

Advanced Technical Bulletin

Modification of Polyolefins with ELASTAMINE[®] Polyetheramines

INTRODUCTION

Polyolefins find use in many applications because of their excellent balance of properties and price. One important characteristic of these polymers is their hydrophobicity, which can be an advantage in many applications, but a disadvantage in others. The low surface energy results in poor adhesion by coatings of all kinds – poor paintability, printability, and dyeability can cause problems in many applications. Low hydrophilicity can result in static problems as well.

Approaches to increasing surface energy and polarity have included plasma and corona treatments, and chlorinated polyolefin adhesion promoters. These can be useful, but improvement of the inherent hydrophilicity of the polyolefin could eliminate the extra processing steps.

One chemical route to improvement of surface energy is grafting of a hydrophilic polymer onto the polyolefin. Use of an anhydride group as a linking point is a convenient approach – the availability of maleated polyolefins, and the reactivity of the anhydride group with amines, makes this a useful tactic, as long as the polyolefins and amines have suitable properties. Huntsman's ELASTAMINE[®] family of polyetheramines includes hydrophilic monoamines that are well-suited to this purpose.

FEATURES

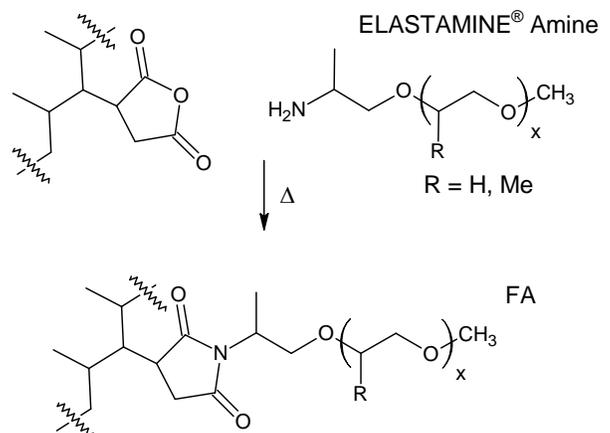
- Increased surface energy
- Increased polarity
- Increased hydrophilicity

BENEFITS

- Improved paintability
- Improved dyeability
- Improved printability
- Improved antistatic properties
- Improved interpolymer adhesion

CHEMISTRY

The utility of this concept has been proven with maleated polypropylene and ELASTAMINE[®] polyethermonoamines. The reaction and product (amine-maleated polypropylene adduct, AMAPPA) are shown below:



EXAMPLES OF COMMERCIAL APPLICATION

Examples of application of this technology fall into two general categories: 1) modification of the polyolefin to make the surface inherently more polar (paintable, printable, etc.), and 2) preparation of dispersions that can serve as primers for polyolefin surfaces to improve adhesion to coatings. In the patent literature examples of each approach can be found.

Polyolefin modification

There are many patents and patent applications around the world describing variations on this chemistry. Three will be summarized here.

The original use, developed at Huntsman, was in modification of TPO to make it more paintable. One of the original illustrations is in U.S. Patent 5,721,315. In this patent various polyetheramines were reacted with maleated polypropylene, and the best results were obtained with a hydrophilic polyethermonoamine. The amine/maleated polypropylene adduct (AMAPPA) was compounded with polypropylene, and paintability was evaluated by crosshatch adhesion.

Variations on this concept are explored elsewhere. Borealis was awarded US Patent 6,716,926, in which a different approach is used. In the Huntsman patent the AMAPPA is prepared separately, and compounded with a TPO. In the Borealis patent the polyethermonoamine is added to an extruder containing a lower molecular weight maleated polyolefin and a higher molecular weight polyolefin; reaction of the amine with the anhydride then occurs in the extruder. In each case, though, improvements in paint adhesion are demonstrated. The amine/maleated polyolefin adduct formed *in situ* is said to migrate to the surface, where it can interact with coatings.

The adduct approach is used in Delphi's US Patent Application 2007/0276094. Here, however, the polymer blend consists of polypropylene, polyolefin elastomers, and varying levels of adduct. Adhesion to polyurethane foam is shown to depend on and increase with adduct content.

Polyolefin dispersions

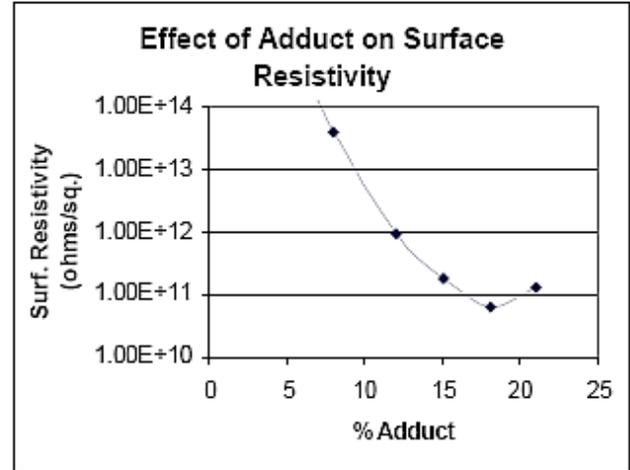
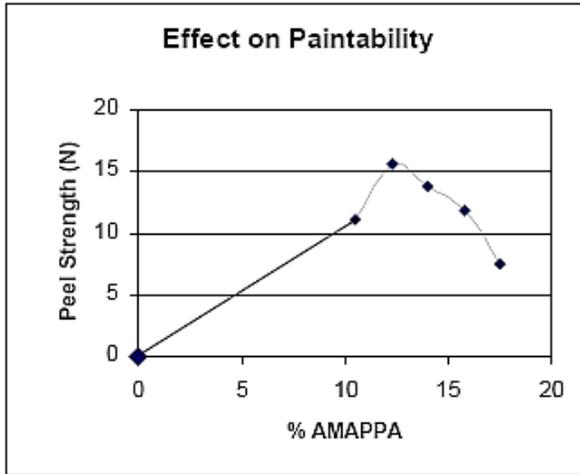
In some more recent uses of this chemistry the polyolefins are not themselves modified, but rather are treated with dispersions of the amine/maleated polyolefin adduct. Two examples will be given here.

In a 2004 patent issued to Crompton (6,774,181) a polyolefin/polyurethane hybrid dispersion is prepared after hydrophilic modification of the polyolefin. A blend of high and low molecular weight polypropylenes is reacted with an MPEG-based polyethermonoamine, and this modified polyolefin is dispersed into water to form a stable aqueous emulsion. A polyurethane dispersion is then prepared in the presence of this polyolefin dispersion to give the hybrid dispersion. Although specific examples of its use are not given, potential uses mentioned include use as a low VOC primer to improve polyolefin adhesion to coatings, and as a sizing for glass, to improve adhesion to polyolefin.

More recently, in US Patent 8,158,727, Mitsubishi outlines preparation and use of a polyolefin dispersion as a primer or as a component of an ink or adhesive. Laminates can be obtained from the dispersions and used as coatings. The hydrophilic MPEG-based polyethermonoamine is heated with a maleated polyolefin prepared *in situ* to generate the modified polyolefin. This is then emulsified to give a white dispersion.

These examples illustrate how a drawback of polyolefins, low surface energy, can be overcome through use of the ELASTAMINE amines. With these amines polyolefins can be made inherently more paintable (printable, dyeable, etc.), or surface treatments can be formulated to achieve the same purpose.

The effects of AMAPPA on paintability and resistivity in TPO are shown in the plots below.



Effect of adduct content on polypropylene dyeability – top row contains 14% AMAPPA

ELASTAMINE[®] RE1-2007 and ELASTAMINE[®] RE1-2005 are hydrophilic polyethermonoamines of approximately 2000 molecular weight.

Product literature is available at www.huntsman.com.

Note: Huntsman does not currently produce AMAPPA – this information is intended as an illustration of the concept.

References: Proceedings of the Additives 2001 Conference (Executive Conference Management); US Patents 6,420,482, 6,154,574, 6,127,480, 6,093,496 (and others) to Huntsman Corp.

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