Viscoelasticity in toner fusing process

Suresh Ahuja, Xerox Corporation, Webster, NY

Abstract

Fusion and fix of images is an important process in digital printing. A base toner is mainly composed of a polymeric binder and a pigment with and without an internal lubricant for fuser roll. Necessary step in fusion of toner after particles melt is coalescence of particles. A review of models of coalescence of particles finds that rate of calescence is dependent on toner particle size, its viscoelastcity and its surface tension. Rolling contact analysis can be used to calculate temperature and shear rate during roll fusing. Temperature and strain rate dependent toner viscoelasticity(viscosity and compliance/modulus)is affected by important variables such as entanglement molecular weight and morphology of a binder polymer. Compared to fusion of toner image, fixing of an image takes place continually as the toner temperature drops. Eventually, adhesion and fixing of the toner image to a substrate is tested at ambient temperature where shear and flexural stresses dominate. Unlike fusion, the effect of molecular weight and morphology of a binder toner is different on image fix because of their effect on brittle - ductile transition and toughness (modulus)of a toner.

Introduction

Image Fix is dependent on three processes 1) Coalescence 2) Adhesion to a substrate 3) Solidification.

Coalescence

There are two ways to cause coalescence of a toner image either through contact with toner image by application of pressure alone or pressure and temperature or by non-contact using radiation, or microwave. Majority of the times, toner particles are subjected to temperature with small pressure. Before toner particles can coalesce, each of the toner particles soften or melt on application of heat. In rolling contact fusing, toner temperature is affected by roll thermal conductivity, thermal conductivity of toner, contact area and contact time. In the nip, toner particles deposited on a media sheet normally paper have capillary pressure from moisture present in the toner.

Coalescence involves several steps: The sintering stages, which vary from the loose powder filling to a final, almost porosity-free, compact part. Transport mechanisms involved in solid-state sintering: 1 Evaporation condensation Surface diffusion, 3 Volume diffusion starting from surface, 4 Grain boundary diffusion, 5 Volume diffusion starting from grain boundary, 6 Volume diffusion starting from dislocation.

Models of coalescence

Viscous models

Frenkel (2) delved the first analytical mode describing the rate of coalescence occurring by viscous flow for two identical spherical particles. Coalescence increases with decrease in viscosity, increase in surface tension, decrease in particle radius and increase in time.

The validity of Frenkel's model is limited to Newtonian flow, and is only valid in the early stages of sintering when the particle diameter remain relatively constant. Newtonian sintering models predict a faster coalescence rate than that observed with many polymers indicating that factors other than the surface tension and the viscosity play a role in polymer sintering. In addition to viscosity, elasticity affects toner coalescence and toner fix. Crosslinked polymers to a varying degree of crosslink density are used as binders in toners. Cross linking increases elastic modulus more than viscous modulus.

Elastic models

Johnson et al. extended the Hertz's analysis of **elastic** deformation by including the influence of surface tension and the adhesion force in an elastic formulation for the **neck** growth between **two** spheres.

Viscoelastic models

Mazur and Plazek (5) proposed a viscoelastic sintering model (MP model) treating the elastic and viscous flows as mutually independent contributions. The elastic contribution for the sintering neck growth is defined based on the **JKR** model. Firstly, the **JKR** model was defined in term of the compliance J with the assumptions that both particles are equal sized and that they are made from an elastic fluid.

With time dependent compliance, predictions have been found to be significantly faster than the observed experimental results for acrylic resins. When MP model is extended to include interfacial forces, the results show that rate of coalescence increases with decrease in particle size, increase in compliance, increase in surface tension and increase in time.

Adhesion to a substrate

JKR model is used to analyze adhesion of polymeric liquids to substrate. Material parameters which affects adhesion most is modulus and surface energy of the melted toner - lower is the modulus greater is adhesion to paper.

Solidification and Brittle-Ductile transition and toner fix to paper

Digital images when solidified are subjected to deformation when evaluated for image adhesion to a media such as paper. A typical stress strain test in bulk of a polymer that goes through yield and then breaks is shown below. A low molecular weight polystyrene below its critical molecular weight is likely to be brittle and ductile above that molecular weight.

In the glassy state the polymer's secondary bonds determine the elastic part of the mechanical properties, modulus and yield stress,while the primary bonds in the network potentially induce the necessary delocalization of local strain that gives toughness. Given this mechanism one can conclude that all amorphous polymers with a Tg above room temperature have roughly the

same elastic, Young's modulus of 3 GPa. the process of plastic deformation in amorphous polymers is controlled by molecular motions on a segmental scale. Thus molecular weight and entanglements should not play a dominant role. Only the secondary interactions and the free volume kinetics could be of primary interest. Once the critical stress is surpassed, the stress to further flow should be constant, until the entanglement network starts to orient, manifesting itself in strain hardening. The entanglements control the modulus and it is the molecular weight that controls the strength at breakage. The combination of strain softening, after yield, followed by strain hardening, at larger deformations, proves to be the key issue in understanding mechanical behavior (6).

Chemical structure of a polymer affects its critical molecular weight and therefore its brittle ductile transition. At a high strain rate (lowering time of deformation or using time temperature superposition lowering of temperature at which material is deformed) in deformation, a polymer becomes brittle. In solid particles going through deformation, particle below a certain size behaves in a ductile manner from less defects or voids. Strain localization can only be stabilized if the stress, or the force, which can be transferred by the polymer network in the localized plastic zone is sufficiently high in order to exceed the yield stress of the surrounding material. However, the polymer network can only be loaded up to a limited stress, the tensile strength. Hence, after a certain ageing time, the stress in the local plastically deformed zone required to surpass the recovered yield stress in the, yet, hardly non-deformed regions, exceeds the tensile strength. Since this tensile strength is related to Mn, both the recovering yield stress and the time-scale, at which fracture occurs, are dependent on Mn

That intrinsic strain softening is dominant in the macroscopic response The macroscopic deformation behavior of amorphous polymers is dominated by localization phenomena like necking an crazing. Finite element simulations show that the details of the intrinsic post-yield behavior, strain softening and strain hardening, determine the severity of strain localizations. In order to perform these numerical simulations an accurate constitutive model such as Lenov model is used. Experimentally it is demonstrated that by a small increase in strain softening (by annealing of polycarbonate) or substantial decrease (by mechanical rejuvenation of polystyrene), transitions from ductile to brittle and, respectively, brittle to ductile can be realized. Extensive work on simulations and experimental has resulted in a conclusion that in order to macroscopically delocalize strain, and thus improve toughness, one has to reduce strain softening or enhance strain hardening, either by improving the intrinsic behavior of polymers, or by creating an optimized annealing conditions. It is shown that an annealed polymer which previously failed in a brittle manner became ductile when subjected to heating above glass transition temperature for half an hour and cooling rapidly to room temperature.

Its implication to digital image deformation is quite significant. A toner material may coalesce or fuse at a low temperature from having low Tg or low molecular weight but the molten image on cooling as a solid material will fail easily in brittle manner. As fix is inversely proportional to adhesion of toner image to a surface, a low molecular weight polymer below a certain modulus would show poor adhesion even though its coalescence rate was quite fast. If the viscosity is lower below a certain threshold, minimum fix temperature increases or correspondingly, strength of image on the surface decreases possibly from having lower molecular weight. Crease fix test involves making an image which is subjected to rolling forces and then flexural forces. Using a simple criteria of fracture by Griffith. The critical stress required for crack propagation in a brittle material is dependent on: modulus of elasticity ,specific surface energy and half the length of an internal crack Increase in modulus, increase in surface energy and decrease in crack length(voids, defects) would increase the critical stress for brittle failure of an image.

Toner fusion and Fix

Heat transfer and toner melting in an electro photographic system was analyzed by Mitsuya etal. for a heated roll comprising a fluoride surface layer and an aluminum core. They found that a sharp rise in heat flux to the toner occurs by conduction from aluminum core to the surface layer. Magnitude of heat flux increases with increase in nip time and pressure . Also shear rate peak should be set late to achieve a good fit between temperature and shear rate (7).

Xerox 5090 toner binder styrene butadiene copolymer shows viscosity dependence on molecular weight linearly below entanglement molecular weight and power law dependence above entanglement molecular weight. Entanglement molecular weight is in the neighborhood of 30K and in the neighborhood of 15K for polybutadiene. Elastic modulus and viscous modulus of a binder resin can be measured at 50C above Tg in the neighborhood of 100C to 180C at 20C interval and using shearing frequency from 0.1radian per second to 100 radians per second.

A reference temperature of 120C can be used and WLF time temperature superposition is applied shifting and getting a master curve at 120C with shearing frequency in seven decades in frequency from 0.001 radian per second 10,000 radians per second (8,9).

The elastic and viscous modulus at various frequencies can be subjected to inverse Fourier Transform or numerical approximations to get relaxation modulus as function of time.

Data can be clearly used to show that as the molecular weight is decreased, relaxation modulus rapidly decreases with time. The slope of relaxation modulus with time can be used to get relaxation time. If the relaxation time is lower than the process time (dwell time), fusing is less dependent on elasticity of a toner. On the other hand if relaxation time is greater than the dwell time, elasticity plays a significant role and slows down coalescence time.

Compared to 5090 toner, EK 1, a toner with cross linked terpolymer of styrene methyl methacrylate and hexyl methacrylate binder resin shows a plateau as the shearing frequency above molten temperature is decreased. A cross linked polymer like Ecta print EK1 is predicted to have a slow rate of coalescence.

Polyesters have been increasing used as a binder resin in toners because of possibility of large cohesive energy, toughness and charging ability. Furthermore, polyesters with soft segment side chain have beta transition and low fusing energy. Since crystalline polyester melts faster than an amorphous polyester, toners with crystalline polyesters have been made by Shiai etal. using fumaric acid and 1 4 -butanediol. and found to require lower fusing energy (10). As the crystallinity was increased, cohesiveness of the toner increased while the lower limit of the fusing temperature decreased significantly. This may be result of significant lowering of melt viscosity of toner with increase in crystallinity. Only a small increase in elastic modulus of the solidified toner image with crystallinity is expected. Crystalline polyesters are ductile on deformation instead of being brittle as is the case in amorphous binder resins in toners. Besides crystalline polymers, liquid crystal polymers and nanostructures have unique rheological properties. Liquid crystal polymers have low melt viscosity and high modulus/ strength at room temperature (11). Compared to large size fillers, nanosize fillers are more reinforcing and have higher modulus and strength for the same concentration (12).

In the toner-paper interface both mechanical and chemical forces are present. Of physical properties of the paper, porosity and roughness have the most pronounced influence on the mechanical adhesion. The toner penetrates in part into the paper structure. The penetration increases with an increase in the fusing temperature, which is clearly because of the lower viscosity levels. When fusing energy is increased even further on uncoated papers, the toner penetrates into the paper to the point that the fibers of the paper appear. This results in decrease in the coverage percentage. The surface of coated or pigmented papers is less porous, which prevents the toner from penetrating into the paper.

The role of surface chemistry is more critical to toner adhesion than to optical image quality. Paper surface energy, which affects the wetting, can be influenced with organic compounds added as internal or surface sizing. On uncoated papers the surface size chemical is known to have an effect on the toner adhesion, when the bonding agents present in the toner resin may chemically react with the surface sizing agent used on the paper. On coated papers the chemical composition of the coating layer is known to be a significant factor.

Conclusion

Digital images on surfaces undergo coalescence and solidification. Most toners show viscoelastic behavior where elasticity and compliance slow rate of coalescence. Toners can show non-monotonic behavior with respect to viscosity and toner elasticity at low molecular weights and low brittle strengths. Both coalescence and fracture models needs to be considered to adequately determine dependence on toner modulus, viscosity, tan delta and surface tension(structure, molecular weight) and substrate properties (modulus, roughness and surface tension).

References

(1). C. T. Bellehumeur, Marianne Kontopoulou, J. Vlachopoulos**,** The role of viscoelasticity in polymer sintering, Rheological Acta, Volume 37,N3 1998 1435-1528(1998)

(2).J.Frenkel, Viscous flow of crystalline bodies under the action of surface tension,J Phys., 9, 385 (1945).

(3) R. W. Hopper, Coalescence of two viscous cylinders by capillarity, J. **Am. Ceram.** Soc., 76, 2953 (1993)

(4) K. L. Johnson, K. Kendall, and **A.** D. Roberts, "Surface energy and the contact of
elastic solids, Proc. R. ***Soc.*** Lond. **A,** 324, 301 (1971).

(5) S. Mazur, Coalescence of polymer particles, in polymer powder technology, John Wiley & Sons, (1995)

(6) E. Han, H. Meijer and L. E. Govaert, Mechanical performance of polymer systems: The relation
between structure and properties, Prog. Polym. Sci. 30, 915–938 (2005)

(7)T. Mitsuya and T. Kumasaka, Heat transfer and toner melting in an electrophotographic fuser system, J. Imaging Sci Technol. 36,(1) 88-92(1992)

(8) S. K.Ahuja, Dynamic melt viscoelastic behavior of random copolymers, Rheol. Acta, 19, 299(1980).

(9) S. K.Ahuja, Viscoelastic behavior of styrene n-butyl methacrylate blends, Rheol. Acta, 19, 307(1980).

(10) E. Shirai, K. Aoki and M. Maruta, The effect of crystalline polyester on toner properties, J. Imaging Sci Technol. 40,(1) 398-403(2004).

(11) L. Lorenzo, S. K. Ahuja and H. Cheng, Visco-elastic properties of polystyrene liquid crystal polyester extrusion blends, Third Chemical Congress of North America, Toronto, 1988.

(12) S. K. Ahuja, Structure property dependence of epoxy nano-composites, Annual Meeting of American Physical Society, 2005.

Author Biography

Suresh Ahuja received her BS in physics and chemistry from the Punjab University (1959), his MS in Soil Physics from Indian Research Institute (1961) and his PhD in Polymer Physics from Polytechnic Institute of Brooklyn (1967). After working over 37 years at Xerox with several years as Principal Scientist he retired. He has several patents including three this year. He has published over 40 publications and presentations at international conferences. He is a member of APS, ASME, SOR and IST.