Rheology and Process Control Minimize Misting

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Presented at the 12th International Coating Science and Technology Symposium
September 23-25, 2004 • Rochester, New York
Unpublished

Introduction

Misting is the generation of droplets (< 50 microns in diameter) upon splitting a liquid film between two counter-rotating rolls. In high-speed coating the mist droplets generated include respirable aerosols. Health and environmental concerns of respirable particulates containing solvent, dispersed particles, and/or polymeric species limit coater speeds. So does the coating non-uniformity that typically accompanies misting. The substantial costs associated with lower production speeds that avoid these difficulties have made misting a significant industrial issue, especially in low viscosity (0.01-1 Pa-s) silicone oligomers and high viscosity (1-100 Pa-s at 70^{o}C) adhesives and inks.

Early researchers investigating origins of misting proposed that during the coating of polymeric solutions or polymer/colloidal dispersions that cavitation of the liquid as it passes through the forward-roll coating film-split leads to the formation of free-standing filaments; that these filaments subsequently become extended, thin, and breakup as the roll surfaces part, and that breakup leads to large droplets, often called spatter or slinging (1,2,3,4). Though there has been no proof of cavitation it is widely believed to be the cause of filamentation and misting. It has also been proposed that increasing liquid elasticity by raising either polymer concentration or molecular weight aggravates misting. However adding high-molecular weight polymer to otherwise Newtonian liquids has been shown to reduce the mass concentration of mist (5,6,7,8). What has been lacking is a mechanistic understanding of the connections of polymer structure, solution rheology, diverging flow leading to droplet formation, and the amount of mist.

In contrast to rheologically complex solutions, Newtonian liquids have been observed to generate mist by failure of septa (9). A septum is a sheet of liquid that extends downstream from the gap and has a curved edge concave in the downstream direction; its formation has been predicted to form by solving the three-dimensional Navier-Stokes equation system for post-ribbing viscous free-surface flow (10). Recently misting of a Newtonian liquid was interpreted to occur by failure of filaments and by "spraying (11)." Septa were not reported. In this case the mass concentration of mist was neither measured nor correlated to the physics-controlling breakup.

We report experimental observations, measurements, and mechanisms by which the underlying molecular structure, acting through rheology and fluid mechanics, controls droplet count, size, and concentration.

Newtonian Liquids

The physics controlling formation and breakup of a septum and how to manage the process to reduce mist can be inferred from flow visualization and mist measurements. We used a pan-fed two-roll coater to generate mist; Fastcam ultima APX high-speed camera (Photron, San Diego CA.) to observe misting mechanisms; and an Aerosizer™ DSP (TSI, St. Paul MN.) to quantify drop size, count, and concentration of mist for Newtonian liquids and polymer solutions.

The origins of mist are in flow instabilities present at conditions prior to and leading up to its formation. At a critical capillary number the otherwise smooth free surface became ribbed. As capillary number was raised further (roll velocity was raised in our experiments) the ribs became unsteady in the cross-roll direction, continually merging and re-dividing. At still higher capillary number the downstream free surface at each rib extended and formed a septum. Once a septum formed the ends of its forward rim slid along the crest of a rib indicating that shear stress was present along the septum's base – shear stress on the order of viscosity η times roll surface speed V divided by the film (coating) thickness h. In contrast, the curved diverging flow in the septum and its swollen rim, and the curvature of the rim suggest that tensile viscous stress and surface tension kept the septum from being pulled further downstream by viscous drag. But as capillary number was raised yet further the septum became more extended downstream and thinner leaving it more susceptible to failure of the rim. Once the leading edge became separated from its structure a new septum was formed behind it. The slender liquid column (by our definition not a filament) remained curved and thinned – evidently squeezed by capillary pressure and stabilized by axial and normal viscous stresses. As the column extended its thickness varied periodically as if it was suffering from a Rayleigh-like instability until the column broke up into droplets of mist. The competition governing septum and rim behavior to breakup into droplets of mist can be represented by a dimensionless number we call the misting number shown in Figure 1. The correlation supports the view that viscosity and the average roll velocity destabilize the flow in septa toward misting while surface tension, roll velocity ratio, and roll diameter tend to stabilize intact septa.

$$\text{Misting Number} = \frac{\eta \overline{V}}{\sigma} \frac{\overline{V}^2}{(\dot{\varepsilon} D)^2 (V_1/V_2)^{0.7}}$$

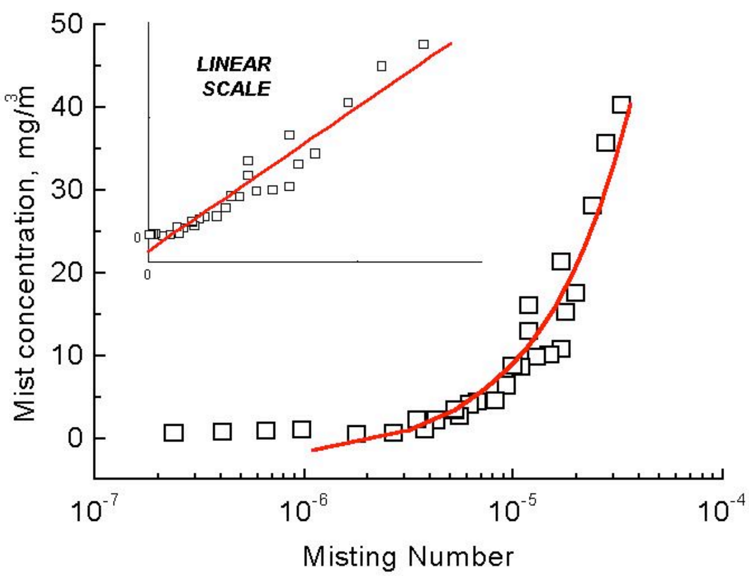

Figure 1: Mass concentration of mist (mg/m^3) versus misting number for Newtonian liquids. The semi-log plot makes clear the data at low misting numbers; mass concentration is actually linearly proportional to the misting number as shown in the embedded plot.

Process Control and Rheology: Boger Liquids

Coating liquids are often weakly elastic polymeric solutions of relatively low viscosity. The misting behavior of Newtonian liquids suggests that shear and extensional rheology are important in controlling that of weakly elastic solutions. Indeed, visualizations made by MacPhee, Glass, and Fernando (2,3,4) indicate that elastic polymer solutions form droplets by breakup of filaments, which suggest that controlling extensional rheology is critical to reducing misting by polymer solutions. Such solutions are difficult to characterize rheologically and their breakup is challenging to visualize.

Using a high-speed camera (up to 3000 frames per second and faster), water-based glycerol/poly(ethylene)oxide solutions, a capillary thinning indexer assembled in the Coating Process Fundamentals Laboratory at the University of Minnesota, and the Aerosizer DSP™ for mist measurement we examined how extensional rheology influences the breakup mechanisms and mass concentration of mist.

Septa was observed to form at lower capillary number than in a Newtonian liquid. As capillary number was raised they evolved as in a Newtonian liquid – up to the moments prior to failure of a septum. Rather than failure of a septum rim and its subsequent breakup to droplets, the septum became unstable, a hole formed, it grew radially outward until a free-standing filament was left downstream of the hole and a new septum formed behind it. It was clear that the hole formation was not due to cavitation, but rather nucleation and growth of a perforation of a thin septum. A filament is defined here to be a cylindrical thread that is straight or nearly so. The integrity of the filaments indicates the presence of normal and tensile elastic stress, which are of course absent from Newtonian liquids. A filament slid atop a ribbing instability indicating the presence of a shear stress at the filament's base, which would act to pull the filament further downstream while the presence of tensile elastic stress apparently resisted extension and downstream translation resulting in the filament sliding back upstream at intermediate roll speeds. As it extended the filament thinned and sooner or later broke - presumably by capillary pressure driving thinning, in one of three ways: formation of beads-on-string followed by detachment of beads as droplets; filament breaks near each roll surface and its retraction into a larger droplets; or a filament break near the mid-plane of the roll surfaces and retraction of each part to its roll surface without a droplet forming. These breakup mechanisms were also seen in experiments with the capillary thinning indexer.

Data from the capillary thinning indexer were used to calculate a (longest) relaxation time of each solution. The number of droplets, droplet size, and mass concentration of droplets were correlated with relaxation times. The rheology and thus the misting behavior of the polymer solutions were controlled by polymer molecular weight and concentration. At the left of Figure 2, at a relaxation time of zero, is the mass concentration of mist for the Newtonian liquid, the standard by which the reduction of misting as relaxation time changes can be judged. There is a range of relaxation times in which misting is less than that by a Newtonian liquid of equal shear viscosity. This range becomes smaller as the average roll velocity is raised. This indicates that there is a limit on adjusting polymer solution properties, by original formulation or by additives.

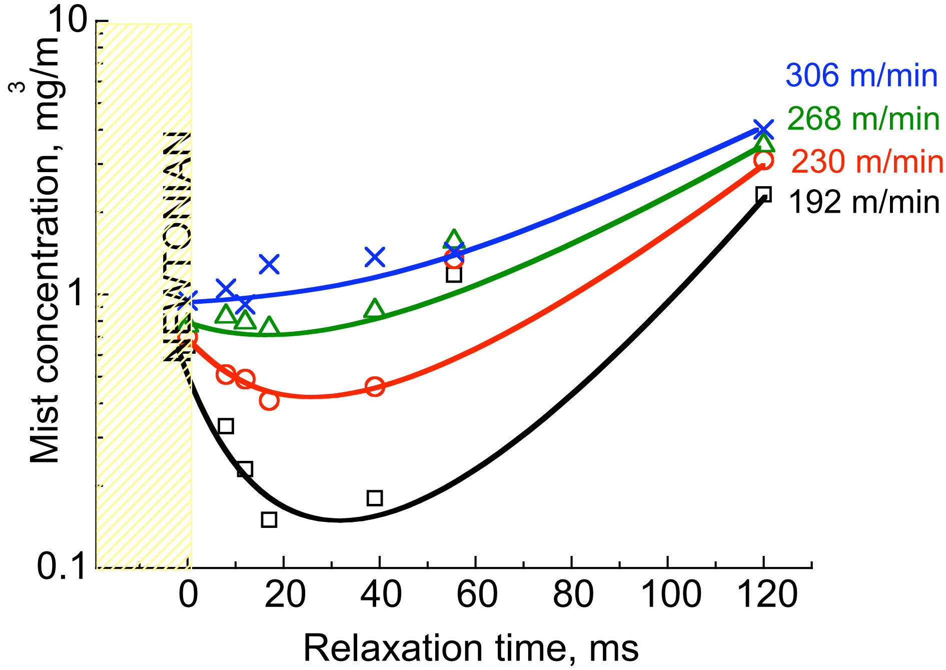

Figure 2: Misting window for water-based glycerol/PEO solutions. The misting window shrinks as the roll velocity rises.

In summary, as capillary number was raised with Newtonian liquids a smooth liquid film evolved into one with ribs. As capillary number was raised further a rib became extended downstream of the film-split and septa formed. As capillary number was raised yet further, the septum became more extended downstream and thinner; and its rim, appear to suffer a Rayleigh-like instability, beaded up into drops that detached. The behavior of the remnant of septum left behind was not clear: it may have re-grown into a full septum, or retracted to be replaced by another growling nearby. What seems particularly significant is that the rim remained curved like a bow as it beaded into drops. The mass concentration of droplets was shown to rises linearly with a dimensionless misting number.

Misting of polymer solutions whose extensional behavior can be detected as a relaxation time in a capillary-thinning rheological indexer can be reduced by adjusting the concentration and structure of polymeric components to obtain a relaxation time in a range of 100 milliseconds. However, the limited data that lead to this inference indicate that the reduction lessens as speed rises in the forward roll test apparatus that was used, and at speeds above about 250 m/min the amount of misting is higher at all relaxation times. It may be that misting at high web speeds can be avoided only by employing other coating techniques.

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