Surface Pattern Formation in UV-Curable Coatings

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Some UV-curable coatings display matte surfaces after cure if they have undergone a certain period of leveling at a temperature above their glass transition temperature and the melting point of any crystalline co-reagents present in the formation. The matte finish of these coatings is due to the presence of coherent surface wrinkles after cure, which are similar in appearance to those induced by differential thermal contraction, when a metal layer is sputtered onto a rubbery or viscous substrate. However, the wrinkles in the UV-cured coatings appear under isothermal conditions, and it is, therefore, inferred that they are due to the dynamics of internal stresses induced by through-thickness variations in the extent of curing.

INTRODUCTION

UV-curable coatings are increasingly used to protect and enhance the appearance of heat sensitive organic substrates, such as wood, and are particularly attractive where rapid processing and the absence of volatiles are at a premium.[1-3] In many applications, it is also important to control the surface topography, and, in particular, to reduce gloss.[4] This gloss reduction can be achieved by texturing the coating as proposed in several patents.[5] We have investigated a number of powder-based coatings that exhibit matte surfaces owing to coherent wrinkling at their surface after a single-step UV cure, provided they have undergone a prior heat treatment. This heat treatment, known as "leveling," is generally necessary to homogenize coatings applied in the form of powders. To account for the surface wrinkling, we ultimately hope to be able to control roughness in such coatings systematically, either by a suitable choice of processing parameters or by adapting their formulation. In what follows, however, we limit ourselves to a presentation of some aspects of the phenomenology of surface wrinkling in a relatively simple model system, and a qualitative discussion of what we believe to be the main physical processes involved.

EXPERIMENTS AND DISCUSSION

The UV-curable model powder coating formulation investigated was a maleate/vinyl ether (MA/VE) system composed of an unsaturated polyester (Uralac XP 3125P from DSM) with a crystalline vinyl ether terminated polyurethane compound (Uralac ZW 3989P from DSM). The polyester oligomer contained unsaturated maleic or fumaric groups which react with the vinyl ether double bonds of the co-reagent.[6] 2,2,-dimethoxy-1,2-diphenylethan-1-one (Irgacure 651) from Ciba Specialty Chemicals Inc., Switzerland, was used as a photoinitiator (1 wt% of the total amount of resin). The components were melt mixed at 80°C in a Buss PR46 extruder. The extrudate was ground into particles, which were then sieved to 125 µm. An EFOS Novacure N2000 UV spot curing system equipped with a high pressure 100 W mercury vapor short arc lamp, and a Fusion I250B UV source equipped with a D-bulb were used as UV sources. Test coatings were prepared on freshly cleaned glass plates by deposition of powder using a spreader or alternatively from the melt using a doctor blade. This resulted in a final thickness of 40 to 190 µm. After melting and leveling on a hot stage, the polyester film was cured using one of the UV sources. A typical "wrinkled" coating is shown in *Figure* 1. This type of surface structure has been reported previously in UV powder coatings[7] and is similar in appearance to those induced by a differential thermal contraction when a metal layer is sputtered onto a rubbery or viscous substrate.[8] It is also reminiscent of the structures that result from geological folding of layers with dissimilar rheological properties.[9-11] As shown in *Figure* 2, the amplitude of the wrinkles was in some cases comparable to the initial coating thickness.

The extent of wrinkling was strongly dependent on the leveling and irradiation procedures. The conditions for sufficient wrinkling to give a matte coating may be summarized as follows. A minimum leveling time was always necessary, this minimum time decreasing with increasing temperature, increased gas flow rate at the surface of the coating and increased coating thickness. No significant modification in the rheological or thermal properties was observed up to the critical leveling time, although thermally induced crosslinking did

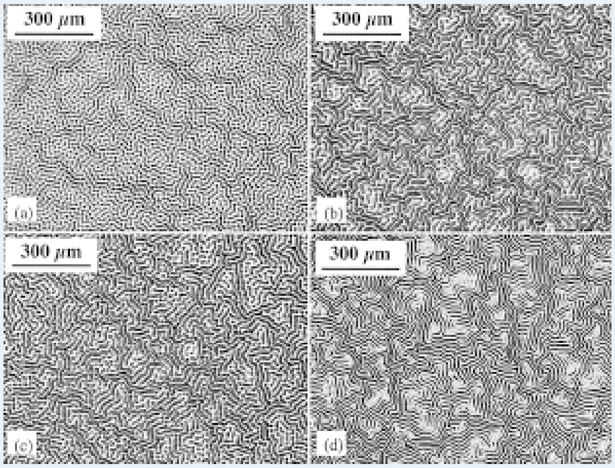

Figure 1—Optical micrographs showing the surface texture of coatings cured at different temperatures and leveling times: (a) T = 150°C, t = 15 min, (b) T = 150°C, t = 22.5 min, (c) T = 160°C, t = 7.5 min, and (d) T = 160°C, t = 17.5 min (coating thickness 80 µm).

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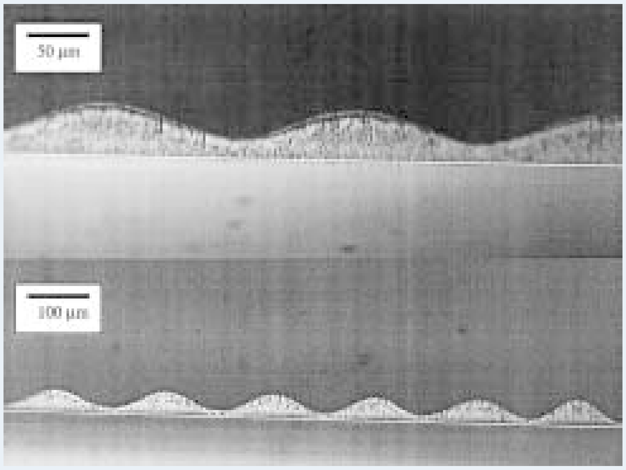

Figure 2—Optical micrographs of wrinkled coating cross-section. The white lines indicate the substrate-coating interface.

occur after longer times. The observation of a maximum in the amplitude (R_a) of the wrinkles after UV irradiation as a function of leveling time (cf. *Figure* 3) and the absence of wrinkles after relatively long periods of leveling may reflect the influence of thermally induced crosslinking. The nature of the atmosphere during leveling was not important, and wrinkles were observed after leveling under nitrogen, oxygen, or air, provided that the surface was submitted to a gas flow. On the other hand, the atmosphere did play an important role during irradiation, no wrinkling occurred during irradiation under nitrogen. The intensity of the UV light was also an important parameter. Too high a UV intensity inhibited wrinkling, whereas reducing the intensity resulted in a increase in the irradiation time necessary to produce wrinkles.

The fact that the wrinkles appeared only after the coating had been submitted to a gas flow before irradiation suggested that they may have been associated with evaporation of a volatile component at the surface, leading to a through thickness gradient in the composition. This was difficult to confirm since no information was available concerning the different additives present in the formulation. However, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) indicated there to be no long-range segregation of the co-reactants themselves during leveling.

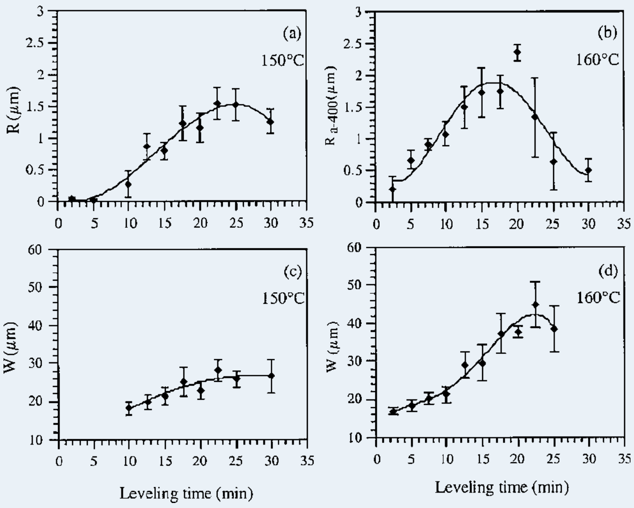

Figure 3—Variation of the surface roughness of coatings (R) cured after different periods of leveling at (a) 150°C and (b) 160°C; (c) + and (d) variation of the corresponding wavelength (W) (coating thickness: 80 μm).

The evaporation of an addition (e.g., a flow promoter) could lead to an increase in the viscosity of a surface layer; the formation of surface wrinkles due to the compressive stresses on this layer induced by shrinkage of the subsurface material. The subsurface material is expected to undergo a more rapid cure than both the surface layer—where the curing reaction is known to be inhibited by the oxygen present in the atmosphere, and the layer in contact with the substrate—where the UV intensity is reduced owing to absorption by the coating. This was confirmed by ATR-FTIR. As a result of these retardation effects, the surface layer will remain viscous during the initial stages of cure of the subsurface material. If it is not sufficiently viscous, any surface deformation will be relaxed by rapid flow. On the other hand, if the viscosity is high, internal stress relaxation will take the form of surface buckling. It is believed that in the case of irradiation under nitrogen, the rapidity of the reaction (less than 2 s for complete cure as measured using photo-DSC and photorheometry equipment[12]), and the lack of inhibition of curing as the surface prevents any relaxation of the internal stresses; hence, no wrinkles are formed.

In samples cured by UV irradiation through a 1 mm thick quartz substrate, which is transparent of UV light, considerable crystallization of the polyurethane was observed in the surface layer after post-cure storage at room temperature but not in the rest of the sample. As the presence of crystallinity is directly related to the presence of unreacted polyurethane, this indicated a step-wise decrease in the extent of cure at the interface between the surface layer and the rest of the sample under conditions of partial UV cure. A reduced degree of cure at the free surface after 90 sec of UV exposure was also demonstrated by ATR-FTIR.

Surface roughening was not seen in samples cured by irradiation through a quartz substrate, presumably since the substrate constrained contraction of the intermediate layers when cure progressed from the bottom up. It is, therefore, noteworthy that coatings cured through the substrate showed substantial residual stresses after cure and long-term storage at room temperature, resulting in upward curvature when the substrate was removed. This was not seen in the wrinkled coatings. It was also possible to obtain uniform through-thickness curing by placing the samples on a reflecting surface (an aluminum foil) during UV irradiation or simply by using very thin coating (<15 μm). Again, no wrinkling was observed under these conditions.

In the absence of precise information on the cure profiles and their evolution during irradiation, it is difficult to account for these effects quantitatively. However, it is well known that a free surface subject to a laternal stress may become unstable with respect to periodic undulations,[13] due to elastic buckling, viscoelastic, or plastic deformation. In the case of surface buckling in polysiloxane metallized at high temperature,[7] the driving force for buckling of the metallic layer is thermal contraction of the rubber as the temperature is reduced. We have also observed similar textures in films of uncured epoxy

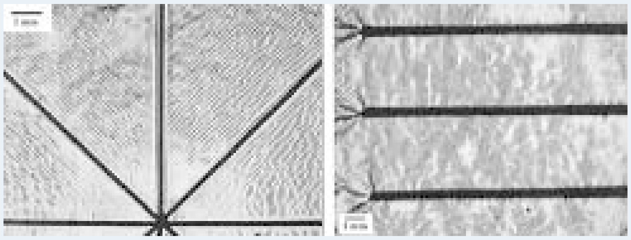

Figure 4—Optical micrographs of a tailored wrinkled pattern obtained by using opaque masks. (Black lines)

resin coated with gold layers of 40 nm in thickness at a temperature of about 60°C. In each case, wrinkling is reversible on reheating. Indeed, the observation of wrinkles in the metallized epoxy resins shows that surface buckling need not require extensive crosslinking below the surface, since little bulk cure took place during gold coating. Moreover, buckling of a viscous or viscoelastic material need not be characterized by a well-defined critical buckling stress. In the partially cured resins under consideration here, the characteristic wavelength of the surface instability is, therefore, likely to depend on the kinetics of the processes responsible for buckling.

As with wrinkling induced by surface buckling in gold coated polymer substrates, the degree of organization in the surface textures of the UV-cured coatings may be increased by tailoring the boundary conditions; wrinkles tend to run at right angles to the edge of coatings, or artifically induced surface steps. This has been exploited to generate the ordered surface structures shown in *Figure* 4 and demonstrates that the patterns are to a large extent controllable. In *Figure* 4 the dark lines correspond to zones where an opaque ink mask has been applied to suppress UV crosslinking locally. Control of the orientation and the amplitude of the surface texture is interesting from the aesthetic point of view. Moreover, applications such as diffraction gratings for optical sensors might also be envisaged.

CONCLUSION

Controllable surface wrinkling has been obtained in coatings based on blends of an unsaturated polyester and a crystalline vinyl ether terminated polyurethane after a certain period of leveling at the final cure temperature, during which a gas flow was present at the coating surface. UV irradiation is suggested to induce relatively rapid contraction of an intermediate layer; layers further into the sample cure more slowly as a result of absorption by the coating itself. Once the global degree of cure is sufficiently high, compressive stresses are induced in the surface layer, provoking a buckling-like instability. The resulting undulations are then frozen as UV cure proceeds. Consistent with the observation, such a mechanism would become ineffective after long leveling times owing to extensive thermal crosslinking prior to the UV cure. These suggestions nevertheless are based substantially on circumstantial evidence. In view of the potential complexity of the phenomenon, further progress in our understanding is likely to require detailed characterization of the local state of the coatings at various stages of leveling and UV cure. Potentially powerful tools in this respect would be confocal Raman microscopy or infrared microscopy of transverse sections. It would also be of interest to expand the range of experimental variables to include the content of different additives, given that the presence of UV stabilizers can strongly affect crosslinking profiles in coatings.[14]

References

(1) Bodnar, E., *Eur. Coat. J*., 1-2, 44 (1997).

(2) Koleske, J.V. and Mazzariello, R.G., in *Plastics Finishing and Decoration*, Satas, D. (Ed.), Van Nostrand Reinhold Co., New York, 1986.

(3) Aspin, S., *Eur. Coat. J*., 4, 288 (1993).

(4) Richart, D.S., *Polymer Powder Technology*, Narkis, M. and Rosenzweig, N. (Eds.), Wiley and Sons, Chichester, 1995.

(5) Hahn, E.A., U.S. Patent 3,918,393 (1975); McDowell, J.R., U.S. Patent 4,169,167 (1979); Troue, H.H., U.S. Patent 4,721,784, (1983), 4,483,884 (1984), and 4,485,123 (1984), Alison, A.D., Koleske, J.V., and Gerkin, R.M., U.S. Patent 5,212,271 (1993); Gorzalski, P.J. and Diehl, D.A., U.S. Patent 5,585,415 (1996).

(6) Witte, F.M., *Eur. Coat. J*., 3, 115 (1996).

(7) Gorzalski, P.J. and Diehl, D.A., (to PPG Industries, Inc.) U.S. Patent 5,585,415, (1996).

(8) Bowden, N., Brittain, S., Evans, A.G., Hutchinson, J.W., and Whitesides, G.M., *Nature*, 393, 146 (1998).

(9) Chapple, W.M., *Tectonophysics*, 7 (2), 97 (1969).

(10) Biot, M.A., *Proc. R. Soc. London*, Ser A., 242:444 (1957).

(11) Ramberg, H., *Tectonophysics*, 1 (4), 307 (1964).

(12) Lee, S.S., Lucian, A., and Månson, J.A.E., “A Rheological Characterization Technique for Fast UV-Curable Systems,” *Prog. Org. Coat*., in press.

(13) Allen, G.H., *Analysis and Design of Structural Sandwich Structure*, Pergamon, New York, 1969.

(14) Schrof, W., Beck, E., Königer, R., Reich, W., and Schwalm, R., *Prog. Org. Coat.*, 35, 197 (1999).