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Studies of the Morphology and Tribocharging Properties of Charge Control Agent (CCA)-Modified Silicas Prepared by the Fluidized Bed Spray Method

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The charging and admix behaviors of a series of surface-modified R972 silicas (modified by two positive charge control agents (CCAs) and nine negative CCAs prepared by the fluidized bed spray process (1:10 wt. ratio of CCA to R972) were studied with unpigmented styrene–butadiene toner (~9 μm). Concurrent to xerographic measurements, the morphologies of the modified silica samples and the resulting toners were examined by TEM and SEM microscopy, respectively. Results showed that when the CCA was homogeneously distributed in the silica sample, it dominated the charging and admix properties of the resulting toner. Because the actual CCA concentration was only 0.05wt%., the observation clearly demonstrated that the approach of using CCA-modified silicas is one of the most effective ways to impart charging in toner. When the CCA was *not* distributed homogeneously in the silica sample, the toner resin dominated the charging and admix properties. The inefficacy of the CCA in this case is attributable to a surface area effect. The importance of the physical state or the distribution of the CCA in the silica sample was further illustrated in the case of KTPB (potassium tetraphenylborate)-modified silicas. Although the silica sample prepared by the fluidized bed spray process was inhomogeneous, we were able to homogenize the distribution of KTPB in R972 using a solution-coating technique. The solution-coated KTBP/R972 sample not only showed great enhancement in negative tribo (e.g., from ~27 to ~95 μC/g), it also reduced the admix time from 15 to 2 min.

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Introduction

The sizes of toner particles used in dry xerography are generally in the range of 10 to 20 μm in diameter.[1] Particle sizes significantly larger than this usually produce ragged lines and dots resulting in poor copy quality. For color copier applications, fine toners, for example ~4 μm in diameter, are known to be beneficial not only to the quality of the print but also in the prevention of paper curling. However, as the size of the toner particles is reduced, the toner's ability to flow decreases. Fumed silicas are commonly known as flow aids for toners. One of the identified approaches to enhance the flow while controlling the charging characteristics of the toner is to use silica modified by a known charge control agent (CCA).[2] Many different preparative methods, e.g., solution coating, vapor phase reaction, fluidized bed spray process, etc., are used to modify silicas. Our experience suggests that the fluidized bed spray process is scalable and large quantities of CCA-modified silicas can be prepared easily. This article reports a systematic investigation of the morphological* and charging properties of a series of CCA-modified silicas prepared by the fluidized bed spray process. Modified silicas of different morphologies were obtained depending on the CCA employed in the surface modification process. The charging properties examined include tribocharging ("tribo") and rate of charge exchange. The latter was studied through the so-called admix time, the time required for the charged toner and a fresh, uncharged toner to become equilibrated chargewise. The tribo and admix time of these modified silicas were studied with model styrene–butadiene toner against polymer-coated metal beads. The variation of tribocharging and admix properties is discussed here in terms of a morphology effect.

Experimental

Materials. Silica R972 was a hydrophobic amorphous fumed silica from Degussa. Distearyl dimethyl ammonium methyl sulfate (DDAMS) and cetyl pyridinium chloride (CPC) were purchased from Hexcel Chemical Products and both were technical grade. Copy Charge NXVP434 was from Hoechst Celanese; salicylic acid (99%), SA, and 3,5-di-isopropylsalicylic acid (98%), iPSA, were obtained from Aldrich; bis(2-hydroxy-3-naphthoato)chromium (tradename Bontron E82), bis(3,5-

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* The term morphology is very loosely defined in this report and is used to describe the "structure" and "form" of the silica sample. It covers physical states from homogenous to nonhomogenous distribution of CCA molecules in the silica sample. In the case of homogenous distribution, the CCA can exist as a fine particulate mixture with silica particles or it can be molecularly adsorbed on the silica surface. We are not distinguishing these two possibilities here.

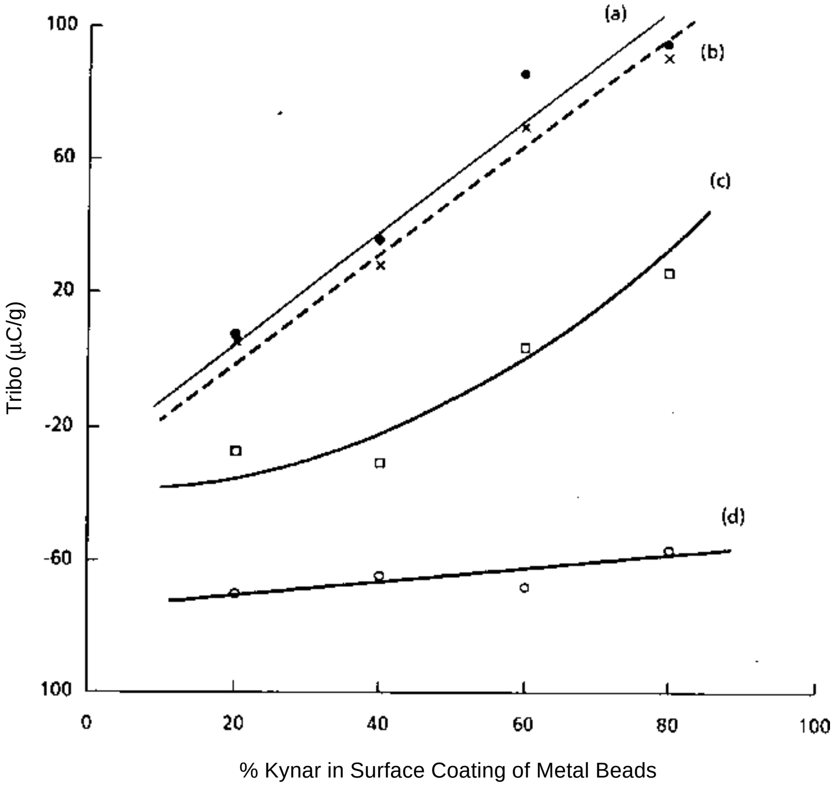

Figure 1. A tribo plot for styrene–butadiene toners incorporating positive CCA-modified R972 silicas: (a) DDAMS/R972, (b) CPC/R972, (c) styrene–butadiene control, and (d) R972/styrene–butadiene control).

di-t-butylsalicylato)zinc (Bontron E84), and tris(3,5-di-t-butylsalicylato)aluminum (Bontron E88) were obtained from Orient Chemical (Osaka, Japan); potassium bis(3,5-di-t-butylsalicylato) borate (LR120) was from Japan Carlit (Tokyo, Japan); and 3,5-di-t-butylsalicylic acid (technical), t-BSA, was from TCI America (Portland, Oregon). Potassium tetraphenylborate (KTPB) was synthesized in-house from sodium tetraphenylborate. All these materials were used as received.

The toner was made of styrene–butadiene (90:10) resin and was prepared by a melt-extrusion and jetting process. It classified to ~9 μm. The polymer-coated metal beads (~130 μm) were prepared by powder-coating a mixture of poly(vinylidene fluoride) (Kynar™ from Pennwalt) and poly(methyl methacrylate) (PMMA) of varying ratios on the surface of the metal beads at a total weight loading of 0.7% (Ref. 3).

Preparation of CCA-Modified R972 Silicas. CCA-modified R972 silicas were prepared by the fluidized bed spray process at a 1-kg level. The weight ratio of the CCA to silica was 1:10 in all the cases studied. Typically, R972 silica (1.0 kg) was charged into the product container of the fluidized bed dryer. The fan was then started and the bed temperature was set at ~10°C above the boiling point of the spray solvent. The CCA solution (5 to 10%) was sprayed into the fluidized bed of the R972 silica with the air atomizer for about 30 min. After the completion of the spray, the fan was left on for another 20 min to allow further drying of the surface-modified silicas.

Preparation and Evaluation of Experimental Toners. The above modified silica (0.063 g), the styrene–butadiene toner (12.5 g), and the steel shots (1/4" in diameter, 125 g) were placed inside a 4-oz bottle. The bottle was roll-milled for 30 min and an experimental toner was prepared.

Developers were prepared using 1.25 g of the above experimental toners and 60 g of the polymer-coated metal beads. All developers were conditioned at an RH (relative humidity) of 20 ± 4% for ~16 h before use. The tribo of the toner was obtained by roll milling the developer for 60 min at a speed of 90 ft/min and was evaluated using the standard blow-off procedure.[4] The admix time was evaluated by adding 1% of the fresh toner into the developer, which had a toner concentration of 2%. The charge distribution of the final developer was recorded on a charge spectrograph apparatus[4] as a function of time, e.g., 15 s, 1, 2, 5, and 15 min. The admix time was defined as the roll-milling time required for the fresh toner to become fully equilibrated in charge with the original developer. A description of the measurement technique and the data interpretation is given in the accompanying paper.[5]

Results and Discussion

Tribocharging of Toners Incorporating CCA-Modified Silicas. ***Positive CCAs.*** The tribocharging properties of the two modified silicas prepared from CPC and DDAMS were examined by first blending them with the styrene–butadiene toner and then measuring their tribo values against a series of polymer-coated metal beads, whose surface coating consisted of a mixture of Kynar/PMMA at varying ratios. The charging properties of the styrene–butadiene toner alone and the styrene–butadiene toner with the untreated R972 silica were studied as controls. The tribo data, plotted in Fig. 1, clearly show that toners containing these two modified silicas charge positively relative to the two controls. The results indicate that the CCAs applied on the surface of the silica dominate the charging of the toner. Considering that the actual concentration of the CCA in each toner was only 0.05 wt%, the attainment of dominance in charging illustrates that using CCA-modified silicas may be one of the most effective ways of utilizing CCA in toners.

Negative CCAs. A series of negative CCAs (nine of them) were used to modify R972 silica, and the charging

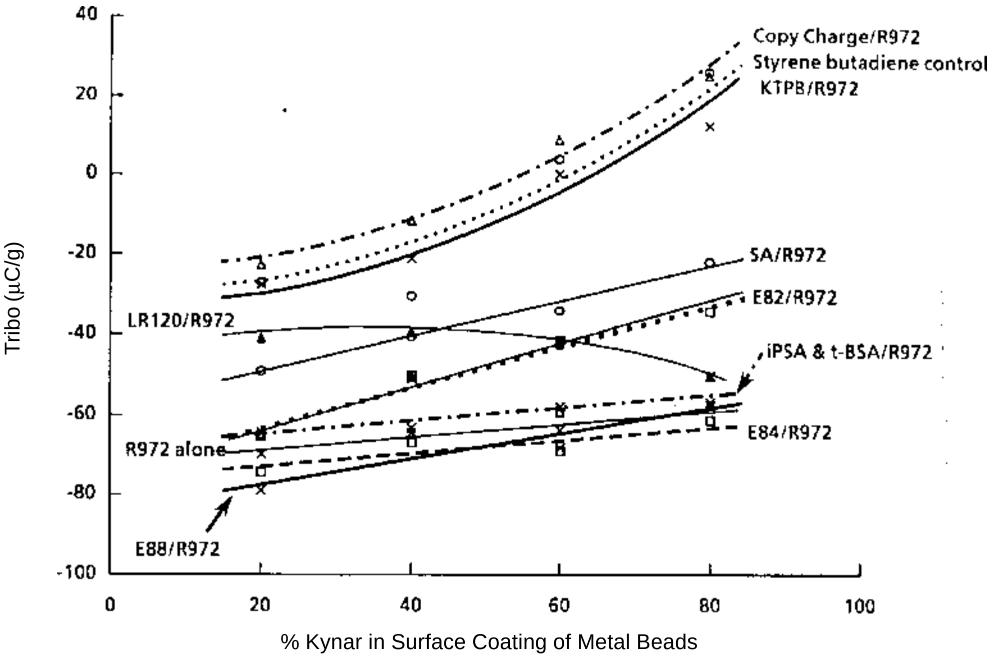

Figure 2. A tribo plot for styrene–butadiene toners incorporating negative CCA-modified R972 silicas (label: CCA used in the modification of the R972 silica).

TABLE I. Charging and Admix Properties of Styrene–Butadiene Toners Containing Various CCA-Modified Silicas

CCA	Charge controlled by	Admix time
R972 alone	CCA	5 min
None	Toner	15 min
Copy Charge/R972	Toner	15 min
KTPB/R972	Toner	15 min
SA/R972	CCA	5 and 15 min*
E82/R972	CCA	15 min
iPSA/R972	CCA	5 min
t-BSA/R972	CCA	5 and 15 min*
LR120/R972	CCA	5 min
E84/R972	CCA	15 min
E88/R972	CCA	5 min
CPC/R972	CCA	15 s
DDAMS/R972	CCA	15 s

* Data from two independent runs.

properties of these modified silicas were studied using the styrene–butadiene toner as described above. The tribo results are plotted in Fig. 2, along with the results of the two controls. At 20% RH, R972 was one of the most negative CCA by itself. A wide range of tribo behavior is shown in Fig. 2. In conjunction with the admix data, which will be presented below, we were able to identify two charging behaviors among these modified silicas. For instance, toners containing the silicas modified by KTPB and the Copy Charge had similar tribo behaviors to that of the control styrene–butadiene toner. The results suggest that these two CCAs are ineffective in modifying the charging behavior of the toner. This is actually quite puzzling. After all, R972 itself is an effective negative charge control agent. The cause of the inefficacy for these two modified silicas remains to be investigated.

A wide range of tribo values was obtained for toners incorporating silicas modified by other negative CCAs, such as SA, E82, iPSA, t-BSA, LR120, E84, and E88. Although the tribo values of these toners were more negative than that of the styrene–butadiene control, there was a sizable spread, ranging from more positive to slightly more negative than R972. The admix time for these toners was 5 to 15 min. The effect on the admix property ranged from no effect to small effect. Nevertheless, the data suggest that the CCAs used in the surface modification process do control the charging of the resulting toners. The different charging behaviors for the toners incorporating negative CCA-modified silicas are summarized in Table I.

The data in Fig. 2 show that the negative tribo achieved by the CCA decreases in the following order [for beads with a Kynar/PMMA (20/80) surface coating]: E88 ~ E84 > t-BSA ~ iPSA ~ E82 > SA > LR120. We recently showed that the tribo achieved by a given CCA is very sensitive to its state of aggregation on the surface of the silica particles. Specifically, tribo values were found to be consistently higher when the CCA was molecularly adsorbed on the silica surface.[6] Hence, comparison of the potency of these CCAs without knowing their precise physical state on the surface of the silica and in toners is not totally meaningful. Without a ranking, the only conclusion one can reach is that E88, E84, t-BSA, iPSA, E82, SA, and LR120 are all effective negative CCAs for the styrene–butadiene toner.

Admix Times. The admix times of all the toners were evaluated on a charge spectrograph apparatus and the data included in Table I. The admix time for the styrene–butadiene control and the R972/styrene–butadiene toner was 15 and 5 min, respectively. The admix data show that surface modification of R972 by CPC and DDAMS improved the admix times of the resulting toners significantly. Of the nine negative CCAs studied, the charging of the Copy Charge and the KTPB toners was shown to be controlled by the toner resin according to tribo data. The admix results supported that conclusion. The admix time for these two toners was identical to that of the toner control.

The admix times for toners containing SA, iPSA, t-BSA, LR120, E84, and E88 ranged between 5 to 15 min. The

Figure 3. A TEM micrograph of a R972 sample.

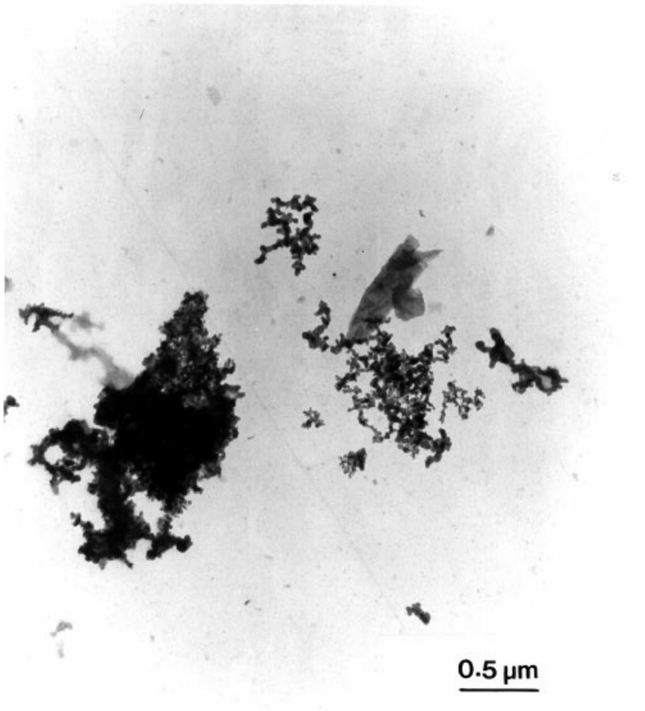

Figure 4. A TEM image of a KTPB-modified R972 silica sample.

results indicate that the CCA-modified silicas have little or no effect on the admix time.

Morphology of CCA-Modified Silicas and the Resulting Toners. The morphological properties of various CCA-modified silicas and the resulting toners at various stages of the study were studied by TEM and SEM, respectively. The properties of the R972 silica itself and the styrene–butadiene toner were also examined as controls.

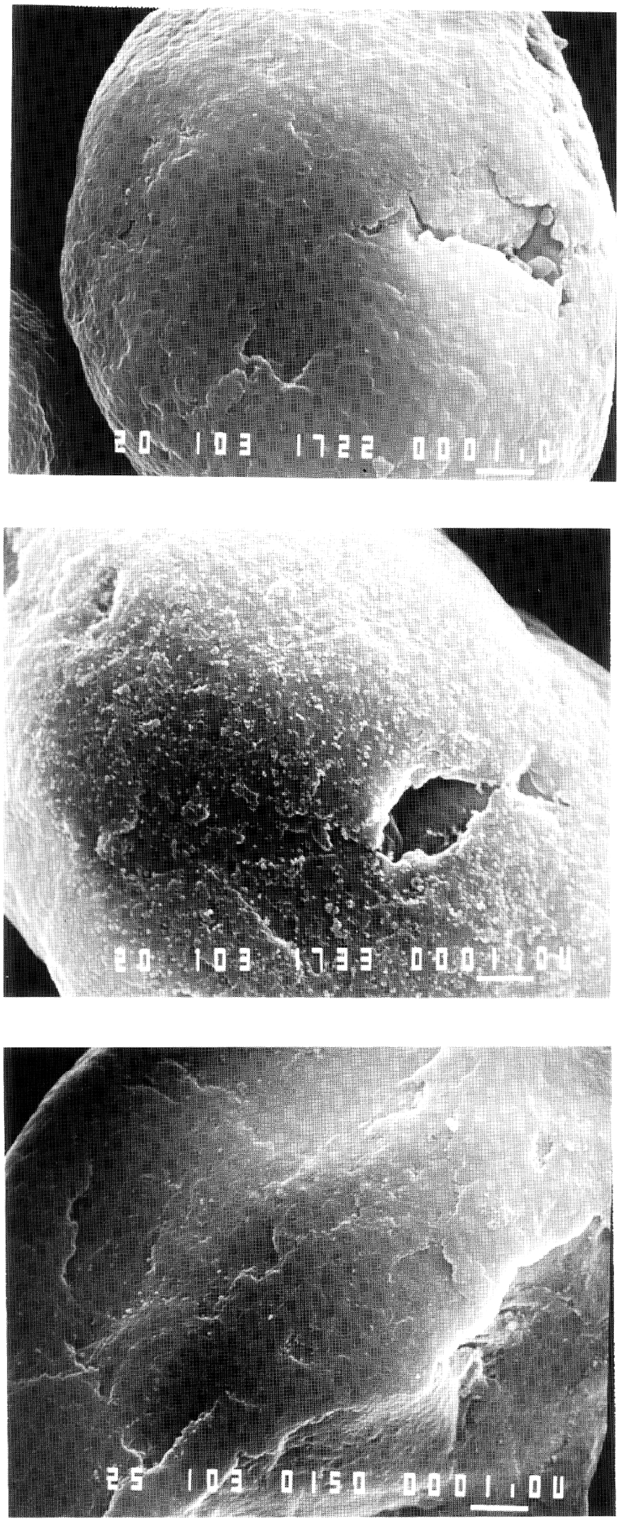

Figure 5. SEM images of (a) styrene–butadiene toner, (b) styrene–butadiene toner with a CCA-modified R972 sample, and (c) styrene–butadiene toner with a CCA-modified R972 sample recovered from the developer.

TEM images reveal that the primary particle size of R972 silica is ~100 Å and the silica particles exist as agglomerates in the powdery state. A typical TEM image of R972 is shown in Fig. 3. Of the eleven CCA-modified silicas, the morphologies of nine (CPC, DDAMS, SA, iPSA,

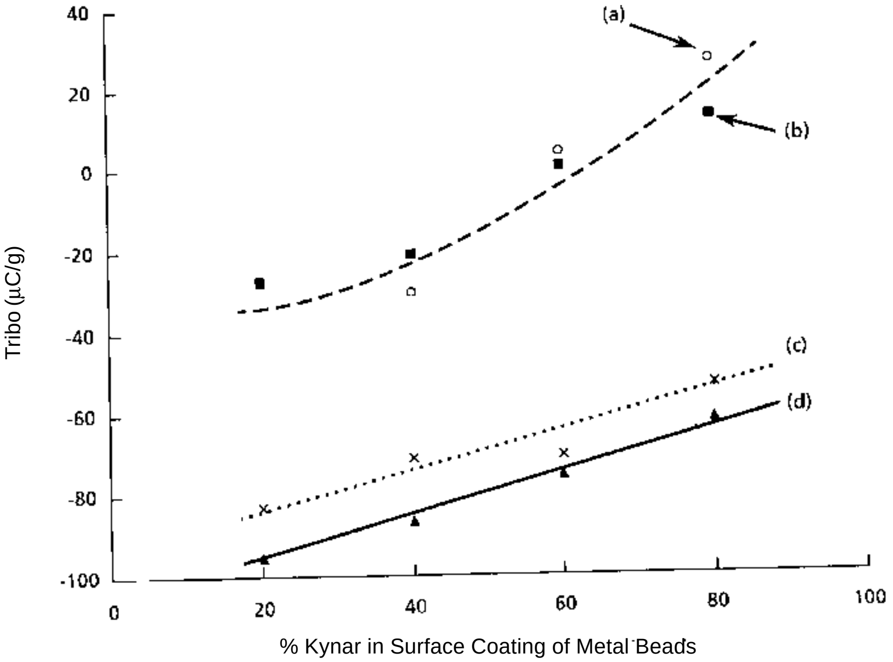

Figure 6. A tribo plot for styrene–butadiene toners incorporating KTPB-modified R972 silicas: (a) KTPB/R972 sample prepared by the fluidized bed spray method, (b) styrene–butadiene control, (c) R972/styrene–butadiene control, and (d) KTPB/R972 sample prepared by solution coating (from a 1:1 mixture of acetone/chloroform).

tBSA, LR120, E84, and E88) appear similar to that of R972. CCA particles are not observable in the TEM images. The results suggest that these CCAs either (1) exist as very fine particulate and mix homogeneously with the silica particles, (2) are molecularly adsorbed on the surface of the silica particles, or (3) are a combination of (1) and (2). Further experimentation is needed to differentiate these possibilities.[†]

In the cases of the KTPB- and the Copy-Charge-modified silica samples, large chunks of CCA materials can be seen. Figure 4 shows a TEM image of the KTPB-modified R972 sample. The results suggest that KTPB crystallizes out of the spray solution during the fluidized bed spray process, resulting in inhomogeneous distribution of CCA in the modified silica sample.

The SEM images of the styrene–butadiene toner control and the toner containing the silica additive are given in Fig. 5(a) and 5(b), respectively. Comparison of the micrographs indicates that silica particles are uniformly distributed on the surfaces of the toner particles. Figure 5(c) shows the SEM image of a typical toner particle in the developer (mixed with metal beads and roll-milled). While the majority of the silica particles seem to disappear from the toner surface, surface elemental analysis reveals that the Si content between the toner in Fig. 5(c) and that in Fig. 5(b) is almost identical. This observation suggests that most of the silica particles may have been buried beneath the toner surface owing to impaction by the metal beads. Although we don't have any measurement on the penetration depth of the silica particles, we believe that it cannot be too deep because the level of Si content before and after the impaction is very similar.

Effect of the Morphology of CCA-Modified Silicas on Toner Performance. A correlation exists when comparing the charging results in Table I with the morphology results in Fig. 3 through 5. For instance, when the CCA is homogeneously distributed in the silica sample, the CCA controls both the tribo and the admix time of the toner. When the CCA is inhomogeneously distributed in the silica sample, such as in the KTPB and Copy Charge samples, the tribo and the admix time of the toner are dominated by the toner resin itself. This finding is by no means surprising. Because the actual concentration of the CCA is only 0.05 wt%, if the CCA is not distributed as broadly as possible, its effectiveness in charging is low. The implication here is that if one can improve the uniformity of the CCA distribution in either the KTPB or the Copy Charge toner, the CCA will dominate the charging and the admix time will improve. This has indeed been achieved. For example, we have been able to deposit KTPB uniformly on the surface of R972 using a solution-coating technique. The uniformity of the CCA distribution was confirmed by TEM microscopy. The tribo data of this solution-coated R972 sample are plotted in Fig. 6, along with the two controls (the styrene–butadiene and the R972/styrene–butadiene toners) and the fluidized bed KTPB sample. The toner incorporating the solution-coated KTPB sample charges significantly more negative as compared to the toner containing the fluidized bed sample, indicating that the added KTPB dominates the charging. This is also indicated in the admix experiment. The admix time for the toner containing the solution-coated KTPB/R972 is only 2 min, significantly shorter than the 15 min admix time for the toner generated from the fluidized bed sample. The critical role of the morphology of CCA in the silica sample on toner performance is illustrated.

Concluding Remarks

We have shown that a variety of morphologies exist for silicas modified by CCA using the fluidized bed spray process. When the CCA is homogeneously distributed in the silica sample, it dominates the charging and admix properties of the resulting toner. The actual concentration of the CCA is only 0.05 wt%. The attainment of dominance in charging demonstrates that using CCA-modified silica additives is one of the most effective ways of utilizing CCA in toner.

[†] Using fluorescence spectroscopy, we have been able to distinguish the different states of aggregation for t-BSA on the surface of R972 silicas. For instance, t-BSA and R972 are in the form of a very fine particulate mixture when the modified silica is prepared by the fluidized bed spray process; whereas t-BSA is shown to be molecularly adsorbed on the surface of R972 when the modified R972 silica is prepared by a solution coating technique (from cyclohexane).

When the CCA is not distributed homogeneously, the toner resin controls the charging and admix. The observation is attributable to the low surface coverage of the CCA in toner. The importance of the morphology of the CCA-modified silica on toner performance is further illustrated in the KTPB system. We have been able to increase the surface coverage of KTPB on R972 using a solution-coating technique. The tribo increases from ~27 to ~95 μC/g (against beads with a 20/80 Kynar/PMMA surface coating), and the admix time decreases from 15 to 2 min.

Morphological data in Fig. 5(c) show that most of the silica particles buried beneath the toner surface in the developer after impaction with the metal beads. The fact that the CCA employed in the initial surface modification process still dominates the charging of the toner implies that CCA molecules must still remain very close to the toner surface. Future experiments are planned involving the use of a fluorescing CCA to probe exactly the whereabouts of the CCA at various stages in the toners/developers. A correlation between CCA location and toner performance would be extremely helpful for the design and synthesis of future toner/developer systems.

Finally, the present work shows that homogeneity of CCA in CCA-modified silicas is critical to the charging and admix properties of the toner that incorporates them. The term homogeneity here covers a range of physical states; from forming a fine particulate mixture between the solid CCA and the silica particles to molecular adsorption of the CCA on the surface of the silica particles. Recent data show that both the charging and the admix time are sensitive to the profound changes of the CCA in the silica sample. The results of these studies will be reported in due course.[6,*]

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