Macromol. Symp. **2001,** *169, 321-328*

Polymeric Film Formation in Spin Coating

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Summary: The results of numerical modeling of polymeric film formation under mass force action are presented. The instability of non-Newtonian liquid front edge at the initial stage of flow over a disk is studied. The quasi-stationary shape of the liquid film (in front edge vicinity) speading over the surface is determined for certain rheology laws. At the modeling of the second stage of coating flow, the special attention was paid to the effects connected with the two-dimensional character of the flow. The impact of rheological properties of a liquid on the free surface shape was studied using codes that calculate the two-dimensional non-stationary flow of non-Newtonian liquid. The factors that determine the final shape of polymeric coating free surface are discussed.

Introduction

The perspective way for hard magnetic discs manufacturing is the spin coating of disc base by ferroliquid lacquer (FL). The coating is formed due to spreading of certain FL amount under the action of centrifugal and Coriolis forces. The front FL edge, as a rule, experiences the finite disturbances during FL movement over the rotating disc. The partial lost of solvent from multi-component FL due to vaporization and other process occurs also. The mentioned factors engender both magnetic and geometric non-uniformity of the coating and are specific for spin coating technology. The FL may be considered as a non-Newtonian liquid. The modeling of both initial and main stages of a multi-component viscous non-Newtonian liquid spreading over rotating disc is considered in the present work.

Various physical processes, which significantly affect final quality of magnetic support, accompany the FL flow over magnetic disc rotating substrate when considered within continuous medium frame. These processes are the solvent vaporization, FL upper layers cooling due to solvent vaporization, the solvent diffusion to FL upper layers, polymer and solvent sedimentation on ferroparticles, new phase germs, FL front edge instability [2-4,10,12-14]. Herein, we discuss the features of mentioned processes. The comparison of referent parameters found at estimation of the processes with the time necessary for FL front reaching rotating disk edge ($t_{flow} \sim \omega^{-1}$) demonstrates

 CCC 1022-1360/00/$ 17.50+.50/0

that the flow process may be divided into two stages. During first stage (at time about ~ t_{flow}), when FL moves to rotating disk edge and the film front edge disturbance is possible, the significant change of FL physics-chemical properties does not occur, so the front edge stability problem may be considered under time independent properties of film. Obviously, the mentioned physics-chemical processes should be accounted at modeling of second, more long, stage of magnetic coating formation, when the film thickness decreases to several microns due to the loss of FL upper layers from rotating disc.

Instability of polymeric film front edge

The analysis of film surfaces stability in the case of Newtonian liquids flow is well studied [1]. Nevertheless, most coatings are formed by the non-Newtonian liquids such as polymeric solutions, multi-component polymeric suspensions, different varnishes, etc. So, we discuss below the non-Newtonian liquid flow over simple form surfaces: inclined plane and rotating disc. The movement of incompressible liquid film over inclined surface with velocity *u,* when inertial members are neglected and under condition of all variables depending only on coordinates along surface *x* and across surface *z,* in lubrication approximation is governed by the following equation (for Newtonian liquid *n=1*):

$$\rho g \sin\alpha + \sigma (\partial/\partial x)(\partial^2 h/\partial x^2) + \eta (\partial/\partial z)(\partial u/\partial z)^n = 0 \qquad (1)$$

Where ρ, σ, h, g are density, surface tension coefficient, film thickness, and gravitation constant, α is the plane slip angle. The viscous shear stress tensor for non-Newtonian liquid is chosen in a form [2]:

$$\tau' = 2\eta S^{n-1} D \qquad (2)$$

In (2), S is the duplicated contraction of deformation rate $D = (1/2)(\nabla v + \nabla v^T)$, η and n are the non-Newtonian liquid parameters. Because the work objective is the analysis of shape and stability of film surface, we substitute the result of Eq. (3) integration into continuity equation averaged over film thickness (V is the velocity averaged over z).

$$dh/dt + \nabla hV = 0 \qquad (3)$$

After transformations we find the equation for surface quasi-stationary shape in the dimensionless form [3,4]:

$$(1-b^{2+1/n})(f_0 - 1)(b-1)^{-1} - 1 + (1+ \partial^3 f_0/\partial \xi^3)^{1/n} f_0^{2+1/n} = 0; \; \xi = x/l, \; f_0 = h/H_N, \; b = H_c/H_N \qquad (4)$$

The transition to precursion film occurs past H_c [4,5] (b<<1), equation (4) is written in vicinity of spreading film front in the region of capillary order length ($\sim [\sigma/\rho g]^{1/2}$) in coordinate system connected with moving front; H_N is film thickness at front, l is referent length that is defined when Eq. (6) is non-dimensionalized (see below). In (4) the time is a parameter since b = b(t). Equation (4) is, as the matter of fact, an ordinary differential equation with following boundary conditions

$f_0 \Rightarrow 1$ at $\xi \Rightarrow -\infty$;

$f_0 \Rightarrow b$ at $\xi \Rightarrow \infty$ (5)

The reference shape of f_0 is presented in Fig. 1. The front edge shape is specified by specific "crest", which intensity depends on the precursion film thickness and physic-chemical properties of spreading liquid [3,4] (compare with [5]).

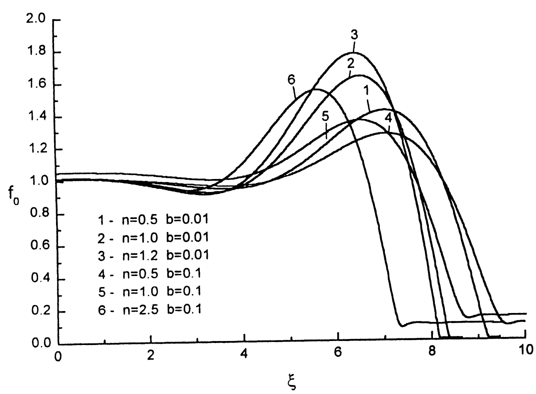

Fig. 1: The dependence of quasi-stationary front agde shape on dimenionless coordinate ξ.

We investigate the linear stability of solution in spreading film front vicinity. For this purpose, we introduce variables $\xi=(x-x_f)/l$, $s=y/l$, $f=h/H_N$ in Eq. (3) rewritten in corresponding coordinate system. We consider f as $f_0(\xi)+f_1(\xi,s,t)$, may $f_1/f_0 << 1$. We pose $\tau= l/u_0$, $u_0 = \rho g H_N^2 \sin\alpha(n/(2n+1))/\mu$, $\beta=(\rho g \sin\alpha/\eta)^{1/n} H_N^{1+1/n} u_0^{-1}$, $v=uu_0^{-1}\beta^{-1}$, μ-const; we note the parameter $\beta=1$ for Newtonian liquid. After substituting in V the sum $f_0 + f_1$ and linearization, we find the equation for investigating of linear stability of spreading non-Newtonian liquid forward edge. The present equation obtained using (4) for f_0 (at $b\Rightarrow 0$) and suitable for qualitative analysis of spreading liquid forward edge should be solved with the following disturbance on the "boundary": $\xi_b = A(s)B(t)$, $A(s)=\cos(qs)$ (where $-\pi/2<qs<\pi/2$ forms so called "finger" that grows at $dB/dt>0$, $B(t)= B_0 \exp(\theta\tau)$); in this case f_l may be presented in a form:

$f_l(\xi,s,\tau)= A(s)G(\xi)e^{\theta\tau}$.

Boundary conditions for f_l follow: when $\xi \Rightarrow -\infty$, ξ_b $f_l \Rightarrow 0$, $f_{l\xi} \Rightarrow 0$. For analysis of linear stability, the spectrum of linear differential equation of the fourth order is studied:

$$\theta G = -(\partial/\partial\xi)\{[(\partial/\partial\xi)(G_{\xi\xi} - q^2 G)]f_0^{\,n+2}/n + (1+1/n)G + (1-\beta)G\}\beta$$
$$- (f_0^{\,2+1/n}/n)(q^4 G - q^2 G_{\xi\xi})\beta \qquad (6)$$

At investigation of present equation, the spectrum f_0 function is assumed to be the simple approximation that allow to reduce the investigation of differential equation of the fourth order to investigation of corresponding algebraic equation and sewing together conditions in point of f_0 piecewise constant function abrupt change. The dependency under the question $\theta(q)$ is found under this approximation that is provided in Fig. 2 and, naturally, is determined by physical parameters (n,b) altogether. In typical case, the curve has a maximum corresponding to most growing disturbances that determine the film forward edge shape at initial stage of disturbance growth. The similar analysis for the case of non-Newtonian liquid flow on the rotating disc, when *rz* component of viscous shear stress tensor in cylindrical coordinates is written in a form [6], also demonstrates the instability of film front edge practically under the same parameters.

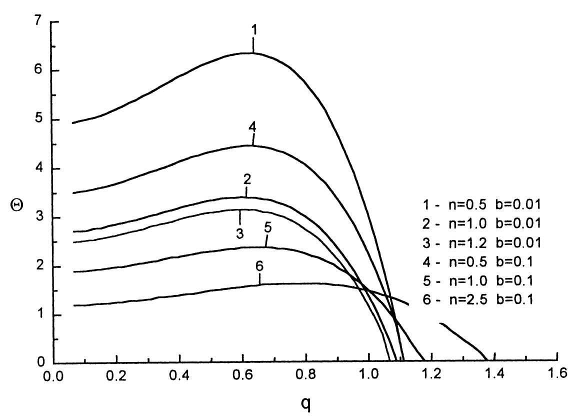

Fig. 2: The dependency of maximum eigenvalue on wave vector (β=1).

It is necessary to account the nature of spreading liquid at experimental check of results of the performed theoretical analysis. Non-Newtonian liquid may, in general, correspond Reiner-Rivlin liquid, demonstrate viscous-elastic properties, etc. The flow of such liquid films is determined by main equations being different from Eqs. (4), (6).

Polymeric coating formation on the rotating disc

We consider second stage of coating flow. At second stage, that is significantly more long in comparison with first one, the film thickness is decreasing to magnitudes of several microns. Hence, all set of physics-chemical processes at the film flow is considered: solvent vaporization from liquid film surface, cooling of coating upper layers due to solvent vaporization, solvent diffusion to upper layers, etc. The comparison of parameters demonstrated the need to account enumerated physics-chemical processes at numerical modeling of flow second stage during which the film properties abruptly change at time variation. The main attention is paid to investigation of the film thickness uniformity along radius during flow of coating, which is, in general, non-Newtonian liquid. It is demonstrated in [6] that the initial non-uniformity of free surface decrease for Newtonian liquid flow on rotating disc and the flow becomes asymptotically uniform along radius. At flow of non-Newtonian liquid with rheological properties [4] (or liquid of Bingham type), the forming film has no constant thickness along radius.

The spatially two-dimensional non-stationary flow model in cylindrical coordinate system (r, z, φ) and under the symmetry relatively φ was chosen for numerical investigation of non-Newtonian liquid flow over the disc rotating with the frequency ω. The Newtonian liquid flow was considered also for numerical algorithm testing. We write the system of conservation equations governing the FL flow over the disc surface. We suggest FL to be two component liquid (solvent + polymer with ferroparticles) under the laminar flow mode and use the appropriate set of boundary and initial conditions. The deviations of polymeric solutions rheology from Newtonian one at modeling of second stage of coating flow over rotating disk were accounted as follows: at first in generalized Newtonian form (2) (similarly to item 1) and in Bingham form.

Numerical experiments at second stage of modeling were performed in two statements: space evolutional and time evolutional [7]. The flow (ω=50 rps, H_0 =0.1-2 mm, $T_W \sim 300$ K) and liquid (viscosity, diffusion etc) parameters were used that are close to [9].

The spatially evolutional problem corresponds to constant fluid inflow in axis vicinity and outflow at disk edge. The flow-field was calculated by marching along radius. At every new step along radius, the flow parameters were determined by the solution of non-stationary equations using quasitemporal relaxation. The calculation field contained about 100 nodes in cross-section direction and about 250-900 steps in the radial direction. Results of Newtonian and non-Newtonian liquid comparison are presented in Fig. 3. The viscosity was decreased by the order of magnitude at certain radius.

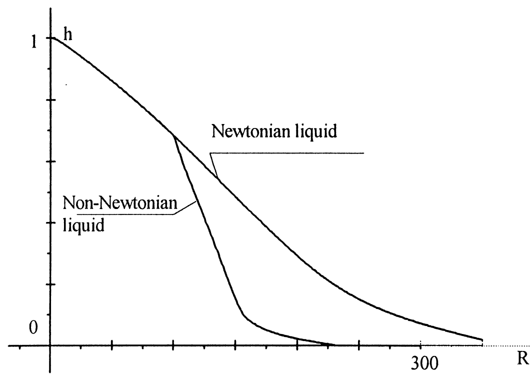

Fig. 3: Thickness variation in R dependence.

Fig. 4: Film thickness at viscosity drop at certain stress magnitude.

Time evolutional problem corresponds to the absence of fluid inflow from outside that correlates the conditions of experiments. The flow-field is determined from the solution of non-stationary equations at every new step. The computational field contains up to 50 nodes in cross-section and about 50-100 nodes in radial one. The code testing was performed using data of [6,8,9,10]. Non-Newtonian properties (effective viscosity dependence on stresses) may cause radial non-uniformity of the film. We may see significant dependence of thickness on radius (Fig.4) at viscosity drop by the order of magnitude at certain stress value. Numerical experiments permit to conclude that dependence of the rheology law on temperature (or solvent concentration) may in certain situations improve free surface uniformity.

Conclusion

The modeling of two qualitatively different stages of polymeric coating flow over the rotating disc is performed. The quasi-stationary shape and stability of forward front of non-Newtonian fluid were studied at first stage that provided forward edge shape determination. At modeling of second stage, the special attention was paid to effects connected with the two-dimensional character of the flow. The impact of rheological properties of liquid on the free surface shape was studied using codes that calculate two-dimensional non-stationary flow of non-Newtonian liquid. The factors determining free surface uniformity: dependencies of rheology low on shear rate, temperature, solvent concentration, and angular velocity ω were studied.

References

1. L.M.Hoking, *J. Fluid. Mech.*, **211**, 373 (1990).
2. O.M.Yachno and V.F. Dubovitsky, *The Fundamentals of Polymers Theory*, Kiev, 1976 . (in Russian).
3. S.M. Baturin and G.A. Pavlov , *Piz'ma v Jurn.Tech. Fiz.*. **22**, N 10, 80 (1996) (in Russian).
4. S.M. Baturin., G.A. Pavlov, and A.A. Shiryaev , In *Strongly Coupled Coulomb Systems*, 429, Plenum PC, NY, 1998.
5. M.A. Spaid and G.M. Homsy, *Phys. Fluids*, **8**, 460 (1996).
6. A. Acrivos, M.J. Shan and E.E. Petersen, *J. Appl. Phys.*, **31**, 963 (1960).
7. O.M. Belotsercovsky, V.Y. Guschin and V. N. Konshin., *ZhVM i MF*, **27**, 594 (1987) (in Russian).
8. C.J. Lawrence, *Phys. Fluids*, **31**, 2786 (1988).

9. T. O'Hara, Y. Matsumoto and H. Ohashi, *Phys. Fluids A.*, **1**, 1949 (1989).

10. A.V. Borkar, J.A. Tsamopoulos, S.A. Gupta and R.K. Gupta,. *Phys. Fluids,* **6**, 3539 (1994).

11. Y. Matsumoto, T. O'Hara, I. Teruya and H. Ohashi, *JSME Int. J., Ser. II*, **32**, 52 (1989).

12. D. Meyerhofer, *J. Appl. Phys.*, **49,** 3993 (1978)

13. H. Inoue., H. Fukke, and M. Katsumoto, *IEEE Transactions of magnetics*, **26**, N 1, 75, 1990.

14. N. Fraysse and J.M.Homsy, Phys. Fluids **6**, 1941 (1994)