

pCBT: A NEW MATERIAL FOR HIGH PERFORMANCE COMPOSITES IN AUTOMOTIVE APPLICATIONS

*David Bank, Peter Cate, Mike Shoemaker
The Dow Chemical Company*

Abstract

Cyclic oligomers of butylene terephthalate (CBT®) represent a new chemical route to semi-crystalline thermoplastic polybutylene terephthalate (PBT). The oligomers of interest melt completely at about 150°C to produce a low-viscosity fluid that is ideal for wetting and dispersing fibrous fillers and reinforcements, thereby enabling the development of composites that were previously not possible when working with high-viscosity commercial PBT. Introduction of catalyst to undiluted molten cyclic oligomer leads to rapid ring opening polymerization and the formation of high-molecular-weight thermoplastic PBT without the generation of volatile organic compounds. The polymer resulting from this polymerization will be hereafter referred to as pCBT. Treatment of cyclic oligomers in this fashion results in pCBT thermoplastic resin with a high melting point (230°C) and physical performance similar to that of other commercially available PBT resins. The low viscosity of these oligomers enables the selection of processing technologies that are typically reserved for thermosetting systems and that work in conjunction with easy flowing monomers or pre-polymers. The combination of excellent mechanical performance and the ability to utilize processing techniques typically reserved for thermosets enables broad uses for these oligomers in a range of applications including interior, exterior and structural automotive components. Additionally, the thermoplastic nature of pCBT holds promise to provide a low-capital route to a new family of pCBT-based recyclable materials made using a range of plastic processing technologies.

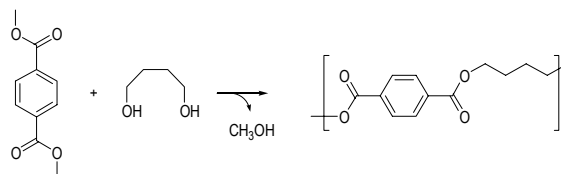
Introduction

A new route to high-performance engineering thermoplastic-based composites is proposed in this paper. The technology is based on the polymerization of the oligomers in the presence of fillers and reinforcement to produce high-performance pCBT based thermoplastic composites. The starting material is obtained by a novel process that converts high-molecular-weight PBT into a mixture of cyclic oligomers.¹⁻⁴ These oligomers are solid, and exhibit no volatility at room temperature or under typical processing conditions. The oligomers are typically melted during processing to form a low viscosity fluid, which when mixed with catalyst at an appropriate temperature, will polymerize to produce high-molecular-weight semi-crystalline pCBT.¹⁻⁴ The low viscosity of the molten oligomers, together with their inherent chemical compatibility with typical coupling systems used with fillers and reinforcements, enables this technology to be considered as a viable approach for the production of a broad range of high-performance thermoplastic composites.

Polymerization

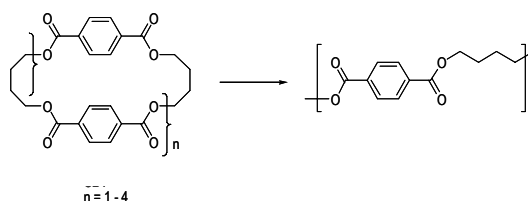
Conventional commercial production of polybutylene terephthalate (PBT) involves a condensation reaction between dimethyl terephthalate and 1,4-butane diol (Scheme 1). High molecular weight polymers are only achieved at very high conversions when the last traces of methyl alcohol co-product are removed.

Scheme 1



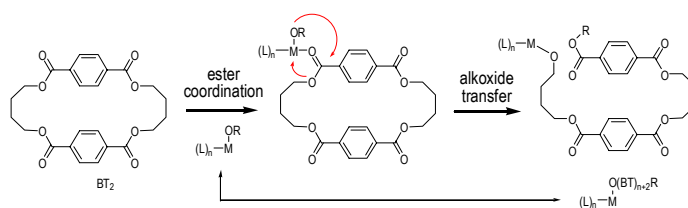
Unlike the conventional material, pCBT is prepared from the oligomers by a metal-catalyzed addition-polymerization process (Scheme 2). As a result, the pCBT polymer's molecular weight is not dependent upon complete monomer conversion.

Scheme 2



The proposed mechanism for polymerization is based on metal-catalyzed ring-opening polymerization. Typical catalysts for polymerization include a range of organometallic complexes based on tin or titanium, especially those with alkoxide ligands. Although we do not yet have specific mechanistic evidence for this system, the generally accepted mechanism for ring-opening ester polymerizations such as these typically involves three steps (see reaction Scheme 3). First, the ester moiety of the oligomer coordinates at the metal center. Following ester coordination, the alkoxide ligand originally on the metal can transfer to the oligomer, thereby opening the ring. The resulting metal complex has a new metal alkoxide bond (from the oligomers), which can then repeat the process of coordination and alkoxide transfer, yielding high molecular weight PBT.³⁻⁵

Scheme 3



A practical demonstration of the transformation of the oligomers into high molecular weight pCBT is provided in Figure 1. In this case a small amount of tin catalyst was mixed with dry oligomers and placed into a differential scanning calorimeter (DSC). Heating the reaction mixture in the pan of the DSC provides a convenient source of energy for polymerization, while

analysis of the data offers a means to view pertinent transitional states as a function of temperature. The curve in Figure 1 labeled “First Heat” indicates the transitional states associated with heating the reaction mixture from room temperature to 200°C. Note the large endothermic transition at about 150°C indicating melting of the oligomers. Upon further heating to temperatures above 170°C, the oligomers begin to polymerize. It is important to note that no exothermic activity is observed in the DSC trace indicating that the heat released during polymerization is negligible. Cooling from the melt results in crystallization of PBT as is evident from the exothermic peak (T_h) observed on cooling. The curve in Figure 1 labeled “Second Heat” indicates the major thermal transitions observed upon reheating the sample to a temperature above the melting point of the polymer, followed by cooling. Notice that the oligomer melting transition has disappeared and a new endothermic peak is present, representing a melting point in the range of 230°C that corresponds to the crystalline melting point for PBT. Upon cooling, this material crystallizes per the exothermic peak (T_h) at about 180°C forming the semicrystalline microstructure associated with PBT.

The significance of Figure 1 is that it clearly illustrates the ability to quickly and efficiently transform the oligomers into high molecular weight pCBT thermoplastic in one simple, thermally activated polymerization step. This capability to thermally polymerize on demand is viewed as a key feature of the technology and holds promise to alter the approach to production of a range of thermoplastic composites in the future.

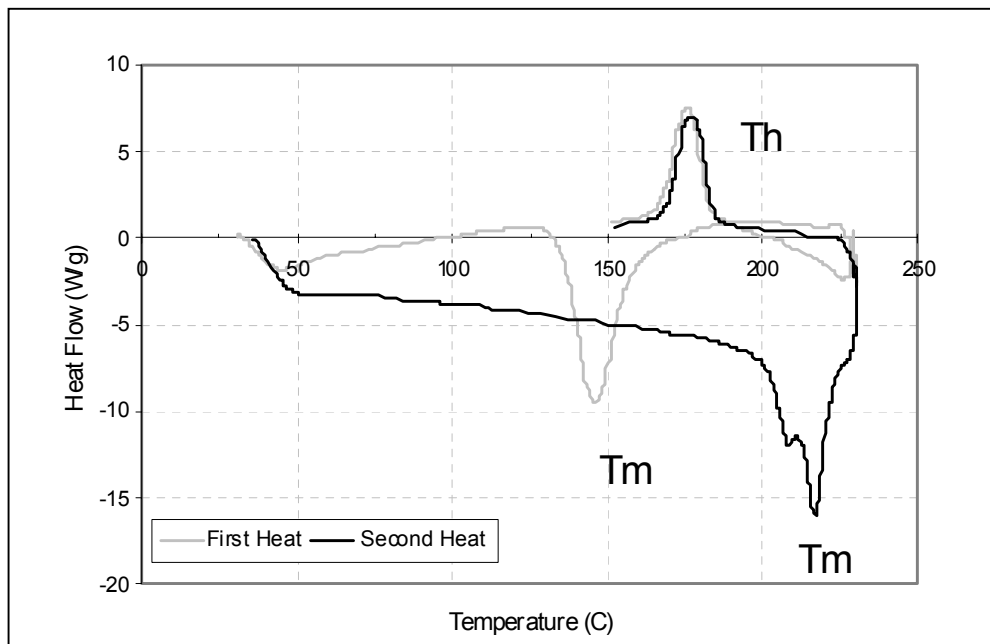


Figure 1. Differential scanning calorimetry (DSC) graph of catalyzed oligomers, indicating the transitional states before and after a simple thermally induced polymerization.

The mechanical and thermal performance of pCBT thermoplastic produced by thermally induced polymerization in the presence of catalyst is compared in Table I to that of commercial linear PBT.⁶⁻⁷ Note that pCBT exhibits nearly identical performance to that of the commercially available system. pCBT should also be expected to perform as a typical thermoplastic with respect to post-consumer recycle and in-plant regrinding operations.

Table I. Mechanical and thermal performance of pCBT in comparison with commercial PBT after injection molding.

Property	Unit	pCBT	Commercial PBT
Melting Temp	°C	220-230	220
Tensile			
Modulus	GPa	1.9-3.0	2.6
Strength	MPa	58	50
Elongation	%	50-300	200
Coefficient of Expansion	10 ⁻⁶ mm/mm/°C	60-95	81
Heat Deflection Temp	°C @ 0.45 Mpa	116-190	154
Specific Gravity		1.31-1.38	1.31
Water Absorption	% (24hr)	0.08-0.09	0.08

The results described in Table I indicate that the oligomers offer a new route to the production of pCBT-based thermoplastic articles with no sacrifice in mechanical or thermal performance when compared to commercial injection-molding grades of PBT. Consistent development of crystalline morphology is an important factor involved with the generation of thermal and mechanical performance in PBT and pCBT. This topic is addressed in the next section.

Crystallinity

pCBT thermoplastic, like commercial PBT, is a semi-crystalline polymer. Crystallinity is important to pCBT because the crystalline material melts at a high temperature (230° C), exhibits a high degree of stiffness and acts to maintain dimensional performance of molded components when subjected to stress at high temperature. With this in mind, a discussion regarding the crystalline morphology of pCBT is presented here in comparison to commercial PBT.

An important attribute of pCBT relative to other polymers used in automotive applications, like polypropylene, is a high crystalline melting point. The DSC result reported in Figure 1 indicates a melting point of 230°C for a fully crystallized sample. Integration of the melting endotherm present in Figure 1 and correction for the heat of fusion of PBT gives a specific heat of fusion for pCBT of 70 J/g and a calculated crystallinity level of 40-50%. Table II provides a comparison of the melting temperature, specific heat of fusion and percent crystallinity for pCBT to that of commercial PBT. In general, results indicate similar melting characteristics; however, pCBT generally exhibits higher specific heat of fusion and the corresponding increase in percent crystallinity as expected from this result.

Table II. Comparison of crystalline melting point, degree of crystallinity and specific heat of fusion for pCBT to that of commercial PBT.

Propert	pCBT	Commercia PB
Meltin Temperatur	23	23
Degree crystallinit	40-	35-
Specific of	70-74	41-45

More detailed analysis of crystallinity was accomplished by wide-angle X-ray scattering (WAXS) to further elucidate the crystalline concentration and structure related issues. The characteristic WAXS pattern for fully crystalline pCBT and commercial PBT are presented in Figure 2, which provides the X-ray image produced by radial integration of the WAXS pattern for each material. Analysis of this result indicates the scattering response expected for highly crystalline polybutylene terephthalate. Integration of the X-ray pattern and treatment of the data confirms a high degree of crystallinity (40-50%) for pCBT and 35-40% for commercial PBT. Analysis of the WAXS patterns reveals sharper, better defined peaks for pCBT in comparison to commercial PBT, indicating larger (more perfect) crystallites for pCBT. This observation is supported by crystalline lamella thickness estimates arrived at via small-angle X-ray scattering (SAXS) measurements made for each material, which indicate a dimension of 90-125 Å for pCBT compared to 70-80 Å for commercial PBT.

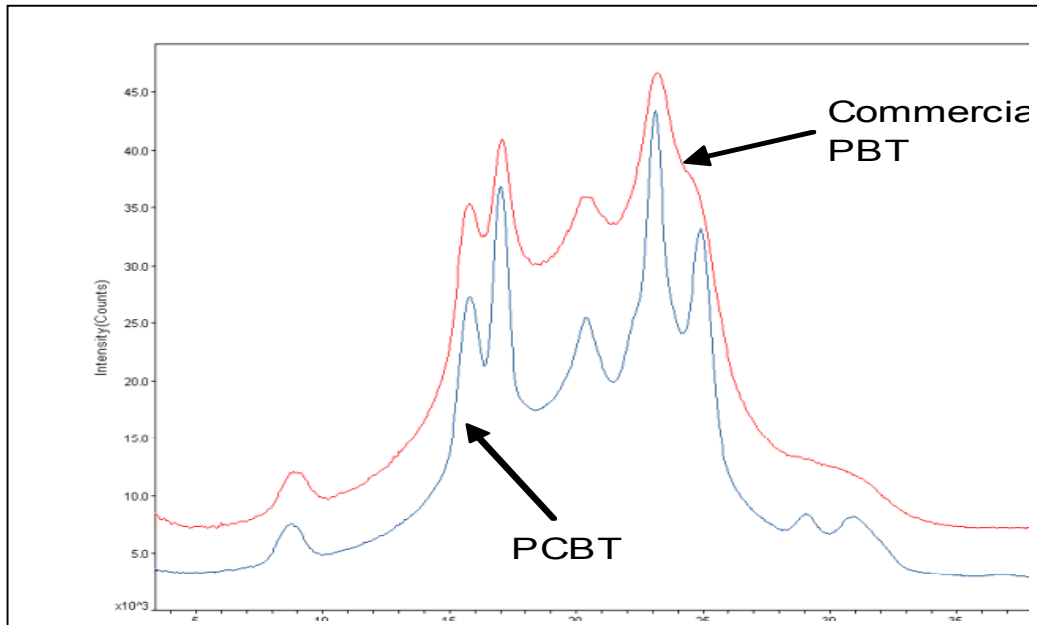


Figure 2. Radial integration of wideangle X-ray scattering pattern for highly crystalline pCBT in comparison to commercial PBT.

Further study of the crystalline morphology of pCBT was accomplished by transmission electron microscopy. In this procedure, a thin sample of polymer was removed from a molded specimen by ultra-microtomy and stained with ruthenium tetroxide. The staining protocol was

employed as a mechanism to increase the phase contrast between crystalline and amorphous regions within the pCBT morphology. The staining methodology results in the amorphous fraction of the pCBT morphology appearing as a dark phase. The crystalline phase, which is unable to associate with the stain, is rendered a light gray or white color in the micrograph. Analysis of the stained sections by transmission electron microscopy (TEM) resulted in the micrograph presented in Figure 3. As the micrograph indicates, the basic crystalline structure of pCBT is lamellar in nature. This observation comes based on the tightly packed highly ordered regions that are evident as lightly colored (light gray or white) structures in the TEM image. A careful look at the morphology reveals a high density of crystalline lamella that appears to be evenly distributed with a characteristic length in the range of about 100 nanometers or more.

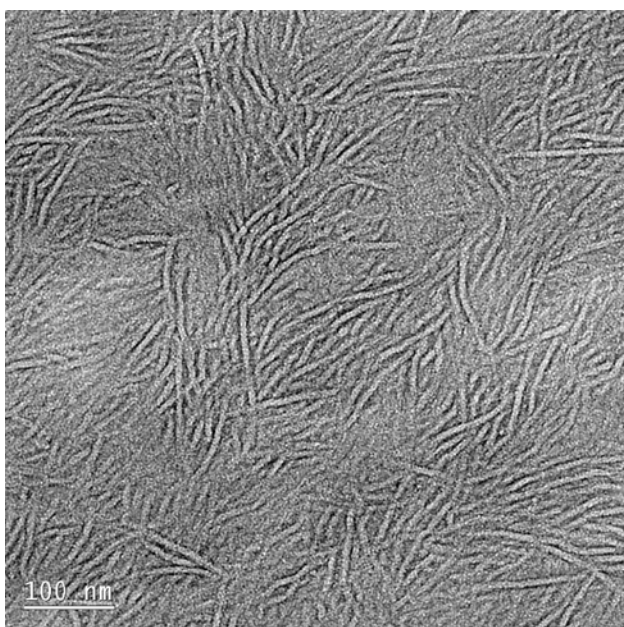


Figure 3. Transmission electron microscopy of pCBT, indicating lamellar crystalline structure.

Probing the nature of pCBT crystalline structure at a higher level via polarized light optical microscopy reveals that the crystallinity manifests itself as a tightly packed spherulitic morphology. The average size of the spherulites is approximately 3-20 microns in diameter. Figure 4 provides a typical polarized light optical micrograph for pCBT. The spherulites are identified as the regular shaped features present in the photomicrograph. It should be noted that pCBT is generally viewed to exhibit smaller and more consistent spherulite size in comparison to commercial PBT, which exhibits spherulite sizes that are much larger. This feature should enable more isotropic shrinkage and over-all better dimensional control of components molded from pCBT in comparison to results obtained from commercial PBT.

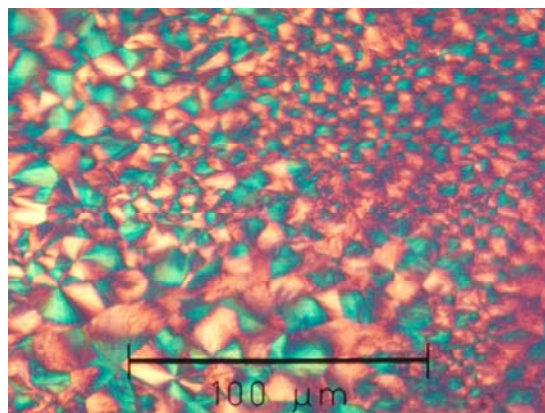


Figure 4. Polarized-light optical micrograph of pCBT showing spherulitic morphology.

Table III provides a summary of the basic crystalline morphology of pCBT in comparison to commercial PBT on the basis of WAXS, SAXS, TEM and polarized-light optical microscopy. Results indicate a lower overall crystalline content for commercial PBT in conjunction with generally larger spherulitic morphology and crystalline lamellae. These results suggest that the crystalline material present in pCBT is of a higher degree of perfection in comparison to that of commercial PBT.

Table III. Comparison of pCBT to commercial PBT based on analysis of the crystallinity of each material via WAXS, TEM and polarized light optical microscopy

Propert	pCBT	Commercia PB
Degree crystallinit	40-	35-
Crystal morpholog	Spheruliti Lamella	Spheruliti Lamella
Spheruliti diamete	3-20	80-16
Lamell thicknes	90-125	70-80

In the next section we will discuss the potential merits of this data based on a range of novel processing routes for polymerization of these oligomers that have historically been reserved for thermosetting materials.

Processing

Molten oligomer exhibits extremely low viscosity making it ideal for a wide variety of plastic processing techniques. To demonstrate this low viscosity, time-resolved rheological properties were measured while curing the oligomers in bulk at selected temperatures from 160 to 350 °C. Viscosity was measured under a nitrogen atmosphere in a dynamic mechanical spectrometer with custom-made 25-mm-diameter disposable aluminum cup-and-plate fixtures. Figure 5 provides a photo of the cup-and-plate fixtures used in conjunction with the rheometer to extract accurate viscosity measurements as a function of time at temperature for the oligomers.

The protocol for viscosity determination involved application of low-strain-amplitude sinusoidal shear flow to the curing material with an actuator attached to the lower cup fixture. The actuator forces the cup to oscillate sinusoidally in a twisting motion about the vertical axis. Some of this motional energy is transferred to the upper plate through the sample. It too will twist sinusoidally and at the same angular frequency of the lower plate after the startup transients dampen away. The material viscosity is estimated from the amplitude of the cup angular displacement, the amplitude of the torque on the upper plate, the phase lag of the plate relative to the cup and the angular frequency of the sinusoidal signals.



Figure 5. Photo of the cup-and-plate fixtures in the rheometer sample chamber.

Results from the experiment described above are presented in Figure 6. As the figure indicates, at temperatures above 170° C, the viscosity of the molten oligomers drops below 10 poise. This viscosity is less than the minimum sensitivity of the rheometer used for the evaluation. The low viscosity suggests a range of potential approaches to pCBT processing that were previously impossible to achieve for conventional commercial PBT. These processes include liquid molding technologies, such as reaction injection molding (RIM), resin transfer molding (RTM) and a range of vacuum-assisted resin infusion processes.

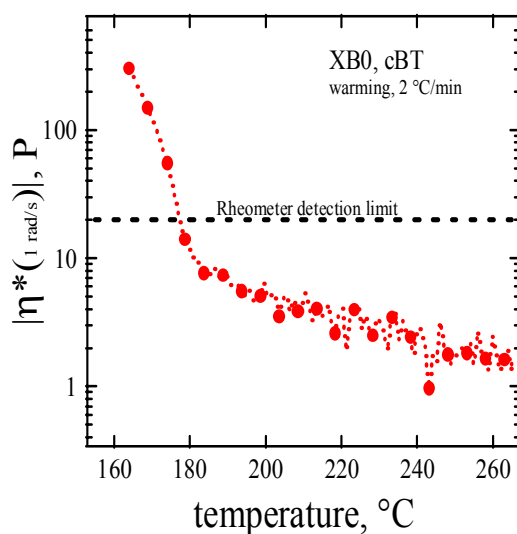


Figure 6. Viscosity versus temperature performance of the oligomers.

Isothermal Curing

An important attribute of catalyzed oligomers is seen in the ability to cure at an isothermal condition. Isothermal curing refers to polymerization and crystallization followed by ejection of a molded part, all at a constant tool temperature. During isothermal curing of the oligomers, the catalyzed resin is heated to the cure temperature followed by rapid ring-opening polymerization and ultimately crystallization. It is important to note that the oligomers are able to polymerize and crystallize under such isothermal conditions. This feature is important because the crystallization process rapidly solidifies pCBT, thereby enabling the demolding of solid parts from hot tooling or molds.

The curing reaction for the oligomers can be studied by time-resolved rheological analysis. Key steps of a typical time-resolved rheological experiment involve:

- (1) Warming the sample chamber with cup-and-plate fixtures to 160 °C,
- (2) Opening the sample chamber to introduce the same amount (about 2-3 g) of dry, catalyzed oligomers into the cup,
- (3) Waiting 1-2 minutes for the material to melt and for the temperature of the sample chamber to return to 160 °C,
- (4) Lowering the plate into the molten material,
- (5) Measuring the distance (about 1-2 mm) between the cup and plate, and
- (6) Measuring the complex shear viscosity at selected times as the material is ramped quickly to, and held at, the targeted isothermal curing temperature 190°C.

The isothermal curing time t_{cure} was set to zero when the cure temperature was reached. The temperature would invariably overshoot by about 2 to 4 °C after this point, and return to the target temperature after about 80 s. The duration of this overshoot was always much shorter than that of the isothermal experiments (>1000 s).

Strain amplitudes of about 10% were selected at the start of the experiment and lowered, as needed to keep the properties in the linear-viscoelastic regime (independent of the strain amplitude). Nevertheless, the viscosities of the curing material at the start of the experiment were often too low to measure reliably with the 25-mm-diameter fixtures. Consequently, these lower viscosities (< 20 poise) data points are not displayed in the figures. Properties measured this way for curing materials, are time averaged over a single period.

Figure 7 presents the curing response for the oligomers with two different catalysts including a relatively fast catalyst system in comparison to a slow system. As the results indicate, the cure of the oligomers typically occurs in conjunction with an initial incubation period where viscosity does not change as a function of time. This incubation time is followed by a period of rapid increases in viscosity followed by a point where the viscosity response becomes time independent. From a practical perspective, the time required for the viscosity response to become time independent represents the point where polymerization and crystallization are sufficiently complete for a given processing scenario, and signifies that enough curing and crystallization has occurred to allow for de-molding of a solid part.

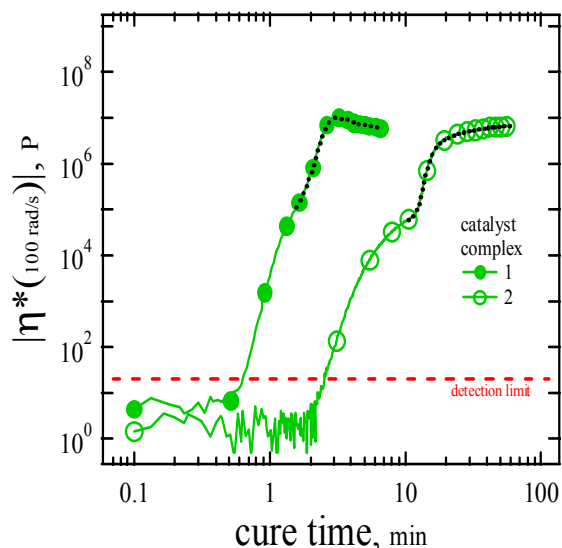


Figure 7. Curing response of the oligomers with a fast catalyst (complex 1) and a slow catalyst (complex 2).

The relationship between molecular weight and viscosity during curing of the oligomers was determined as a mechanism to describe the correlation between these variables. The approach to this experiment involved conducting the polymerization reaction in the rheometer for a specific time at 190°C followed by rapid quenching to terminate the reaction. The protocol used for polymerization was identical to that described above for curing with the additional step of thermally quenching the system after specific times to terminate polymerization. Molecular weight was determined via size-exclusion chromatography. Results from this experiment enable the direct comparison of viscosity to molecular weight during curing of the oligomers to form pCBT. Figure 8 presents the comparison of viscosity versus molecular weight based on polystyrene equivalents as a function of curing time at 190°C. Note the rapid increase in molecular weight as a function of increasing viscosity for a fast catalyst (complex 1) and the corresponding slower increase in molecular weight as a function of viscosity change for a slow catalyst (complex 2). Further analysis of this information illustrates the ability to directly correlate molecular weight and viscosity for pCBT based on cure time, temperature and catalyst type.

The low viscosity and controlled polymerization reaction of the oligomers enables a range of plastics processing options to be considered. These options include the entire list of possibilities described in Table IV. As the table indicates, the oligomers are viable material for consideration in processing technologies that span traditional thermoplastic as well as thermoset approaches. The flexibility imparted to the end user to select the most appropriate process for a given application is thereby improved greatly.

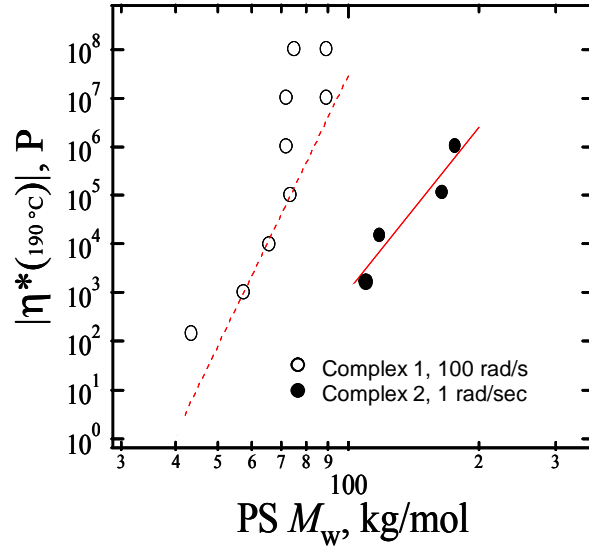


Figure 8. Comparison of viscosity versus molecular weight based on polystyrene equivalents for a fast catalyst (complex 1) and a slow catalyst (complex 2) during polymerization of CBT® oligomers at 190°C.

Table IV. List of viable processing options for use with these oligomers

Process	Specific Process Type
Injection molding	
Compression Molding	Powder based prepreg Melt based prepreg Sheet molding compounds Bulk molding compounds
Reaction Injection	Reaction Injection Molding (RIM) Resin Transfer Molding (RTM) Structural Reaction Injection Molding (SRIM) Vacuum Infusion
Pultrusion	
Thermoforming	
Rotational Molding	
Slush Molding	
Fiber Winding	

These oligomers clearly enable a wide variety of processing methodologies to be considered. However, for the purpose of this paper, the authors intend to focus on one form of processing to enable greater depth of discussion. With this in mind, the thermal spray process for manufacture of net-near-shape oligomer-based prepreg will be reviewed along with the compression-molding process required to produce final molded composite parts. In this example the authors intend to illustrate how a process designed for use with classical thermoset epoxy resin can be applied to these oligomers in a manner that results in the production of a thermoplastic composite part.

Thermal Spray Processing

Oligomer -Based Thermal-Spray Composites with Random Fiber Reinforcement

Thermal spray processing is typically employed in the production of net-near-shape pre-forms for use in subsequent liquid molding operations. In this processing scenario, a fiber chopper gun is integrated with a heat source and resin delivery system such that chopped glass or carbon fiber is co-mingled with small amounts of resin binder during the spray process to form a net-shape pre-form. The result is a highly porous pre-form that is ready for use in a number of liquid-infusion processes. While this approach to pre-form production is viable for use with these oligomers, our main interest has been the creation of high-solids prepregs where all of the resin and fibrous reinforcement is in place in the final net-shape prepreg. To accomplish this, an identical approach to that described above for the pre-form process was taken; however, in this case, all of the resin and reinforcement required for production of the final part were applied during the spray process.

Execution of the thermal-spray prepreg process involves delivering a stream of powdered oligomer to the process by blowing it through a heat source along with chopped reinforcement. The heat source acts to melt the oligomer and form a cloud of droplets, which commingle with the chopped reinforcement and adhere to the fibers as they are blown onto a screen with the desired net-shape. A high-velocity blower provides suction to inhibit movement and allow for consolidation of the prepreg on the screen. A process schematic is provided in Figure 9. The thermal-spray process is further documented in Figures 10, 11 and 12, which provide photos of various parts of the process. Figure 10 gives a close look at the co-mingling of the oligomers and glass reinforcement as they move through the air just prior to deposition on the screen surface. This figure also clearly shows the chopper gun, the powder-delivery hose and the cylindrical heater that is attached to the bottom of the chopper gun. The heater works in conjunction with a blower that facilitates the ability to blow hot air into the mixture of the oligomers and glass fiber to allow for melting of the resin. Figure 11 shows a large pre-form that is nearing the end of the spray process. Note that minimal overspray and waste are created with this process. The resultant high-solids prepreg is pictured in Figure 12. The final prepreg exhibits the net-shape of the desired component. One of the strengths of this approach is that all of the resin and reinforcement are present in the prepreg in close proximity to where they will end up in the molded component. With this in mind, little or no movement of reinforcement is anticipated during compression molding, thereby yielding highly consistent mechanical performance from the molded component.

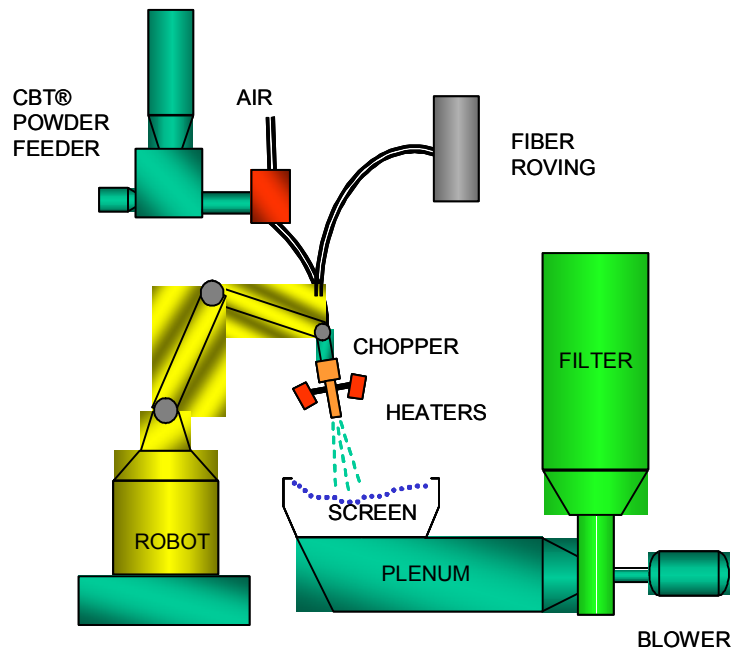


Figure 9. Schematic illustration of the thermal spray process



Figure 10. Photo showing the co-mingling of oligomers and glass fiber during the thermal spray process for prepreg manufacture.



Figure 11. Photo showing the final stages of the thermal spray process for manufacture of a large prepreg component.



Figure 12. Photo showing a high-solids prepreg based on the oligomers following thermal-spray processing but before compression molding.

Compression Molding

Final consolidation of the oligomer-based prepreg into a composite part is accomplished by first drying the prepreg to remove moisture and then placing the prepreg into a tool cut to the precise final dimensions of the part, followed by compression molding. During the compression-molding process, heat and pressure are applied to cure the matrix resin and shape the system into the final desired part. Typical drying and compression-molding conditions are provided in Table VII. It should be noted that drying is of special importance and that all prepregs must be thoroughly dried prior to in-mold polymerization of the oligomers.

Table VII. Typical drying and compression-molding conditions for the oligomer-based prepregs.

Process Parameter	Time / Temperature
Dessicant Drying	
Time	< 8 hours
Temperature	85°C
Curing / Polymerization For Fast Catalyst	
Time	< 5 minutes
Temperature	190°C
Curing / Polymerization For Slow Catalyst	
Time	> 30 minutes
Temperature	190°C
Pressure	
Minimum Cavity Pressure at 50 Volume % Reinforcement	14 psi

Mechanical Performance of pCBT Composites Produced Via Thermal spray and Compression Molding

The performance of pCBT composites produced by thermal-spray processing and subsequent compression molding is presented in Table VIII in comparison to that of a toughened vinyl-ester composite produced with a similar level of reinforcement. As the table indicates, the pCBT composite exhibits comparable strength and stiffness, but offer a major improvement in toughness. This unique toughness / stiffness balance offers a source of mechanical performance advantage that will enable the success of oligomer-based composites in a range of high-performance composite applications in the future. Comparison of the heat-distortion temperature under load indicates a lower maximum performance temperature for the oligomers-based composite due to melting of the PBT crystalline material at 230°C. However, it should also be noted that the pCBT composite enjoys the benefit of its thermoplastic nature in terms of recyclability, processing, and durability in comparison to a more limited performance spectrum for the thermoset-based system. The fact that the oligomers exhibit little or no

volatile organic compound (VOC) emissions either before, during or after processing also bodes well for this material in comparison to the thermosetting technology. With these oligomers, no containment devices or special exhaust fans are necessary during thermal spray processing or compression molding.

Table VIII. Mechanical and thermal performance comparison of a thermally sprayed oligomers-based PBT composite in comparison to that of a toughened, glass-reinforced vinyl-ester thermoset composite.

	Unit	Method	pCBT Composite	Toughened Vinyl Ester Composite
Reinforcement Level	%	ASTM D5630	57	57
Tensile		ASTM D638		
Modulus	Mpa		13237	13,306
Break Stress	MPa		191	108
Break Strain	%		1.7	1.1
Flexural		ASTM D790		
Modulus	MPa		10,865	11,713
Break Stress	MPa		192	239
Dart Impact				
Total Energy @ -40°C	J	ASTM D3763	30	11.3
Izod Impact				
Izod @ 23° C	J/m**2	ASTM D-256	107	103
Izod @ -40°C	J/m**2	ASTM D-256	194	156
Heat Distortion Under Load	°C @ 1.8 Mpa	ASTM D648	221	>300
CLTE	(mm/mm/C)X10**-6	ASTM D698	28	38

Oligomer- Based Thermal-Spray Composites with Continuous Fiber Reinforcement

It is also possible to utilize the thermal-spray process to create preregs based on woven or stitched fabric reinforcements. This approach can be further developed by combining with chopped fiber spray to enable the production of cost-efficient sandwich structures. Table IX provides the comparison of a thermoplastic oligomer-based PBT composite to that of an analogous epoxy thermoset composite. Both systems were produced by preparing prepreg from a stitched carbon fabric with a 45°/45° fiber orientation. The preregs were fabricated by placing a layer of fabric on the screen during the thermal-spray process and using the suction from the process to hold the fabric in place. In this case, powdered resin was sprayed at the fabric along with heated air to melt the powder and create a cloud of oligomer droplets that hit the fabric and infuse into it prior to freezing due to the air flow through the fabric and screen combination. Individual layers of fabric were cut and impregnated using the thermal-spray process as described above. The fabric was cut to facilitate easy stacking of the resultant prepreg to allow the creation of multi-axial reinforcement based on specific placement of the

layers. In this case, the prepregs were cut and stacked such that the carbon-fiber reinforcement scheme employed off-axis reinforcement in the $0^{\circ}/90^{\circ}/45^{\circ}/45^{\circ}$ configuration. Figure 13 provides a schematic illustration of how the prepreg layers were stacked to achieve specific off-axis carbon fiber reinforcement within the prepreg layers. The target level of carbon fiber reinforcement was 50 percent by volume and the part thickness was 3.0 mm. Composite parts were produced by drying the prepreg, followed by in-mold polymerization during compression molding. The resultant pCBT composites exhibit comparable performance to that of the epoxy-based system with regard to the stiffness/toughness/strength balance of the composite as illustrated in Table IX. Additionally, the oligomer-based system exhibits the added benefit of thermoplastic durability and less than 5 minute isothermal curing time. By comparison, the epoxy system required 10 minutes to cure and could not be processed isothermally

A final advantage of the oligomer-based prepreg is the observation that very little mold closing pressure is required due to the low viscosity of the resin, offering new alternatives in tooling and presses to be explored with dramatic implications for capital reduction.

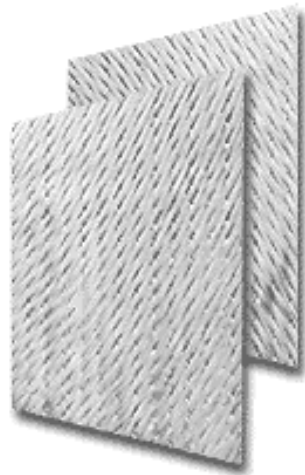


Figure 13. Schematic of the prepreg organization required to achieve off-axis reinforcement with stitched carbon fiber fabrics.

Table IX. Mechanical performance comparison of an oligomer-based PBT composite with 50 volume-percent carbon fabric reinforcement and off-axis fiber orientation arranged in the 0°/90°/45°/45° configuration in comparison to an epoxy-based composite produced in the same manner.

	Uni	Metho	Thermal pCBT Composit	Thermal pCBT Composit	Thermal Epoxy Composit	Therma Spray Epoxy Composit
Laminate Constructio			0/90/45/45	0/90/45/45	0/90/45/45	0/90/45/45
Testing Orientation			0°	90°	0°	90°
Reinforcement Leve	Volume %		47	47	43	
Specific		ASTM D792	1.48	1.48	1.44	1.44
Tensile		ASTM D638				
Modulu	Mpa		51274	47902	44938	45076
Break Stress	MPa		635	717	768	564
Dart Impact						
Total Energy @ -40°C	J	ASTM D3763	677		765	

Applications For Oligomer-Based Composites

Composites based on these oligomers are suitable for use in a variety of structural applications, as a means to address fuel efficiency and emissions targets by drastic reduction of vehicle component weights.

These oligomers are of particular interest where traditional thermosetting composites are already considered (but are not viable for toughness, cycle time or recycling considerations) or where thermoplastic composites are considered (but are not viable for temperature or stiffness considerations).

The advantages of oligomer based composites allow a diverse range of applications to be addressed, including:

- engine undertray (where increasing temperatures mean heat resistance becomes critical)
- bumper beams / side impact beams (requiring good stiffness and toughness balance)
- driveshafts (where these oligomers can drastically improve cycle times versus existing composite driveshaft solutions)

Long term, visible body panels, complete floor pan or side frame assemblies will be possible, as further design and engineering information is built up around oligomer composites. These large components will necessarily be designed with recycling in mind, the thermoplastic nature of these oligomers in assisting car makers to meet forthcoming end-of-life vehicle directives.

Conclusion

The combination of unique physical properties plus processing ease and versatility of pCBT based composites offer the automotive market an exciting family of thermoplastic materials. Implementation of pCBT will enable cost and weight reduction with improved styling, durability, high-heat performance and dimensional stability in applications such as exterior body panels and structural components. Dow Automotive is actively working to develop this new family of oligomer materials and deliver this novel technology to the industry in the near future.

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