of carbon black particle size distributions. We made sampling of specimens for particle size measurements at upper and lower parts of the test tube, which contained

the dispersed solution.

Appearances of the solution in the test tube are shown in Figure 6. In the case of the non-grafted carbon black, sedimentation of the carbon black occurred. This result suggests aggregation of the carbon black particles.

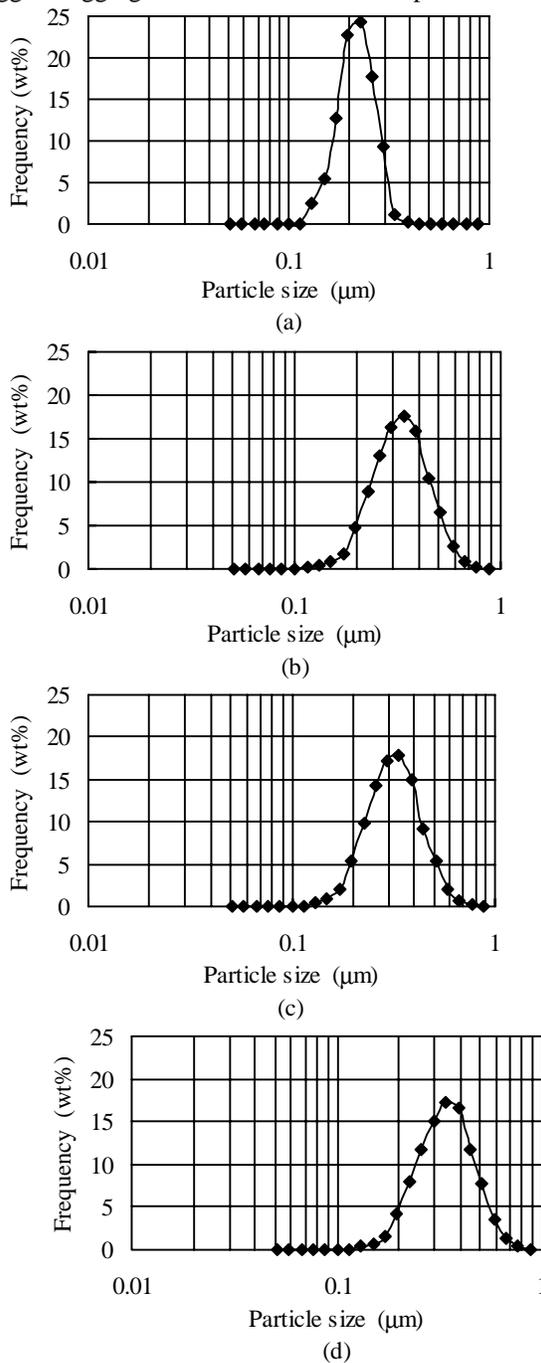


Fig. 7. Change of particle size distribution of non-grafted carbon black kept at -5°C for different parts of the solution and elapsed time.

- (a) 2 h after the synthesis, upper part of the solution,
- (b) 2 h after the synthesis, lower part of the solution,
- (c) 24 h after the synthesis, upper part of the solution,
- (d) 24 h after the synthesis, lower part of the solution.

The change of the carbon black particle size distributions with the elapsed time is shown in Figure 7. The mean particle size of the non-grafted carbon black was 240 nm at the end of the synthesis but those at 2 hours after the synthesis were 140 nm (Figure 7(a)) and 320 nm (Figure 7(b)) at the upper and lower parts of the test tube, respectively. Further the mean particle size at 24 hours after the synthesis were 310 nm (Figure 7(c)) and 330 nm (Figure 7(d)) at the upper and lower parts. These results indicate that the non-grafted carbon black particles attract each other and precipitate. It should be noted that the upper part of the solution of the non-grafted carbon black changed clear after 48 hours.

On the other hand, the grafted carbon black particles did not attract each other and did not precipitate even after 48 hours at -5°C . The particle size distribution at the upper part is almost the same as that at the lower part.

Next we observed the spreading of the drops of the non-grafted carbon black solutions on filter paper to examine their dispersion stability. The results are shown in Figure 8. Each small circle in Figure 8 corresponds to the upper and lower parts of the test tube. The spread of a liquid-drop of the upper part was almost the same as that of the lower part at the end of the synthesis (Figure 8(a)). The spread of a liquid-drop of the upper part was somewhat cleared and the lower part deepened 2 hours after the synthesis (Figure 8(b)). The change of the spread proceeded further 24 hours after the synthesis (Figure 8(c)).

On the other hand, in the case of the grafted carbon black particles, the spread of a liquid-drop of the upper part was almost the same as that of the lower part, independent of time after the synthesis.

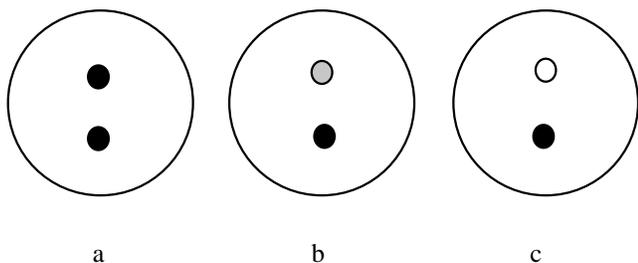


Figure 8. Change of spreading of drops of polymer non-grafted carbon black solution kept at -5°C on a filter paper with time. The upper and lower circles on the filter paper correspond to the upper and lower parts of the solution respectively.

- (a) just after the synthesis process,
 (b) 2 h after the synthesis process,
 (c) 24 h after the synthesis process.

Application of polymer grafted carbon black to ink for ink jet printers

Inks for ink jet printers were prepared by using the polymer grafted and non-grafted carbon blacks. An ink of good quality could be formed from the polymer grafted carbon black. The ink was stable and gave good printing performance under any environmental conditions. On the other hand, an ink of reasonable quality could not be formed from the polymer non-grafted carbon black. As mentioned above, the non-grafted carbon black showed similar behavior as the grafted carbon black at room temperature, however, aggregation of the carbon black occurred when some agents for inks were incorporated into the ink solution.

Conclusion

High dispersibility and stability of carbon black particles in ethanol were obtained by polymer grafting. Cases of polymer grafted and non-grafted carbon black are discussed. The following conclusions were obtained.

1. Both the polymer grafted and non-grafted carbon blacks showed high dispersibility just after the synthesis process.
2. Both the polymer grafted and non-grafted carbon blacks were stable for more than 10 days at room temperature.
3. The polymer grafted carbon black was stable even at low temperature.
4. The polymer non-grafted carbon black was not stable at low temperature.
5. The ink made of the polymer grafted carbon black was stable and gave good printing performance.

References

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