The Effects of pH, Molecular Weight and Degree of Hydrolysis of Poly(Vinyl Alcohol) Suspensions on Slot Die Coating

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Abstract

Slot die coating technology is currently the most widely used method for production of optical films. The main advantages of this coating method are its ability to pre-determine the product film thickness and to produce uniform film under prolonged operation. In the present study, a laboratory-scale slot die coating equipment was used to investigate the effects of pH, molecular weight and degree of hydrolysis of TiO_2 in polyvinyl alcohol (PVA) suspensions on the coating window. Measurements of steady shear viscosity, surface tension, and amount of PVA adsorption on particle surfaces of different suspensions, together with observations of coating bead by means of a flow visualization technique, were used to analyze the coating flow behavior. Changing pH affected the suspension rheology and its stability. Increasing the amount of PVA adsorbed on the TiO_2 surface resulted in an increase in surface tension, which was responsible for the expansion of the coating window or an increase of the maximum coating speed at which flow defects occurred. Four different PVA with varying molecular weight and degree of hydrolysis were used in the suspensions. Higher degrees of hydrolysis resulted in an increase in polymer adsorption, and hence larger surface tension. By contrast, higher molecular weight PVA resulted in a higher viscosity and a smaller surface tension, thus causing air entrainment to occur at a much lower maximum coating speed.

Introduction

In recent years, many hi-tech industries have focused their research and development on high performance materials. There is a huge demand of hybrid organic-inorganic materials for applications in flat panel display panels and long-life battery productions. Many coating materials contain added particles in polymers to produce value-added products. For example, in the coating of light diffusing backlit film, TiO_2 particles are normally added in the PVA solution to produce a film with high gloss, good light diffusion and uniform dimensions.
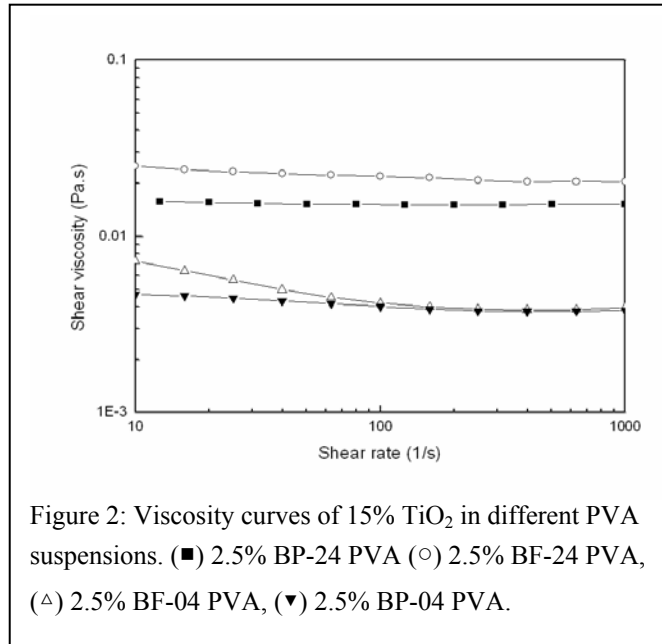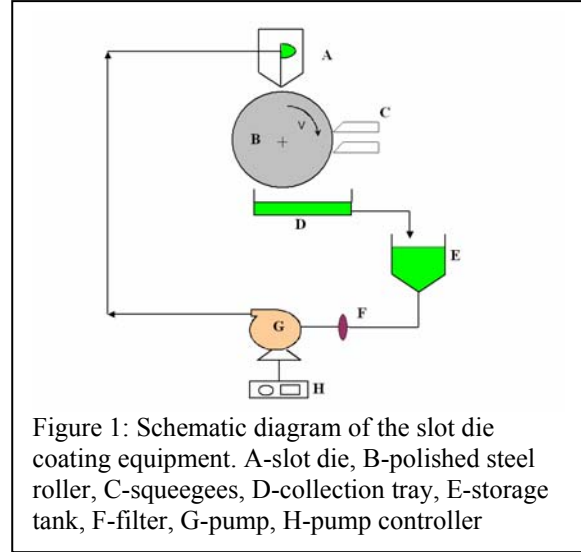
The slot die coating technology has the advantage of pre-metering a stable coating film thickness under prolonged operating conditions. The process involves the delivery of coating solution at a constant flow rate through a pump to a precision slot die. The die produces a wide, stable coating bead onto the substrate. This coating method is used in the present study to examine the effects of added particles in polymer solutions on the coating performance.

Adding polymer in suspension to control the colloidal dispersion has been the subject of extensive research because of its importance in industrial applications. The stability of a uniformly dispersed suspension is determined by the relative magnitude of various inter-particle forces such as Brownian, van der Waals, electrostatic, steric, and hydrodynamic forces. In the present study, polyvinyl alcohol (PVA) is chosen as the base fluid, since it is not only hydrophilic, non-toxic, and easy to handle, but is also an industrially important ingredient which is widely used in coating industry such as in ink-jet media. Despite numerous studies

Figure 1: Schematic diagram of the slot die coating equipment. A-slot die, B-polished steel roller, C-squeegees, D-collection tray, E-storage tank, F-filter, G-pump, H-pump controller

on the adsorption and rheological behavior of adding PVA in inorganic particle suspensions, very little information is available on the coating behavior of these polymeric suspensions. Chu et al. found that the coating window is enlarged with the addition of inorganic particles such as TiO_2 and SiO_2 in PVA solutions, and the coating window size increases with the solids concentration. The strong interaction between particles and polymer appears to delay the occurrence of flow instability to a higher coating speed. It was also shown that the influence of surface tension is more dominant than the suspension viscosity. The evidence was further supported with flow visualization measurements. Since the stability of the coating bead is paramount in achieving a good coating, many researchers have attempted to relate the shapes of the upstream and downstream menisci of the coating bead to coating stability. Yamamura et al. observed a higher onset velocity of air entrainment when PMMA particles were added to silicon oil, but it was dependent on the particle number density. The onset velocity appeared to reach

a maximum at the particle diameter of 30um, and then decreased with further increase in the particle diameter.

Experimental

A schematic diagram of the slot die coating equipment is shown in Fig.1. A non-pulsating, high precision constant rate screw pump (NEMO Pump, Heishin Ltd., Japan) was used to deliver the coating suspension. The flow rate was adjusted with a regulator and the suspension was coated on a chrome-plated steel roller (radius: 0.1m, width: 0.2m). The squeezes were

Figure 2: Viscosity curves of 15% TiO_2 in different PVA suspensions. (■) 2.5% BP-24 PVA (○) 2.5% BF-24 PVA, (△) 2.5% BF-04 PVA, (▼) 2.5% BP-04 PVA.

positioned on the roller surface to scrape off the coating solution and collect it. The coating die was arranged vertically in order to facilitate the visual observation of the coating bead. The roller speed was controlled between 2 to 30m/s, and the coating width was 0.1m, which was the width of a dual cavity T-die. The slot gap was 0.0002 m, and the distance between the die exit and the roller was 0.0003 m. The experiment was first carried out to determine the maximum and minimum speed limits for stable operation. Flow rates were then adjusted using the flow regulator to complete the stable coating window.

Results and Discussion

The effect of molecular weight and hydrolysis of PVA on the coating window was studied by using suspensions of 15% TiO_2 in four different 2.5% PVA solutions. The degree of hydrolysis of PVA is defined according to the relative quantities of hydroxyl and acetate groups on the polymer chain. The four types of PVA used in the present study were supplied by Chan-Chun Petrochemical under the trade names of BP-24, BF-24, BP-04 and BF-04. It is noted from Fig.2, that the 15% TiO_2 suspensions with different PVA are only marginally shear-thinning, except the BF-04 suspension, and the viscosity increases with increasing molecular weight. All suspensions approach a constant viscosity at high shear rate. For PVA with the same molecular weight, the viscosity of BF-24 is about 35% higher than that of BP-24. This is due to the stronger hydrogen-bonding between the TiO_2 particles and the polymer (BF-24) with a higher degree of hydrolysis (more –OH group). To understand the mechanism of polymer adsorption on solid particle surfaces, it is important to consider the role of the functional groups present in the polymer. For example, the main function group in PVA is the hydroxyl group, but due to the presence of a small residual of non-hydrolyzed acetate group after polymerization, the adsorption of PVA onto TiO_2 surface is greatly influenced by the acetate group. Since the affinity of the acetate group with TiO_2 is greater than the hydroxyl group, more segments of PVA chains will be attached to the particle surfaces, resulting in a flatter conformation. By contrast, PVA with a higher degree of hydrolysis contains less acetate groups, and the adsorbed segments form loops and tails arranged perpendicularly on the particle surface. This allows more surface area available for polymer adsorption, resulting in more BF-24 adsorbed on the TiO_2 surfaces.

Figure 3 shows the coating windows obtained for the four TiO_2/PVA suspensions with different molecular weights and degrees of hydrolysis. It is clear that the maximum coating speeds, which mark the onset of air entrainment, are significantly different for PVA with similar molecular weight but different degrees of hydrolysis. Comparison of the windows obtained for BF-04 and BP-04 (98% and 88% degree of hydrolysis, respectively) reveals the maximum coating speed for the former suspension is about 2.5 times that of the latter suspension. Similar results are obtained for BF-24 and BP-24, although the extent of the increase in the maximum speed is not as large as the lower molecular weight PVA. Apparently, there appears to be a counter-effect due to the difference in molecular weight.

To examine the effect of molecular weight, the shear viscosity and the surface tension of the BP-04 and BP-24 suspensions were compared. Their physical properties are listed in

Table 3. The molecular weight of BP-24 is about 5 times that of BP-04, and they have the same degree of hydrolysis (88%). Their respective viscosities are 15.1 mPa.s and 3.78 mPa.s at a nominal shear rate of 1000 s^{-1}, and their surface tensions are 0.0364 N/m and 0.0421 N/m. It is seen from Fig.3 that the maximum coating speed increases by about 45 % for the BP-04 suspension as compared to the BP-24 suspension. Similarly, the maximum coating speed obtained for the BF-04 suspension (μ= 3.84mPa.s and σ= 0.0427N/m) is about 1.5 times that for the BF-24 suspension (μ= 20.4mPa.s and σ= 0.0393N/m). A flow visualization technique was employed to observe the shape of the coating bead. It was found that the dynamic contact angle approached 180° when air entrainment occurred at the maximum coating speed. It has been previously reported that for Newtonian fluids, the air entrainment velocity V_{ae} decreases with increasing viscosity and increases with increasing surface tension. Hence, the BP-04 suspension yields a higher maximum coating speed and thinner coating film than the BP-24 suspension. The same argument applies for BF-04 and BF-24 suspensions.

Acknowledgements

References

1. M.J. Lubar, US Patent 5,888,629, 1999.
2. E. Katoh, Y. Tsubaki, US Patent 6,699,536, 2004.
3. E.D. Cohen, E.B. Gutoff, Modern Coating and Drying Technology, VCH Publishers, New York, 1992.
4. K.Y. Lee, L.D. Liu, T.J. Liu, Chem. Eng. Sci. 47 (1992) 1703.
5. B. Vincent, Adv. Coll. Interf. Sci. 4 (1974) 193.
6. T. Sato, R. Ruch, Stabilization of Colloid Dispersions by Polymer Adsorption, Marcel Dekker Inc, New York and Basel, 1980.
7. A. M'Pandou, B. Siffert, Colloid. Surf. 24 (1987) 159.
8. L.K. Koopal, V. Hlady, J. Lyklema, J. Colloid Interface Sci. 121 (1988) 49.
9. W.B. Chu, J.W. Yang, Y.C. Wang, T.J. Liu, C. Tiu, J. Guo, J. Colloid Interface Sci., 297 (2006) 215.
10. C.K. Yang, D.S.H. Wong, T.J. Liu, Polym. Eng. Sci. 44 (2004) 1970.
11. P.M. Schweizer, J. Fluid Mech., 193 (1988) 285.
12. M. Yamamura, H. Miura, H. Kage, AIChE J. 51 (2005) 2171.

Figure 3: Coating windows (q vs. V) for the 15% TiO$_2$ in different PVA suspensions. (■) 2.5% BF-04 PVA, (●) 2.5% BF-24 PVA, (□) 2.5% BP-04 PVA, (○) 2.5% BP-24 PVA.