

Degradation of Polymers During Aerosol Formation from Antimisting Polymer Solutions

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Synopsis

Degradation of polyisobutylenes as a consequence of spraying jet-fuel solutions of these polymers was studied as a function of polymer molecular weight and concentration and the spray conditions. Assessment of the degradation was made by measuring the maximum ductless siphon height h^* for sprayed samples and comparing this with prespray values. Two polymers, L-160 from Exxon and B-288 from BASF ($M_w = 4.1 \times 10^6$ and 11.9×10^6), were studied to concentrations of 3000 and 2000 ppm, respectively. Degradation was found to be extremely sensitive to the air speed used in wind-shear spraying, above a critical value of approximately 30–40 m/s. At the highest air speed employed, 135 m/s, degradation was so severe that h^* values were reduced nearly to Newtonian (solvent) values, for all concentrations of both polymer additives. The implications of these results are important for designing effective antimisting fluids.

INTRODUCTION

Addition of trace amounts of polymers having very high molecular weight M to solvents is known to create solutions with unusual rheological properties. Although these fluids are quite ordinary in laminar shear flow, with only a slight enhancement of shear viscosity η due to the polymer presence, their behavior in nonlaminar and nonshear flows can be anomalous and unpredictable. One example of this is the well-known "Toms effect," a reduction of frictional drag in turbulent pipe flow.¹ Another is the "antimisting (AM) effect," an alteration of aerosol particle size (in the direction of suppressing small particles and producing large ones, even filaments) when the solutions are sprayed.^{2–4} The latter phenomenon has received special attention recently because of efforts to develop additives for jet fuel that would render the fuel less likely to ignite when released accidentally from aircraft fuel tanks in a survivable crash landing.

In a previous report, we proposed² that the controlling rheological property leading to fine particle mist suppression was the *elongational* viscosity $\bar{\eta}$. Even in dilute solutions, in which η exceeds the solvent shear viscosity η_s , only slightly, it is known that $\bar{\eta}$ can vastly exceed the corresponding solvent value $3\eta_s$ at sufficiently high elongational (tensile) strain rates. The dependence of the antimisting effect on M and on solvent character is con-

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sistent with this explanation, as is the fact that aerosol formation itself is a complex hydrodynamic phenomenon involving elongational strains.

However, detailed study of the mist formation process is complicated by uncertainty about the stability of the polymer molecules in these severe and complex flows. High- M polymers degrade substantially in shear flows of high intensity, and they are expected to be even more susceptible to breakup in elongational flows because these "strong" flows tend to unravel the polymer coil. Therefore, the experimental investigation described here was launched to determine the extent of polymer degradation in the type of mist creation situation employed earlier² to test the effectiveness of AM agents. The present exploratory work examines the roles of liquid flow rate, air velocity, and polymer M and concentration c on the degradation of polyisobutylenes (PIB) in jet fuel during spraying by wind-shear action.

EXPERIMENTS

Materials

The two PIB samples used in this study were L-160 (from Exxon Chemical Co.) and B-288 (from BASF), with viscosity-average molecular weights $M_v = 4.1 \times 10^6$ and 11.9×10^6 , respectively. The commercial product L-160 was part of our earlier study² and was found to be a moderately good antimisting agent, and B-288 is a recently developed material provided for research purposes only and probably represents the highest- M PIB available today. Molecular-weight distributions were earlier measured for many PIB grades,^{2,5} but such information was not obtained here for B-288.

Jet-A aircraft fuel was the solvent for all PIB solutions. A commercial product (from Shell Oil Co.), with a density of 0.81 g/mL, was used as in our previous studies. Stock solutions of both polymers were prepared and then diluted in one step to the desired concentration; stock concentrations were 3000 ppm for L-160 and 2000 ppm for B-288. To avoid degradation during the stock preparation, no mechanical agitation was used. Tiny pieces of the bulk polymer were immersed in the requisite amount of solvent, the stoppered container then being suspended in a 45°C water bath for several days to achieve sample dissolution without any stirring or imposed fluid motion of any kind.

Creation and Collection of Sprays

The spray creation apparatus used in the earlier AM investigation² was employed here. The liquid fuel was metered from a syringe pump, through a transfer line, and emerged vertically from a circular tube of 1 mm inner diameter (ID). Air was blown horizontally across the surface of the fuel from a 2 mm ID tube to produce mist particles by a wind-shear effect. Fuel rates Q ranged up to 77 mL/min and air speeds V up to 135 m/s. The spray was formed in a sheet metal chamber that exhausted into a fume hood during normal operation. Spray samples were collected by placing an inclined sur-

face (at 10° from horizontal) into the spray trajectory and allowing the impacted liquid to drip into a dish.

Characterization of Degradation

A ductless siphon device, also used in our previous work,² was employed as a measure of elongational viscosity. Because of strong M dependence in $\bar{\eta}(M)$, the siphon functioned as a sensitive detector of polymer degradation; no M measurements were made directly. Since the highest rise height h^* of the fluid column in a ductless siphon before breaking is very M sensitive,^{2,5} the differences in h^* between prespray and postspray (collected) samples were taken as the measure of degradation. Values of h^* can be replicated within about 5% with this device, so that the larger changes found (e.g., from 30 cm to 5 cm) represent very significant changes in the solutions.

Experimental Program

Three types of effects were examined in these experiments. First, the degradation (if any) due merely to pumping the polymer solution through the syringe and transfer lines to the spray creation chamber had to be established as a reference from which to assess subsequent degradation during spraying. If it existed, then its dependence on flow rate was needed for the various concentrations being employed. Second, the effect of air velocity was examined for each concentration, for a standard liquid rate $Q = 46$ mL/min. Third, the effect of liquid rate was found for each concentration, with a standard air speed $V = 100$ m/s.

RESULTS AND DISCUSSION

Transfer-Line Degradation

The baseline behavior of $h^*(c)$ for solutions of both polymers in their unpumped condition is shown in Fig. 1 by the solid lines.⁺ Solutions of L-160 displayed no reduction of h^* as the result of being pumped through the transfer lines, which meant that any degradation seen with sprayed samples had to arise from the mist creation event itself. The situation was more complicated with B-288 solutions, however, as seen in Fig. 2. When $Q > 14$ mL/min, degradation occurred in the lines. Liquid collected from this process was tested for its $h^*(c)$; two examples are shown as dashed lines in Fig. 1b, evidencing depression relative to the baseline curve for B-288 solutions. Under the most severe condition ($Q = 77$ mL/min), this depression of $h^*(c)$ was about 15% at $c = 1000$ ppm. Far greater h^* reductions were found after aerosol formation (see below), so the pumping degradation was only a minor factor even for B-288 solutions.

⁺ Values of h^* for both curves are somewhat lower than determined in a preliminary study.⁶ Examination of numerous possible explanations suggested that the major influence was the change of the siphon (inlet) tip; such sensitivity has apparently not been recognized before and shows the importance of reproducing the siphon geometry precisely.

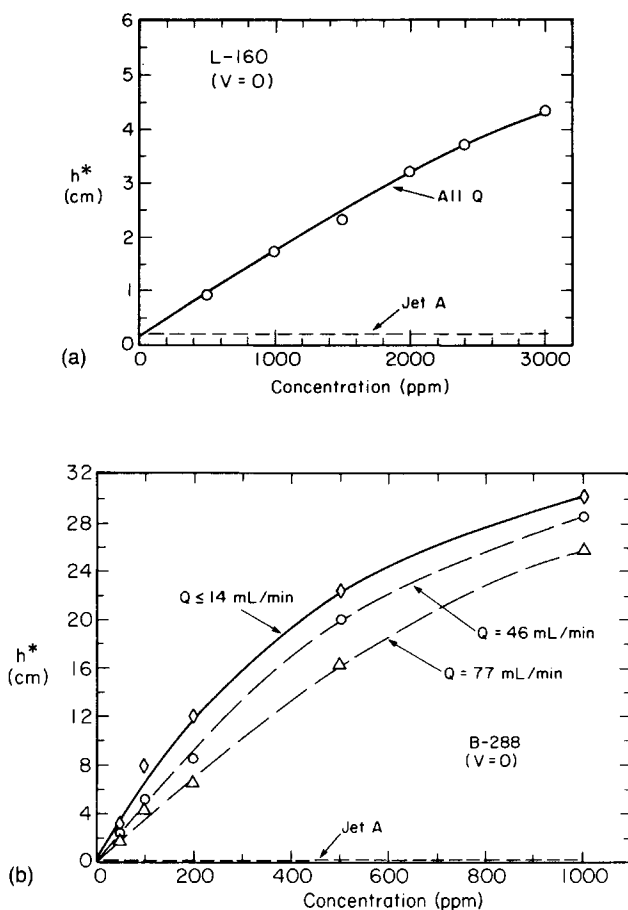


Fig. 1. Dependence of ductless siphon limiting height h^* on polymer concentration. (a) L-160, for unpumped solutions and also those delivered at all flow rates. (b) B-288. Solid line represents behavior of solutions prior to being pumped through the liquid delivery system, and the dashed lines indicate behavior following pumping at the given flow rate Q .

Effect of Air Speed

The degradation curves $h^*(V)$ for each concentration (at fixed Q) are given for L-160 solutions in Fig. 3 and for B-288 solutions in Fig. 4. In each case there is a low- V plateau where no degradation occurs in the spray process, followed by a rather abrupt drop as degradation commences. The drop seems to occur at the same V for all concentrations of a given polymer: 40 m/s for L-160 solutions and 30 m/s for B-288 solutions. Qualitatively, the lower- V threshold for the higher- M solute is expected, since high- M polymers are known to be more susceptible to degradation in general. That the threshold is independent of concentration suggests that the droplet production process undergoes a change associated more closely with airstream hydrodynamics than with the liquid resistance to it.

At values of V exceeding the threshold, degradation was severe for both polymers. For the more dilute solutions ($c \leq 1000$ ppm for L-160; $c \leq 200$

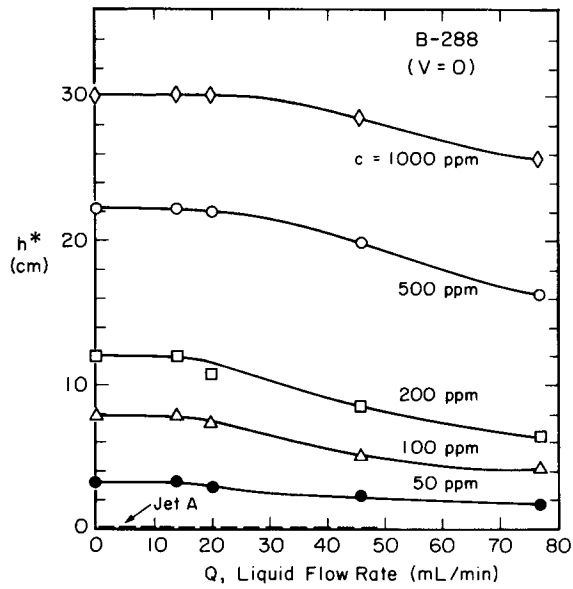


Fig. 2. Degradation of B-288 solutions caused by their being pumped through the transfer lines but not sprayed ($V = 0$).

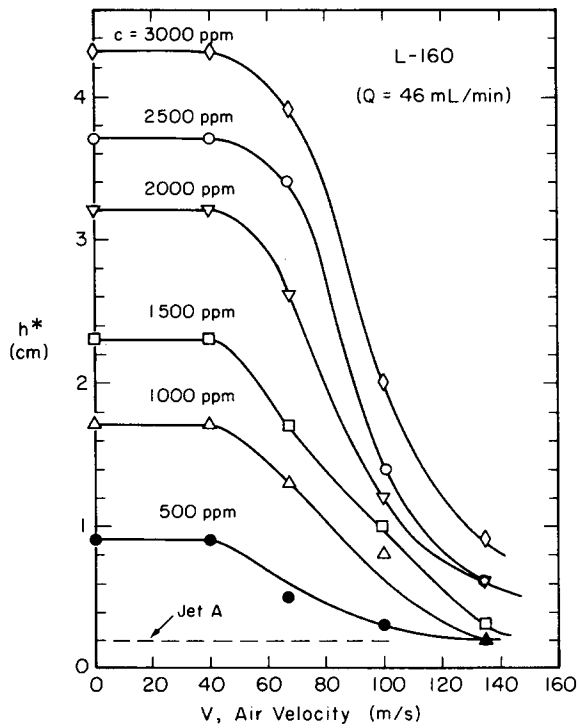


Fig. 3. Degradation of L-160 solutions caused by their being sprayed with an airstream at average velocity V , for liquid flow rate $Q = 46$ mL/min.

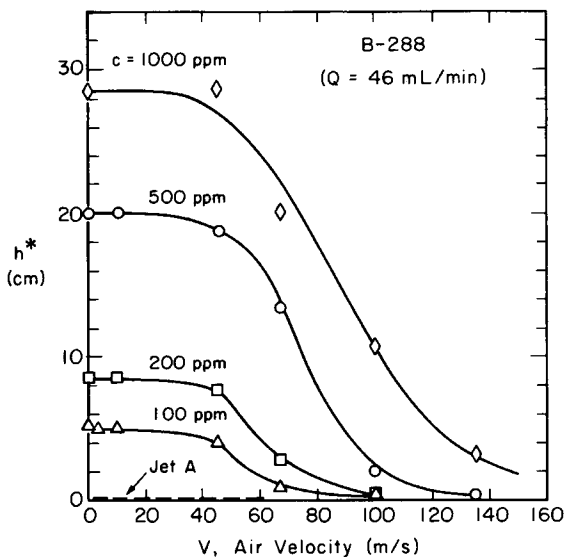


Fig. 4. Degradation of B-288 solutions caused by their being sprayed with an airstream at average velocity V , for liquid flow rate $Q = 46$ mL/min. Because B-288 solutions undergo some transfer line degradation (see Fig. 2), all data, including the $V = 0$ intercepts, represent the behavior of partially degraded polymer.

ppm for B-288), "complete" degradation was achieved at or before $V = 135$ m/s; that is, values of h^* became identical to those registered by any purely viscous Newtonian fluid (about 0.2 cm).² Even the most concentrated solutions were degraded in large measure, on the order of 80–90%, at this highest speed. However, the residual capability possessed by such fluids for effecting further antimisting behavior is still significant. It should also be noted that the AM function was accomplished despite the polymer degradation.

The transfer line degradation of B-288 (see Fig. 1b) that prevailed for tests shown in Fig. 4 (with $Q = 46$ mL/min) seems to have had no qualitative effect and very little quantitative effect on the wind-induced degradation process. At low V , the mildly predegraded B-288 solutions gave a $h^*(V)$ plateau just as did the L-160 solutions that suffered no measurable transfer line degradation (Fig. 1a). However, the level of that plateau was slightly lower because of that predegradation, and the point of the $h^*(V)$ dropoff may have occurred at slightly higher V than if predegradation had not been sustained.

Effect of Fuel Rate

Although no degradation occurred in L-160 solutions during flow in the transfer lines at any liquid flow rate, this did not mean that changes in flow would not influence degradation during the spray process. This influence is displayed in Fig. 5, for the case $V = 100$ m/s, which represents conditions in which major degradation was occurring (see Fig. 3). All curves in Fig. 5

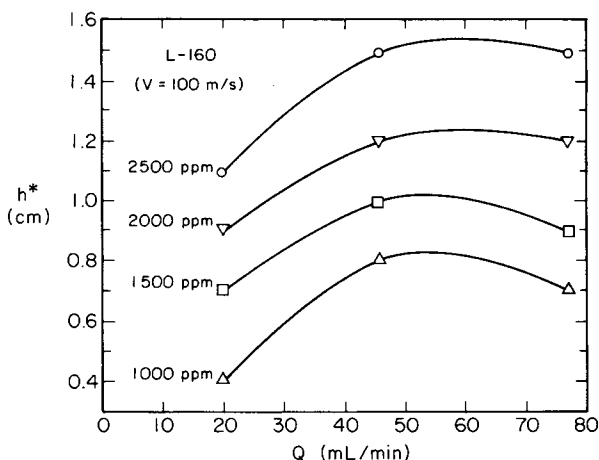


Fig. 5. Variation of degradation with liquid flow rate for L-160 solutions, for an air speed $V = 100$ m/s. Because L-160 solutions suffer no degradation in the transfer lines, all of the Q dependence seen here is due to its role in the spray process.

are drawn to show a maximum in h^* near $Q = 50$ – 60 mL/min, guided by data from the two lowest concentrations, but not enough data points are available to be certain of this. However, it seems clear that $h^*(Q)$ does decrease as Q decreases at lower Q values; thus, more polymer degradation occurs although liquid flow rate is diminished.

The explanation for the drop in h^* at both high and low Q is not clear. At low Q one can speculate that a smaller volume of liquid (per unit time) is more completely atomized than a larger volume, when deformed by an airstream of a given kinetic energy; the greater atomization would imply greater droplet strain rates and consequent polymer degradation. However, this argument cannot explain the existence of a maximum in $h^*(Q)$ —as drawn in Fig. 5—or even a plateau at high Q . Such behavior might result from changes in the nature of the spray action at these higher flows, with the liquid jetting farther into the airstream before being dispersed; at low Q , the wind shear strips the spray directly from the liquid surface emerging from the feed tube.

CONCLUSION

The antimisting phenomenon, the ductless siphon behavior, and the material property $\bar{\eta}$ all display great sensitivity to M values of AM additives. Thus, the mechanical degradation of only the highest- M species in an M -distribution induces major changes in all three, even though many other fluid properties (e.g., η) would be insensitive to alterations in such a small weight fraction of the solute material. It is therefore important to understand the sensitivity to degradation of each polymer being viewed as a candidate as an AM additive.

An approach suggested earlier² for selection of an optimum additive and concentration was to maximize M because then the required concentration

(and corresponding costs) could be low and η would be least affected. The present study suggests that we may also need to take into account that higher- M polymers degrade more easily (e.g., even under routine handling procedures) and very low concentrations lead to a more complete approach to total degradation (as measured by our standard h^* experiment) than do higher concentrations, for comparable spray conditions. However, it is important to remember that additive degradation is the *result* of the action of the polymer in suppressing mist formation. As shown in measurements of flammability of jet fuel-PIB solution sprays,^{2,5-7} effective anti-ignition takes place even when spray conditions (Q and V) and solution parameters (M and c) are in ranges corresponding to those found here to represent almost complete polymer degradation in *postspray* tests.

To the extent that degradation limits AM agent effectiveness, then the strategy of using the highest- M polymer available could lead to diminishing returns. That is, one could envision a situation in which, beyond a certain high- M , the handling and prespray processes might degrade all the higher- M molecules to the point that their special AM effectiveness was not available. If this occurred, then the required concentration would have to be just as high as for lower- M polymers that are less subject to degradation. At this time, however, no such limit is visible for PIB in jet fuel,^{6,7} so the general strategy of choosing the highest- M sample for best results still prevails.

Finally, the ultimate application of polymers as AM agents will determine whether degradation is viewed as undesirable. For aircraft crash-fire prevention, the AM fuel additive must be degraded deliberately in the engine feed lines in order that proper misting and combustion occur in the engines. Here, a relatively easily degraded polymer, such as PIB, may be most attractive. An alternative case would be agricultural chemical spraying from aircraft, where economical AM effectiveness (i.e., for reduction of spray drift from intended application sites through drop size control) would be the only objective and any degradation would probably be deleterious. In such cases, polymer additives that resist breakup should be sought, especially considering that pumping and transfer systems would likely not be specially designed to minimize handling degradation.

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