



Poly(acrylic acid)–poly(vinyl pyrrolidone)-thickened water/glycol de-icing fluids



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ABSTRACT

In this study we consider the use of poly(vinyl pyrrolidone) (PVP) in conjunction with poly(acrylic acid) (PAA) as a thickener for water/glycol solutions. PAA in water/glycol formulations has wide application in the aviation industry for aircraft de-icing and prevention of ice build-up. Routinely sprayed onto the surface of wings and fuselage of aircraft in winter, they are designed to be retained on surfaces under zero shear and actively removed under high shear corresponding to take-off velocities. PAA deposited in aerodynamically quiet regions can produce gel deposits which have adverse effects on the performance of aircraft control systems. In this study we examine the rheological properties of solutions produced using a combination of PAA with PVP, with the aim of reducing the sensitivity of the solutions to added electrolytes. Various PVP–PAA formulations were examined rheologically and in a wind tunnel, across a range of sub-zero temperatures. The conclusions were that these blends can be used as alternative de-icing fluids. In these fluids, hydrogen bonding between the PVP and the PAA achieves the required level of polymer–polymer interactions to exhibit viscoplastic flow at lower electrolyte content. Gels which are formed are less stable than those formed with PAA alone.

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1. Introduction

Ice is a major challenge to all aircraft, particularly in the winter where operations rely on de-icing fluids to clear aircraft and runways and maintain flight schedules. De-icing operations can be broadly divided into two types: those involved in runway clearance and those involving aircraft de-icing. De-icing is required when the temperature falls below 0 °C but there are also conditions where ice can form above this temperature. After a long flight at high altitude or if re-fuelled with very cold fuel at temperatures between –20 °C and +15 °C in the presence of high humidity, the wings can gain deposits of ice. Ice on flight control surfaces reduces their aerodynamic efficiency, reducing lift and maneuverability during or after take-off. Industrial best practice in relation to de-icing and anti-icing is summarized in the Association of European Airlines and US directives (Blau, 2011; Simonot et al., 2004).

De-icing of runways usually involves using aqueous mixtures of sodium and potassium ethanoate salts. The run-off, however, can have significant effects on the environment. A number of alternative formulations have been proposed based on glucoside, ethoxy and protein structures which, in combination with various inorganic salts, depress the freezing point of water (Sapienza et al., 2009, 2011; Stanley and Smith, 2003). The driving force for the development of these alternative formulations has been the desire to reduce biological oxygen demand

[BOD] of the waste water run-off. These fluids are not normally used for aircraft de-icing.

For aircraft de-icing glycol-based aqueous mixtures are used, the composition of which depends on the application for which they are to be used. Type I fluid is used for simple de-icing and is usually based on ethylene glycol or 1,2-propylene glycol, water, corrosion inhibitors, surfactants and pH regulators. Spraying Type I de-icing fluid onto an aircraft surface at around 65–80 °C effectively removes ice (Paredes et al., 2010; Ritter, 2001). However, the period of time for which ice formation is prevented (hold-over time) is relatively short and is approximately 3 min in freezing rain and 20 min in frost-forming conditions. If a longer hold-over time is required, a two-step de-icing process is often used, which involves the initial use of a Type I fluid followed by application of Type II, III or IV fluids.

The hold-over time achievable designates the fluid type. Type I fluids are recommended for operation from the freezing point of the fluid of +10 °C and Type II, III and IV fluids +7 °C. Changes in the ratio of the glycol-to-water mix allow the operational temperature to be progressively lowered. The de-icing fluids will usually be applied hot and precautions have to be taken to avoid water loss.

The principle difference between Type I and the other fluids is the presence of a thickening agent in the latter (Coffey et al., 1995; Jenkins et al., 1995, 1997). With appropriate thickening agents, hold-over times of 30 min for a Type II fluid in freezing rain and 240 min in frost-forming conditions are prescribed by the EAD (Blau, 2011; Simonot et al., 2004). While ethylene glycol has, in principle, the right physical characteristics for use in de-icing fluids, it is, however,

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potentially harmful to humans and animals. Propylene glycol has a lower toxicity and is usually used as a base for most formulations. Aqueous mixtures of propylene glycol containing 40% w/w glycol have a melting point of $-5\text{ }^{\circ}\text{C}$; at 50% this is lowered to $-25\text{ }^{\circ}\text{C}$ and at 60% it is $-60\text{ }^{\circ}\text{C}$. However, at the lowest temperatures its viscosity is too high for use. Below $-32\text{ }^{\circ}\text{C}$ ethylene glycol is still usually used. The use of 1,3-propylene glycol as a more environmentally acceptable fluid has, however, been proposed for use in de-icing fluids (Ross, 2011).

1.1. Principle of aircraft de-icing

De-icing fluids have multiple functions:

- 1) The hot applied fluid is used to disperse ice which has been deposited on the fuselage or wings of the aircraft.
- 2) The de-icing fluid should suppress ice build-up while the aircraft waits at the gate and travels to the holding position. In a small airport this period may be a matter of minutes whereas in large airports a significant period of time may elapse between the points at which de-icing takes place and the aircraft starts to take-off.
- 3) The de-icing fluid should form a stable film which, when the aircraft starts to take-off, aids the efficient clearing of the wings and fuselage of ice before the aircraft reaches rotation and avoids reduction of the aerodynamic efficiency at lift off.

Choice of fluid type depends on the hold-over time, which is the lapse time between de-icing and take-off, and can depend on operating conditions. While de-icing will mainly involve the upper areas of the wing and fuselage, de-icing under wing areas and, in particular, flaps may be necessary.

Simple mixtures of glycol and water form the basis of Type I fluids, but are not easily retained on the aircraft surface and hence only provide protection for short periods of time. To achieve longer hold-over times, Types II, III and IV fluids have higher viscosities to develop a stable fluid layer on the surface to be protected. However, during the initial stages of take-off this thin surface layer should be rapidly depleted and ideally be completely removed prior to rotation. To achieve the desired viscoplastic characteristics small amounts of high molecular weight polymers are added to the base glycol mixtures. Hydrophilic polymers – poly(acrylic acid) (PAA), hydrocarboxylic acids, and various acrylic acid copolymers with hydrophobic monomers – are commonly used as polymer additives (Coffey et al., 1995; Jenkins et al., 1995, 1997; Ross, 2011). By adjusting the molecular weight and concentration, these thickened fluids with appropriate glycol mixtures are able to provide the desired hold-over and shear-thinning characteristics for effective use as de-icing fluids and achieve the desired performance when subjected to simulation of the conditions found during take-off. These formulations, however, have the potential of gel formation when water and glycol evaporation occurs; this can become a particular problem to the wings in aerodynamically quiet areas. This problem has been encountered with Type IV fluids where powder-like residues remain in balance bays, under wings, and rear spar stabilizer areas (Cal, 2008; Dow, 2005; Hille, 2007; Kotker, 1999). These residues can absorb moisture, for example when the aircraft descends through a cloud, swell to many times of their original size, and freeze, potentially restricting movement of flight control surfaces and making it become partly uncontrollable. Dendritic (hyperbranched) polymers used in conjunction with silica and clay particles are used to reduce the extent of re-swell on hydration (Seiler and Bernhardt, 2011).

In this study, we evaluate the use of poly(vinyl pyrrolidone) (PVP) as a co-thickener with PAA in an attempt to produce a de-icing fluid with similar characteristics to those obtained with PAA but with lower gel-forming potential and enhanced ease of removal if the gel is formed.

PVP was used after the 1950s as a blood plasma expander for trauma victims and is now used in many pharmaceutical tablet and liquid formulations (Ferguson and Sundar Rajan, 1979; Haaf et al., 1985;

Oechsner and Keipert, 1999). The potential use of PVP in conjunction with various salts as a runway de-icing medium has been proposed (Samuels et al., 2005). In a typical PAA formulation, salt is added to control the viscosity, making the product sensitive to changes in ionic strength as a consequence of dilution with water during application, or in the subsequent evaporation of solvent. Conceptually, partial replacement of PAA by PVP would allow achievement of the viscoplastic characteristics through hydrogen bonding between the PVP and PAA. In PAA, gel formation can be associated with electrostatic interactions with salts, and achieving structure formation through hydrogen bonding rather than electrostatic interactions should reduce the sensitivity to changes in salt concentration and reduce deposits of insoluble gel building up on the control surfaces (Nurkeeva et al., 2004). It is believed that the addition of PVP will effectively block the interaction between PAA and calcium ions and thus reduce the possibility of forming insoluble gel.

Previous studies have shown that PVP/PAA miscible blends can be formed at any molar ratio and are sensitive to low pH (Jin et al., 2005). The hydrogen bond is not affected by small molecular salt, which only affects those carboxylic groups without forming a hydrogen bond on the PAA chain. Reversibility of the complex formed between PVP/PAA has been shown for pH values above 4.5, and the interaction between PAA and PVP at pH 7 is minimal (Pradip et al., 1991). On the other hand, the molar ratio of PVP/PAA complexes has always to be greater than 1.5:1 to form a stable complex (Lau and Mi, 2002). The stability of the complex depends on pH and as it is raised there is a tendency for the mutual interactions to be reduced (Devine and Higginbotham, 2003; Henke et al., 2011; Kaczmarek et al., 2001; Lau and Mi, 2002). To avoid the creation of insoluble deposits, the ratio of the two polymers is held below the critical value for gel formation, hence allowing the benefits of dynamic interaction enhancing the rheology without promoting gel formation.

In this paper, we report a study of the rheological behavior of a PAA/glycol/water mixture similar to that used in conventional Type II, III and VI de-icing fluids and measurements on two high molecular weight PVP species which potentially can exhibit similar rheological characteristics to those of the standard fluid. To assess the performance of these mixtures, wind tunnel measurements are reported which determine the rate at which a thin film of the mixture is removed from the wing as take-off is simulated according to AS 5900, which is the standard test method for aerodynamic acceptance of SAE AMS 1424 and SAE AMS 1428 aircraft de-icing/anti-icing fluids, for which all de-icing fluids are required to pass and include High Humidity Endurance Testing, HHET. In addition, the hold-over times are determined using the WSET test (Laforte et al., 1990, 1992). This test involves the observation of ice build-up and growth on a metal surface subjected to a moisture spray at low temperature and is used to determine the hold-over time for the fluids.

2. Materials and methods

2.1. Materials preparation

The PAA was supplied by Lubrizol (Brussels, Belgium) and has a molecular weight of 3 MDa (Chu et al., 1992). A solution of $1.22 \pm 0.001\text{ g/dL}$ was prepared by dispersing the solid powder in de-mineralized water using a Silverson L4R laboratory mixer operating at approximately 4800 rpm for 5 min, followed by 3600 rpm for 55 min. Two PVP polymers used in this study were of nominal molecular weights of 360,000 Da and 700,000 Da, supplied by Aldrich Chemical Company Limited (Gillingham, UK) and BDH (Poole, UK), respectively. Each was prepared by dispersion in de-mineralized water also at a concentration of $1.22 \pm 0.001\text{ g/dL}$ and stirred until fully dissolved using a magnetic stirrer. A water/1,2-propylene glycol mixture was prepared at a 50:50 wt/wt ratio. The PAA gel intermediate was first added to the water/glycol mixture and fully mixed; the PVP solution was then added and fully mixed. The solutions were prepared to a total polymer

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