Materials Compatibility Assessment via Temperature-Controlled Contact Angle Measurements

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Abstract

We evaluated the temperature-dependent rheological behaviors of several resin polymers in an environment-controlled chamber by monitoring the spreading dynamics of polymer melts on various substrates to understand their interfacial interactions at different processing temperatures upon contact with materials of interest. To the best of our knowledge, this is the first report on the study of polymer-pigment interaction via contact angle measurement of toner resins on substrates constructed from pigment nanoparticles.

Introduction

Identifying materials with the optimal compatibility is an important prerequisite to many developmental practices that involve the assembly of different counterparts. For example, failure to identify the appropriate colorants and additives in ink development can lead to unstable formulations which often lead to poor image quality and poor print attributes. One of the approaches to assess materials compatibility is through determining their surface energies via contact angle measurements.

The extrapolation of contact angles of reference liquids interfacing with the materials of interest can be modeled based on theories proposed by Young, Zisman, Fowkes, Wu, Owen-Wendt-Rabel-Kaelble, and Schultz to determine the surface free energies [1]. Although theoretical models can provide quantitative predictions of the nature of a particular surface, they determine surface energies based on the materials interfacial energies with the test liquids and on the assumption that materials of interest are unique in nature. For example, the Schultz model is particularly suitable for high-energy solid surfaces; while Wu, Fowkes and Owen-Wendt-Rabel-Kaelble models are more suitable for materials which exhibit both dispersive and polar characteristics. Although these models are useful in providing information regarding the surface energy of materials, they cannot provide any direct indication of the surface interactions between two materials having temperature-dependent properties.

Motivation

Polymeric materials such as toner resins and engineering plastics have temperature-dependent rheological behaviors. These physical properties are intrinsic to the performance of the printing ink, giving them important properties such as fusing, film formation, adhesion, cohesion, particle size and morphologies. They are typically subjected to thermal treatment during processing such as extrusion, milling and injection molding in which polymers are softened or melted. In these conditions, the surface energy and the wetting behavior of polymers could vary significantly with temperature, but these changes are difficult to assess using contact angle measurements with standard test liquids because the operational temperatures at which these polymers are handled often exceed the boiling point of the standard test liquids. To the best of our knowledge, the surface tension of various polymer melts such as PP, HDPE, PS, PMMA and star polymers have been explored on molded substrates [2], but the polymer melt behaviors on discrete materials such as pigment have not been reported.

Organic pigments are typically composed of one type organic chromophore and are often poly-crystalline. In the manufacturing process, they are synthesized and grinded to different sizes to maximum light scattering to give them the most vibrant color efficiency for each specific application. Like other organic molecules that can be recrystallized, they can be compacted under pressure to form a large poly-crystal, similar to the preparation of salt plates for IR absorption measurements. Here we report a macroscopic analysis of polymeric hot melt wetting on discrete material surfaces such as organic pigments. We demonstrate the feasibility of assessing the wetting behavior of polymer melts on pigment discs that are produced under high pressure to form a macroscopic reconstruction of pigment surface under controlled-temperature environment. The ability of reconstructing a substrate representative of the pigment surface without roughness is critical to an accurate assessment of the pigment's surface energy [3]. Our approach provides a direct comparison of the wetting behaviors of polymeric materials such as thermoplastics on different types of pigment surfaces.

Approach

Based on the assumption that the constructed surface with pigment particles is representative of the surface of each discrete particle, we are survey the average surface energy of these surfaces in a macroscopic scale. To assess the properties of these constructed surfaces, we utilized a die which is typical for the making of crystal discs for IR absorption measurements. Under approximately 10 tons of pressure, most materials can be compressed to form a bulk sample. Depending on the materials utilized, the interfacial energy holding them together could arise from Van der Waals, electrostatic, ionic and hydrogen bonding. These are common in polymeric and organic materials, such as those containing hydrocarbon chains, charged atoms, or materials containing both hydrogen acceptor and donor.

Experimental

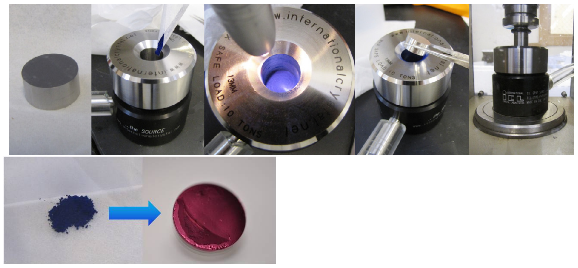

Figure 1. *From left to right, we have one of the two plastic lined anvils, next to it is the die we used to prepare our pigment disc. Approximately 100 – 200 mg of sample is typically loaded into the die then smoothed and compressed under 10 ton pressure to form a pigment disc on the lower right.*

To construct a sufficiently large sample surface from discrete materials such as organic pigment, we utilized a die which is a common sample preparation tool for creating salt discs used in IR absorption measurements. In a typical setup, 100 – 200 mg of pigment powder is deposited into the cavity of the die, smoothed between two plastic-lined anvils, and compressed under 10 tons of pressure for 10 – 15 minutes at room temperature. Upon release of pressure, a solid pigment disc measuring 1 cm in diameter and 1 mm in thickness is formed. It requires some practices to obtain a well constructed disc, and the choice of plastic liner has a big effect on the release of the materials because some plastics yield under pressure, causing failure of the pigment disc to be released after its formation.

We examined four representative samples of off-the-shelf pigments from the four major colors, cyan, magenta, yellow and black. Interestingly, we were unable to compress black pigment into pigment disc, regardless of how much pressure and preparation time was used. Among the four pigments, only black is an amorphous material. This explains the failure of crystal formation under pressure which is the major mechanism holding the materials together. While cyan, magenta and yellow were organic materials made of one small molecule as a chromophore, they could be compressed into poly-crystals. The crystal formation was particularly pronounced with cyan, which showed a slight shift in color due to close packing of the nanostructures which is known in optically active materials as bathochromic or hypsochromic shift due to the new orientation of the relative molecular orientation

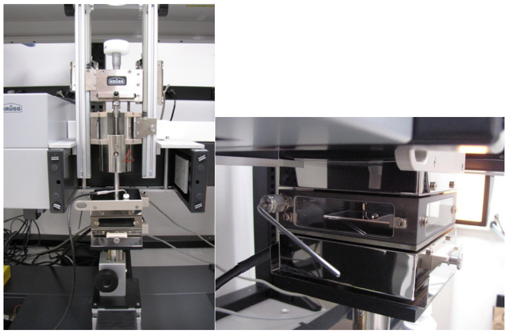

Figure 2. *(Left) Contact angle measurement device Kruss DSA100 equipped with a high temperature dosing system for dispensing high viscosity materials and the environmental chamber (right).*

in space.[4,5]

The equipment we used to carry out the measurements are shown in Figure 3 & 4. It is a high precision contact angle measuring device by Kruss equipped with a high temperature dosing system and an environmental chamber which allows control over both temperature and the type of atmosphere in which the experiment can be conducted. With the capability of video recording evolution of events that happen during the experiments, we examined the melting behaviors of some commercially available toner resin on both reference substrates and the pigment samples discs prepared in-house. The reference materials chosen are Teflon and glass. These two materials represent two distinct types of surface energies, with Teflon being completely hydrophobic due to the halogen and hydrocarbon chains, while glass is hydrophilic with oxygen atoms on the materials surface available for hydrogen bonding.

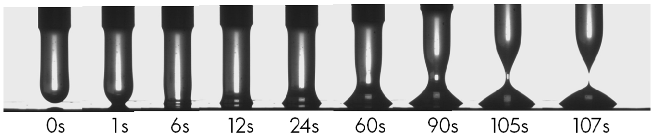

Figure 3. *The chronological changes and dosing behavior of a low molecular weight polymer while being dispensed inside the environment-controlled sample chamber.*

Figure 3 shows the evolution of a low melting polymer and its behavior upon dosing onto glass with respect to time. In a typical experiment, the experimental chamber is equilibrated to the melting temperature of the material being examined. A drop of the melted resin polymer was then dispensed in 10 uL increments until a sessile drop is formed and can be deposited onto the testing substrate.

Results & Discussion

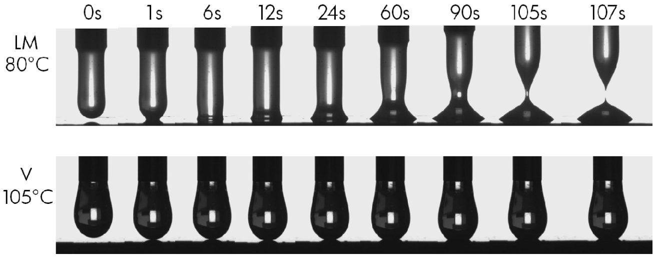

Figure 4. *The direct comparison of two polymers having almost identical melting point exhibit different rheological behaviors while dosing at different temperatures due to viscosity difference.*

The behavior of one toner resin can have different behaviors on different substrates, which directly indicates the compatibility of the resin with the substrate we are interested in at a specific temperature. It is particularly useful to examine the rheological behaviors of materials at the actual process temperature because it may be under or above the transition temperatures of the materials and we can gain insight to how to control the process.

We examined several polymers that have similar melting temperatures but different viscosities and their behaviors on the pigment discs at or near the polymer's melting temperature. The dosing behaviors of different polymers even having the same melting temperature are different due to viscosity. As shown in Figure 4, a low molecular weight (LM) sample and a higher viscosity sample (V) having almost identical melting point have completely different behaviors. At 105 °C, which is above its melting temperature, the dosing of V was still not complete, while LM dosing was completed in 107 seconds.

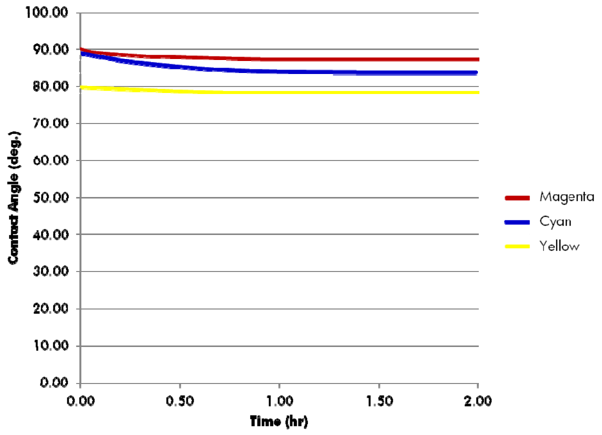

Figure 5. Plots of contact angles changes of the viscous polymer (V) at 80°C over the course of 2 hours.

When we observe the spreading behavior of V at 80 °C as shown in Figure 5, the changing in contact angle seized after 1 hour and it clearly shows that this resin has a higher affinity for the yellow pigment since its contact angle is almost 10 °C smaller than magenta and 5 °C smaller than cyan. From this experiment we can conclude that this particular polymer is likely to coat the yellow pigment better than cyan or magenta.

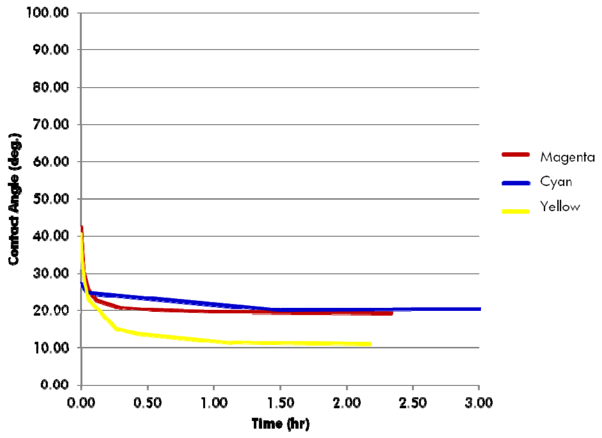

Figure 6. Plots of contact angles changes of the low molecular weight (LM) polymer at 80°C over the course of 3 hours.

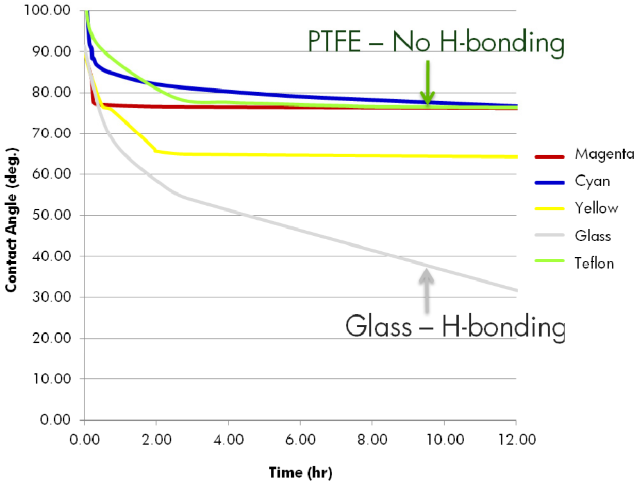

Figure 7. Plots of contact angles changes of the viscous polymer at 80°C over the course of 2 hours.

When we examine the low molecular weight (LM) polymer on the same pigment surfaces (Figure 6), we observed a similar trend that the resin once again exhibit better wetting on the yellow pigment compared to cyan and magenta. The discrepancy is once again 10 °C, however, in this experiment, cyan and magenta appear to have more similar surface energies relative to the LM polymer.

To compare the performance the same materials on different materials in perspective, a different polymer having a higher melting point and viscosity was dosed on all three pigments and the references, namely glass and Teflon. As shown in Figure 7, we can see that due to the high surface energy of glass, this polymer can wet the glass surface better than it does with low surface energy Teflon. Toward the end of the 12-hour experiment when the contact angles of the samples had seized to change, it appears that the pigment surface of cyan and magenta have very low surface energy and the curves coincide with Teflon. As we have seen with prior samples, yellow once again appear to have a higher surface energy compared to cyan and magenta. A likely explanation is due to available atoms in the yellow chromophore for hydrogen bonding.

Conclusion

We reported a method to systematically examine the temperature-dependent behaviors of materials such as resin polymers with substrates constructed from discrete materials such as organic pigments. Using high and low surface energies substrates as standard for reference, we can indirectly infer potential mechanisms that the wetting behaviors may have arise from. It is possible to extend this investigation method to explore other materials systems involving fine particles to assess the compatibility of various parts that may not be able to otherwise.

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Author Biography

Doris Chun is a senior research scientist at Hewlett Packard Laboratories in Palo Alto, California. Her current research focuses on the development of novel liquid toners through the investigation of new materials and production processes. Doris received her Ph.D. in organic chemistry from UCLA and B.S. in bioengineering from UCSD. At UCLA, she studied the synthesis and application of electronic materials for OLED, OFET and photovoltaic; and the self-assembly of polymeric nanoparticle during her stay at IBM-ARC.