ATSP Innovations Estherm© Oligomer for Enhancing Properties of Certain Thermoplastics

By

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Abstract

ATSP Innovation's Estherm C-series oligomers are a high temperature and chemical resistant thermoset polyesters specially processed to be used as modifiers and hardeners for thermoset and thermoplastic resins. Applications of C-series oligomers imparted to thermoplastic resins such as polyamides, polyesters, and polyurethanes including reduction in viscosity, improved fiber wet-out, and improvements to mechanical and properties. C-series oligomers can also serve as a hardener phase for thermoset epoxy and polyester thermosets.

History

Under the guidance of Dr. James Economy, Chairman of Materials Engineering, University of Illinois – Champaign, a new generation of thermosetting resins was developed. An all-aromatic oligomer was introduced in 2010 that paved the way to provide many innovative solutions that face issues the polymer materials industry. Classified as "Vitrimers," crosslinked polymers featuring dynamic covalent chemistry – termed "bond exchange reactions" – BER, offer a mechanism for reversible or on-demand assembly of thermosets. Developed and manufactured by ATSP Innovations, Inc., Houston, TX, a versatile platform of materials. Several of the most significant performance characteristics ATSP resins offers are:

- Designed for **high temperatures** (up to 350 °C in air, with Tg of up to 310°C)
- **Liquid crystalline** character results in lower residual stresses at interfaces – producing stronger bonds and tougher composites
- **Flammability resistance** superior to aramids, epoxies, phenolics and other high temperature polymers (LOI: 40%)
- Strong **adhesion** to metal surfaces

- **Tribological** performance combining low friction and low wear
- **Versatile** processing and application forms such as composites, films, coatings and additives to both thermosets and thermoplastics

A significant performance behavior characteristic is the ability of ATSP to behave as a thermoplastic while maintaining it thermoset characteristics. This means several interesting ATSP capabilities. First, it can be recycled and reformed. Second, it can be alloyed with thermoplastics as an additive to produce enhanced properties and performances. It is to its ability to alloy with certain thermoplastics and composites that is of significant interest.

Thermoplastic resins synthesized via condensation reactions are widely utilized as engineering polymers. These include polyamides, polycarbonates, thermoplastic polyurethanes (TPU), and polylactic acid (PLA). These resins are heavily utilized within industry due to their ease of process, low cost and versatile application interest. However, they suffer from modest heat deflection temperatures, thermal stability, modest tensile and modulus properties, and fire resistance properties. ATSP oligomers offer a method for modifying properties of thermoplastic engineering resins via use of bond exchange reactions.

Bond Exchange Reaction

When the polymer is stretched, Bond Exchange Reactions, BER, lead to stress relaxation and plastic deformation, or the so-called **reforming**. In addition, ATSP, with its high BER (dynamic covalent energy potential) will enable two pieces of polymers that can be rejoined together without introducing additional monomers or chemicals on the interface, enabling welding and reprocessing. This conversion is understood to occur via the exchange at end points between the carboxylic acid caps of the crosslinkable aromatic copolyester oligomers and the linkages in the thermoplastic. Additionally, direct ester-thermoplastic exchange may also contribute to this topological conversion

PTFE/ATSP

The early development of combining ATSP oligomers with thermoplastics led to ATSP's NOWE® Coatings, a member of the ATSP family of oligomers, for metallic substrates for high temperature & wear durability, chemical & corrosion resistant, polyester powder coatings processed to be used as a filler alloy for polytetrafluoroethylene (PTFE) polymers. When used with PTFE the composite coating will have excellent temperature, improved wear resistance, and chemical durability along with low coefficient of friction surface performance. It is also likely that NOWE coated molds and dies would reduce or eliminate the frequent application of applying process mold release.

Nylon PA6/ATSP

The early development of ATSP alloyed certain thermoplastics enabled us to believe we could enhance the resin's properties and performance. Alloyed with thermoplastic resins synthesized via condensation reactions are widely utilized as engineering polymers. These include polyamides, polycarbonates, thermoplastic polyurethanes (TPU), and polylactic acid (PLA). These resins are heavily utilized within industry due to their ease of process and low cost but suffer from modest heat deflection temperatures, thermal stability, and fire resistance properties.

Initial experiments have been conducted on polyamide (PA6) with ATSP's CB oligomers. These were compounded via a screw extruder operating at 275C. This evidenced a decrease in viscosity in the extruder process at 5% mass ratio of CB: polyamide. This also included a reduction in viscosity in the product as measured by increase in the spiral flow metric. Flex modulus improved from 2974 MPa to 3326 MPa following ISO 527. Per ISO 178, flexural strength improved from 117.20 MPa to 128.96 MPa with an increase in flex modulus from 2974 to 3384 MPa. This is understood to occur by conversion of the polymer into a network structure that can constrain chain movement and thereby produce the increase modulus and strength values observed. The important spiral flow measurement increased from 44 to 53 inches, a 20.4% improvement. Fig 1 illustrates the comparison of neat vs. 5% ATSP CB oligomer.

Next Steps

Thermosets have lower melt viscosity and enable better fiber wet out vs. higher viscosity thermoplastics. By reducing the ATSP/Thermoplastic alloy's melt viscosity, spiral flow, we now may improve the fiber "wet out" of certain thermoplastics. This will will increase tensile and modulus properties, especially with LFT (Long Fiber Thermoplastics). Experiments alloyed with Nylon (PA6)/5% ATSP are now being conducted with high long fibers. Improvements in tensile properties would be beneficial for higher performing alloys in many market segment applications.

Fig. 1

Test	Test Standard	Units	AVG	AVG
MFR (250C/2.16kg)	ISO 1133	g/10 min	95.4	107.37
Density	ISO 1183, A	g/cm²	1.113	1.14
Spiral Flow (Distance - Inches)	Measured	Inches	44 in.	53 in.
Tensile Strength at yield, Mpa; 50 mm/min	ISO 527	Mpa	73.86	57.98
Tensile Strength at break, Mpa; 50 mm/min	ISO 528	Mpa	71.68	
Elongation at Yield, %; 50 mm/min	ISO 527	%	4.09	2.07
Elongation at Break, %; 50 mm/min	ISO 527	%		
Tensile Strength at yield, Mpa; 5 mm/min	ISO 527	Mpa	73.86	69.02
Tensile Strength at break, Mpa; 5 mm/min	ISO 527	Mpa	71.68	
Elongation at Yield, %; 5 mm/min	ISO 527	%	4.09	2.32
Elongation at Break, %; 5 mm/min	ISO 527	%		
Tensile Strength at yield, Mpa; 50 mm/min	ISO 527	Mpa	80.96	68.02
Tensile Strength at break, Mpa; 50 mm/min	ISO 527	Mpa	71.64	
Elongation at Yield, %; 50 mm/min	ISO 527	%	4.37	2.32
Elongation at Break, %; 50 mm/min	ISO 527	%		
Tensile Modulus, Mpa 1 mm/m	ISO 527	Mpa	2912	3190
Flexural Modulus, Mpa 2mm/m	ISO 178	Mpa	2974	3326
Flexural Strength, Mpa 2mm/m	ISO 178	Mpa	117.2	128.96
Impact Strength, Charpy, 23C notched kJ/m2	ISO179/1eA	kJ/m2	1.37	1.74
Impact Strength, Charpy, -40C notched kJ/m2	ISO179/1eA	kJ/m2	1.58	1.40