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Structure−Activity Relationship of Organic Acids in Titanium Dioxide Nanoparticle Dispersions

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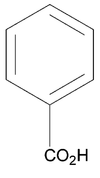
Aromatic carboxylic acids have been shown to effect dispersion properties of titanium dioxide nanoparticles. Addition of small amounts of aromatic acids with more than one carboxylic acid group has significant effects on dispersion viscosity. Structure−activity relationships are explored and possible mechanistic implications are discussed.

Introduction

Titanium dioxide films are used in a number of applications, including dye-sensitized solar cells,[1,2] light-emitting devices,[3] and as solid-phase catalysts.[4−6] The construction of these films consistently requires use of a high temperature (in excess of 450 °C).[1,2] This places serious limitations on the choice of substrate and manufacturing conditions. Frank[7] has reported the effects of temperature annealing of materials prepared from $TiCl_4$ hydrolysis. A low-temperature processing alternative for nanostructured films would be beneficial for both economic and environmental reasons. When considering these processes in relationship to the principles of green chemistry,[8] it is often found that energy use and requirements can have significant environmental and economic implications. We have found that the use of certain nontoxic aromatic carboxylic acids can allow for significantly lower temperature processing. Previously we found that adding small amounts of terephthalic acid, **2**, or trimesic acid, **5**, to the growing colloidal dispersion during a sol−gel preparation allowed us to prepare dispersions and films of titanium dioxide at near ambient temperatures.[9,10] In an effort to expand the general utility of this process, we decided to investigate the effect of these types of acids in the aqueous milling of preformed titanium dioxide nanoparticles. There has been some work reported in the past discussing the use of citric acid as a coating additive.[11] Other uses of carboxylic acid group-containing polymers in titanium dioxide coatings as binders and rheological modifiers have been described.[12] We have found that the viscosity and film-forming quality of titanium dioxide dispersions can be significantly modified by the use of aromatic acids. Although the effect of pH on TiO_2 aqueous dispersions has been described previously,[13] the relatively small amounts of additives used in this current work and the similar pK_a values of the acids employed, lead us to believe that these effects are not governed by pH. However, we have discovered some structure−activity relationships that lend some insight into the mechanism of action of this phenomenon.

Results and Discussion

The effect of benzoic acid, **1**, on the viscosity of a colloidal dispersion of titanium dioxide is negligible. The viscosity remains unaffected until about 2 wt % has been added. Additional amounts of benzoic acid initiate severe foaming of the dispersion to the point where it is not viable for coating purposes. Terephthalic acid [1,4-benzenedicarboxylic acid], **2**, shows a significant increase in viscosity. After addition of only 0.4 wt % of this diacid, the viscosity increases to about 4500 cP. Increasing the amount of added diacid up to 4.0% does not further increase the viscosity. Isophthalic acid [1,3-benzenedicarboxylic acid] ***3*** shows a similar, but reduced, behavior as the terephthalic acid. The 1,3-diacid requires the addition of 0.8 wt % of the isophthalic acid to achieve a maximum viscosity of about 2000 cP. Thus, twice as much of the 1,3 isomer is required relative to the 1,4 isomer to reach approximately half the maximum viscosity (Figure 1).



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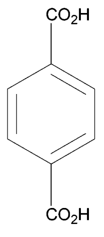

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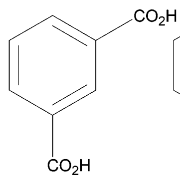

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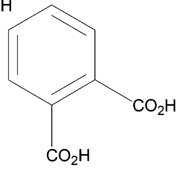

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Phthalic acid [1,2 dicarboxylic acid], **4**, continues this trend in that a full 2 wt % of the 1,2-diacid is required to reach maximum viscosity of, again, about 2000 cP. In this case a 4-fold excess of 1,2-diacid relative to the

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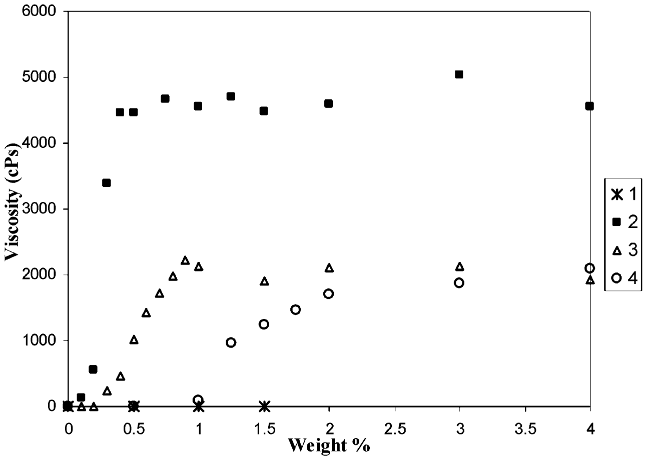
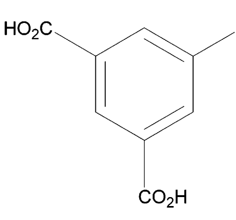


Figure 1. Viscosity vs weight percent of additive: benzoic acid (**1**), terephthalic acid (**2**), isophthalic acid (**3**), phthalic acid (**4**).

1,4 derivative and a 2-fold excess relative to the 1,3 derivative is required to reach maximum viscosity. The maximum viscosity of the 1,2 derivative is, however, similar to that of the 1,3 derivative (Figure 1).

This behavior reveals a possible mechanism of action of the carboxylic acids in these systems. It has been well-documented in the literature that carboxylic acids form covalent, mixed acid anhydride bonds on the surface of titania particles.[14−16] It is likely that one of the carboxylic acid groups in the diacids form a covalent linkage with the surface of the titanium dioxide particle. The magnitude of the effect on viscosity depends on the steric availability of the second carboxylic acid. Obviously, benzoic acid lacks a second carboxylic acid group and thus has no effect on the viscosity. The foaming that is observed in this system is due to the increased hydrophobicity of the particles imparted by the benzoic acids. The 1,4-diacid derivative **2**, having the second carboxylic acid group positioned at an angle of 180° from the titania bound acid, is the most available in the series for interparticle interactions. The 1,3-diacid derivative **3**, having the second carboxylic acid group positioned at an angle of 120° from the titania bound acid, is less available. The 1,2-diacid derivative **4**, with its second carboxylic acid positioned at an angle of 60° relative to the titania bound acid group, is least available in the series.



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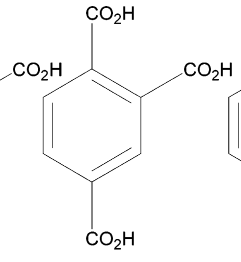

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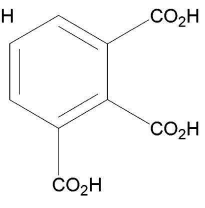

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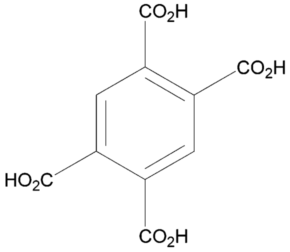

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When compounds with three carboxylic acids are used in these dispersions, the behavior is a bit different from that of those with 2 carboxylic acids (Figure 2). Trimesic acid [1,3,5-benzenetricarboxylic acid], **5**, shows a rapid increase in viscosity upon its addition to the titanium dioxide dispersion. The addition of approximately 0.7 wt % of this triacid brings the viscosity to around 3500 cP. This viscosity is less than that of the 1,4-dicarboxylic acid, **2** (~4000 cP), but more than that of the 1,3-dicarboxylic acid, **3**, and the 1,2-dicarboxylic acid, **4** (~2000 cP). When additional amounts in excess of 0.7 wt % of the 1,3,5-tricarboxylic acid, **5**, are added to the dispersion, however, a *decrease* in viscosity is observed. From 0.7 to 2.0 wt % the viscosity steadily decreases to about 1400 cP and then holds steady upon further addition. When trimellitic acid [1,2,4-benzenetricarboxylic acid], **6**, is used, the same trend as with the 1,3,5-triacid **5**, is observed, but with reduced effect. A maximum in viscosity is achieved with approximately 0.8 wt % of **6**. The decrease in viscosity is then observed upon additional amounts of the 1,2,4-triacid **6**, declining to a minimum of 1000 cP at 3 wt %. Hemimellitic acid [1,2,3-benzenetricarboxylic acid], **7**, does display the same type of trend as the other two acids but to a lesser extent. In this case, the viscosity reaches a maximum of 1600 cP at about 1.5 wt %, while the viscosity decreases only slightly to 1200 cP upon further addition. Interestingly, pyromellitic acid [1,2,4,5-tetracarboxylic acid], **8**, behaves almost exactly the same as trimesic acid **5**. In this case, a maximum in viscosity of 3500 cp is observed at approximately 0.75 wt % of added tetraacid. The viscosity decreases to about 1100 cp upon further addition of up to 3 wt % of **8**.

The effects on viscosity of the titania dispersions by the tricarboxylic acids seem to be consistent with the steric availability of the pendant carboxylic acids. One could propose that the interactions of the two pendant carboxylic acids with each other—and with excess unbound tricarboxylic acids—interfere with attractive interparticle interactions. In the case of the 1,3,5-tricarboxylic acid **5**, with one carboxylic acid covalently bound to the titania surface, the two other carboxylic acid groups present themselves at 120° angles from the particle surface. Because the acid groups are *meta* to one another there is minimal intramolecular hydrogen bonding. However this 1,3-*meta* pattern does allow for significant intermolecular interactions, so that additional 1,3,5-tricarboxylic acid **5** can passivate the surface and compete with the interparticle interactions. In the case of the 1,2,4-tricarboxylic acid **6** there are

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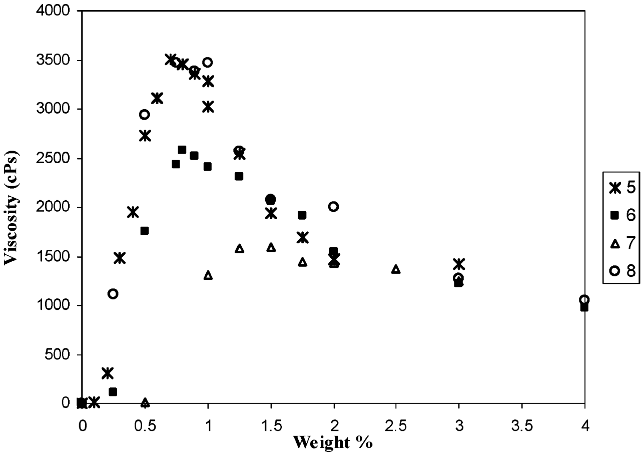

Figure 2. Viscosity vs weight percent of additive: trimesic acid (**5**), trimellitic acid (**6**), hemimellitic acid (**7**), pyromellitic acid (**8**).

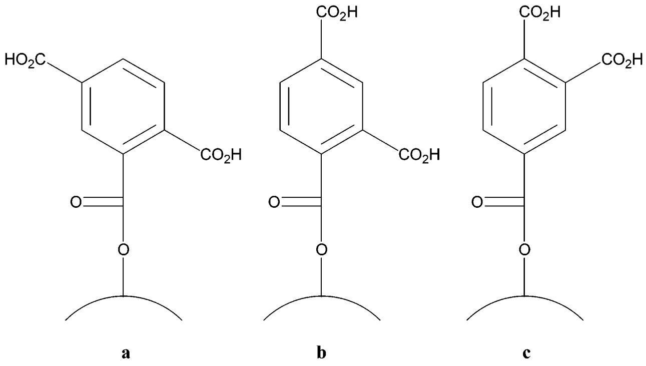

Figure 3. Bonding schemes of 1,2,4-benzenetricarboxylic acid, **6**.

three possible bonding scenarios. The covalent bond between the titanium dioxide and the triacid could be through the 1-position, leaving the 2- and 4-positions free (Figure 3, bonding scheme a). The bonding could occur through the 2- position, leaving the 1- and 4-positions free (Figure 3, bonding scheme b). And the bonding could be through the 4- position, leaving the 1- and 2-positions free (Figure 3, bonding scheme c). Considering the intermolecular interactions available between the 1- and 2- positions, and literature precedent regarding relative reactivity,[17] it seems likely that bonding scheme c will predominate. This is consistent with the behavior of 1,2,4-tricarboxylic acid **6**. The pendant carboxylic acids not bound to the titanium surface will present themselves at angles of 180° and 120°. Being *ortho* substituents, significant intermolecular interactions will reduce the interparticle interactions, and thus we see a reduction in viscosity with respect to that of the 1,3,5-tricarboxylic acid **5**. These two groups, however, still serve to form significant intermolecular interactions with unbound triacid reducing interparticle interactions with excess unbound triacid.

In the case of the 1,2,3-benzenetricarboxylic acid **7** there are two possible bonding schemes. The 1- position can be covalently linked to the titania particle leaving the 2- and 3-positions unbound (Figure 4, bonding scheme d). Alternatively, the 2- position could be covalently bound to the titania surface, leaving the 1- and 3-positions free (Figure 4, bonding scheme e). Again, because of intramolecular interactions, it seems likely that bonding scheme d dominates. In this case, the two pendant carboxylic acids at 120° and 60° are not particularly available for intermolecular association with free triacids, and thus do not show the surface passivation as does the 1,3,5-triacid **5** and the 1,2,4-triacid **6**.

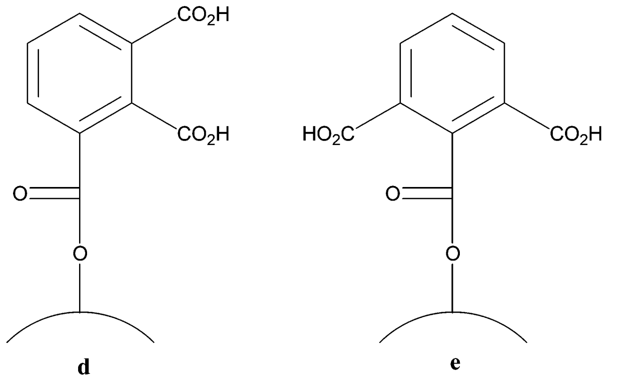

Figure 4. Bonding scheme for 1,2,3-benzenetricarboxylic acid, **7**.

With pyromellitic acid **8**, there are significant intermolecular interactions between the 1- and 2-positions and the 4- and 5-positions in this system. Covalent bond formation between any of the four carboxylic acids will give rise to the same bonding scheme. The intermolecular interactions between the free tetraacids and the interparticle interactions of this system, while certainly complicated, result ultimately in a system that behaves like the 1,3,5-tricarboxylic acid **5**.

By understanding the structure−activity relationships of these systems, it is possible to design specific aggregation motifs of titanium dioxide nanosystems. Work is underway to create specific spatial orientation of nanoparticles in films designed for solar energy and catalysis applications.

Experimental Section

All aromatic carboxylic acids were purchased from ACROS and used without further purification. 1,2,3-Benzenetricarboxylic acid hydrate ($C_9H_6O_6{\cdot}H_2O$) was utilized for the studies with hemimellitic acid (**7**). The amount utilized in the grinding studies was calculated to compensate for the hydrated form. Degussa P25 was received from Degussa and used as received. A ball mill grinder, ceramic jars, and beads by U. S. Stoneware (New Palestine, OH) were used for all studies. A LVF Brookfield viscometer was used for all studies.

General Procedure for TiO_2 Aqueous Milling. A 15-g portion of Degussa P25 was added to a ceramic jar. The carboxylic acid was added in the appropriate amount by weight percent of TiO_2 (0.015−0.600 g). Water (85 mL) was added to the jar along with 20 ceramic beads. The jar was sealed and placed on a ball mill grinder to be rotated at 85 rpm for 18 h.

General Procedure for Viscosity Measurements. Using the LVF Brookfield viscometer, spindle number 3 was used at 30 rpm. Measurements were taken after one minute of rotation to ensure equilibration of the reading. Readings were taken in triplicate and averaged.

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