Fast-Curing Structural Polyurethane Adhesive Increases Manufacturing Throughput

WHITE PAPER

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Introduction

Manufacturers have benefited from replacing mechanical fasteners with structural adhesives when bonding composites, plastics and painted metal. Additional benefits—such as lower exotherm, lower odor and higher elongation-accrue when structural polyurethane adhesives replace acrylic and methyl methacrylate adhesives (MMA). A historic barrier to urethane adoption, however, has been its slower cure rate of cure. Specifically, most urethanes have a linear relationship of open time to cure time, so adhesives that offer reduced handling time also present a very short open time, leaving inadequate time for product assembly. Conversely, adequate open times are associated with slow cure times for polyurethanes. In this way, polyurethanes have traditionally been at a disadvantage compared to the fast rate of cure which allows for quicker production rates when using MMAs. Adding heat to cure urethanes has been a common solution, but this adds the cost of heated tooling to the manufacturing costs as well as creating potential quality issues with 'cold spots' in heated tooling. (Cold spots are complex shapes and thicknesses of the component that are sheltered from the heat applied for curing or in the tooling itself.) Polyurethanes requiring heat to fully cure can experience incomplete cure.

A step-change in addressing this situation is LORD 7800 fast-curing structural polyurethane adhesive. The LORD 7800 family has a range of open times followed by a rapid cure. The product family's cure profile is similar to an acrylic and it cures at room temperature. (If desired, low heat can accelerate curing.) It also offers a solution to cold spots in composite tooling.

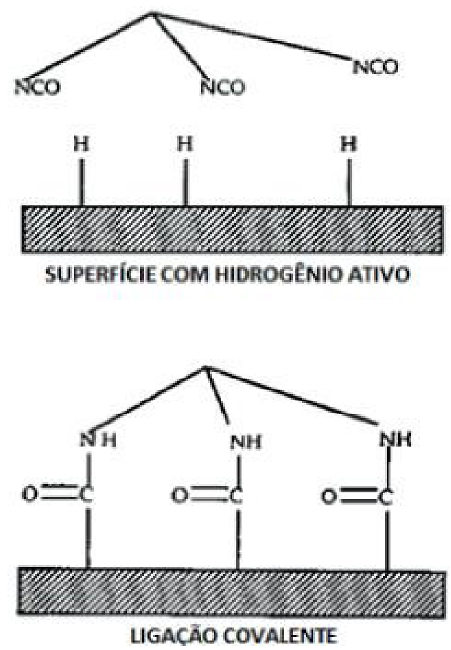
Benefits of Urethanes

Urethane formulas are good adhesives for several reasons:

- They have good wettability on most substrates.
- They form hydrogen bonds with the substrates.
- Their small molecular size allows them to penetrate porous substrates.
- They form covalent bonds with substrates that have active hydrogens.

Figure 1 shows the forming of covalent bonds in the process of adhesion of urethanes to polar surfaces.

Figure 1: Forming of covalent bonds in the process of adhesion of urethanes to polar surfaces. (Image courtesy of A. Pizzi and K. Mittal)



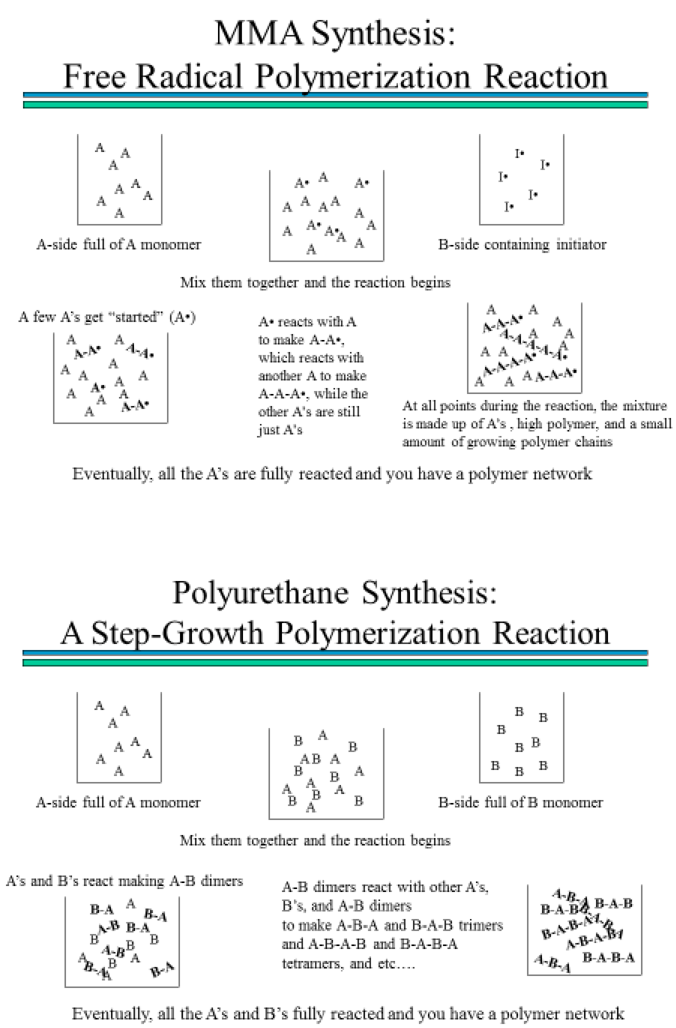
Polyurethanes are not only versatile in their molecular configuration, they are compatible with many other polymers, such as phenolic compounds, urea, epoxy, thermoplastic resins, and elastomers. This increases polyurethanes' usefulness in the area of adhesives.

Chemistry of Polyurethanes

The term polyurethane (PU) is used to refer to a class of polymeric materials containing urethane linkage, regardless of whether there are other chemical bonds present. In addition to the urethane groups, aliphatic, aromatic, ester, ether, amide, urea groups, and others may also be present in their structures. Two-component polyurethane adhesives (generally composed of polyol, isocyanate, and other additives) are formed by an NCO-terminated prepolymer consisting of a chain with a urethane group in its structure which is obtained by the reaction of a polyol with excess di- or polyisocyanate. In a second stage of the process, the prepolymer reacts with the remaining polyol to form the polyurethane.

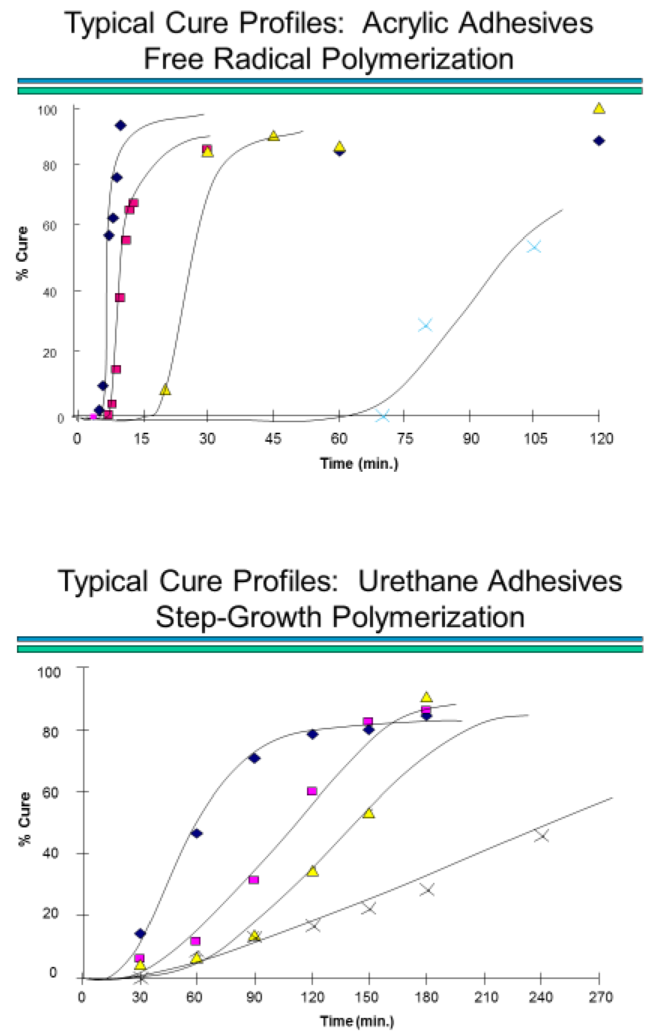
This form of polymerization is known as step growth polymerization. It is characteristic of polyurethane adhesives and is different from MMA adhesives, which undergo free radical initiation. The figures below simplify the differing mechanism of free radical polymerization and step growth polymerization.

Figure 2: A comparison of MMA and polyurethane polymerization reactions.



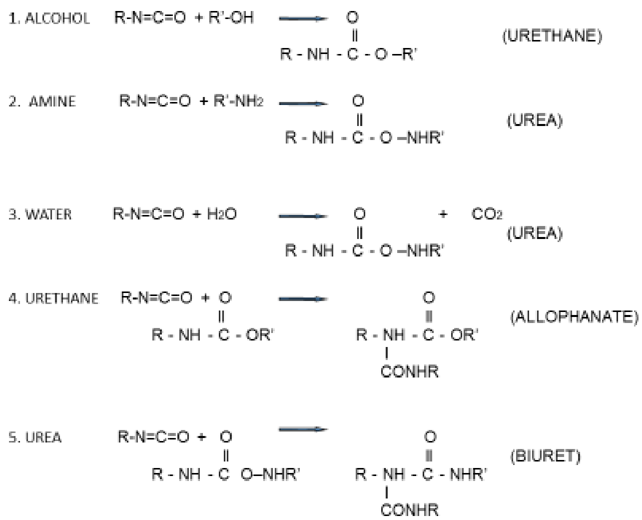
Step growth polymerization tends to be a slower mechanism than free radical polymerization. The two charts below serve to illustrate the desirable nature of MMAs versus older polyurethane adhesives. MMAs reach a higher percentage of cure in a shorter amount of time. It is beneficial when manufacturers can shorten the time between subsequent steps in a manufacturing process, because doing so translates to shorter production cycles. MMAs have traditionally offered shorter times to achieve a higher percentage of cure or a shorter time to attain sufficient strength to perform the next step in the manufacturing operation (such as cutting to size, removing flashing, inserting additional components, and painting of finished components).

Figure 3: Net effect of different polymerization mechanisms with respect to percent of cure when cured under ambient conditions.



There are five major isocyanate reactions in the polyurethane technology, as shown in Figure 4. The isocyanate reacts with: (1) polyols forming polyurethanes; (2) amines resulting in polyureas; (3) water originating polyurea and releasing carbon dioxide; (4) urethane groups and (5) urea resulting in the forming of crosslinked allophanate and biuret, respectively.

Figure 4: Main reactions of isocyanates. (Image courtesy of W.D. Villar)



Translating Chemistry Into Manufacturing Methods

In applications where composites are utilized, two-component polyurethane and epoxy adhesives are widely used in original heavy-duty truck and automotive equipment manufacturer assembly lines (OEMs). However, due to the slower rates of cure for these adhesives, many manufacturers resort to additional methods of heat (such as hot air impingement, heated tooling, or ovens) to accelerate the rate of cure and shorten manufacturing cycle times.

Adhesive manufacturers define the amount of time OEMs have from the initiation of mixing of the two components to mating of the parts as the work time or "open time" of the adhesive. However, the amount of time bonded components need to sit in a fixture before they can be removed and free the tool for reuse (known as handling time) is subject to interpretation. Factors influencing an adhesive's handling time include the usual variables of temperature, humidity, and adhesive's mass, as well the individual assembly's required strength or level of cure needed to prevent a bonded assembly from coming apart when removed from the fixture or moved down the assembly line. Various adhesive manufacturers define handling strength as being between 0.345 to 0.689 MPa (50 and 100 psi). A more useful time increment may be "processing strength." Processing strength can be defined as the length of time an adhesive needs to reach 50 percent of the ultimate yield strength of the bonded joint, or 6.89 MPa (1000 psi). When the adhesive has cured to 50 percent of ultimate strength or 6.9 MPa (100 psi), parts can generally be processed in whatever manner is necessary for the OEMs next manufacturing operation without the concern of debonding the parts. This includes cutting to size, attaching additional components, continuing assembly, etc.

The introduction of fourth-generation structural polyurethane adhesives offers OEMs the ability to utilize structural urethanes in place of MMAs while retaining the short cycle times needed for productivity in their operations. Furthermore, since the LORD 7800 fourth-generation structural adhesive is a room-temperature-cured adhesive, additional capital expenses of heating tooling and fixtures, ovens and hot air impingement are not needed unless the manufacturer wants to further realize cycle time gains or drop in a new adhesive into an existing bonding cell.

The following graph illustrates the advantage of the fourth-generation structural polyurethane in terms of time to reach processing strength.

Figure 5: Comparison of cure rate for structural polyurethane adhesives. (Materials tested via ASTM D1002 Single Lap Shear on 0.037" thick E-Coated Steel.)

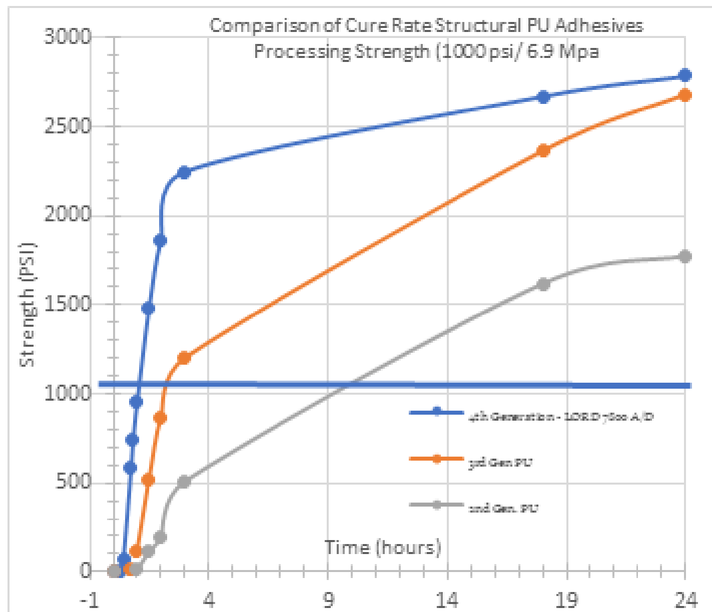


Table 1: Times needed to achieve processing strength of the preceding graph.

Adhesive	Open Time (min)	Handling Time (min)	Processing Strength (hours)
4th Gen – LORD 7800 A/D	5-7	25	1
3rd Gen	6-8	60	2 1/2
2nd Gen	4-7	60-120	9-10
LORD MMA	2-4	4-6	1

As illustrated in the graph and in Table 1, the fourth-generation polyurethane adhesive, LORD 7800 A/D, offers a good balance of open time while improving performance over previous generations. More importantly, the processing strength is achieved in an amount of time equivalent to that of MMA adhesives.

Fourth-Generation Polyurethane Adhesive Properties

The LORD 7800 family of polyurethane adhesives has excellent adhesion when bonding GFRP, sheet molding compound (SMC), bulk molding compound (BMC), and thermoplastics, as well as when cross bonding. The main features and advantages are:

- Non-sag paste: provides excellent gap filling and good thixotropy, allowing for vertical application.
- Versatility in curing: higher capital cost systems are not required but may be used. Room temperature (ambient) cure, forced air and gravity convection ovens, heated tooling and fixturing, and IR heating elements are all acceptable (with a maximum temperature of 104 °C (220 °F).
- Gravity feed system for bulk dispensing: low viscosity A- and B- components allow for the material to utilize gravity to feed into metering pumps. This negates the need for the additional cost of pail or drum pumps for the metering system.

Tables 2 and 3 present the main physical properties for the LORD 7800 family of adhesives.

Table 2: Main physical properties of the LORD 7800 A-component (isocyanate).

Appearance	Black Liquid
Viscosity, 25 °C, cP	8,000-25,000
Density, kg/m3	1282-1420
Flash Point (°C)	> 93

Table 3: Main physical properties of the LORD 7800 polyols (C/D/E)

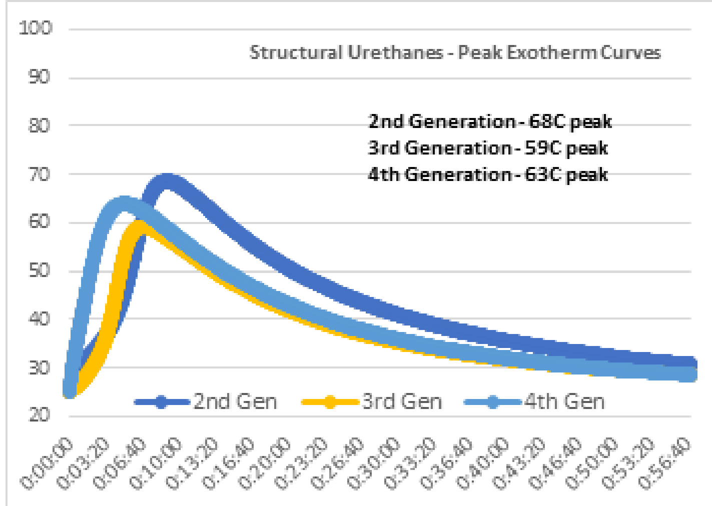
Appearance	Tan Liquid
Viscosity, 25 °C, cP	33,000 – 60,000
Density, kg/m3	1198-1282
Flash Point (°C)	> 93

Fourth-Generation Polyurethane Adhesive Characterization

Exothermic Peak

The exothermic peak for LORD 7800 was obtained by measuring the temperature of the adhesive curing reaction with a thermocouple inserted into standard mass (25 grams) of mixed adhesive. The maximum temperature found during the adhesive curing process was considered to be the exothermic peak.

Figure 6: Exothermic peak during the curing process for LORD 7800 fourth-generation adhesive versus earlier generations.



The peak exotherm test, where mass is 25-50 g, is often presented as a measure of time, after which handling strength will begin to be achieved. However, peak exotherm testing, while useful for measuring the rate of reaction in quality testing of a given batch, represents an artificial construct. This is because the adhesive's mass helps to drive the rate of reaction and acts as a thermal mass for the continued reaction. In most manufacturing cases, the mass represented in the peak exotherm test does not represent the mass of adhesive initially laid down in bead form nor does it take into account the thermal insulative properties of the substrates being bonded (either positively or negatively affecting the reaction). It also does not consider the final, compressed bondline, which tends to reduce the mass accelerated effect. As can be seen in Table 4, the peak exotherm temperatures reached (between 59 and 68 °C) tell us nothing about the time needed to reach the handling or processing strength (see Table 4).

Table 4: Open time, handling time and peak exotherm for various generations of structural polyurethanes.

Adhesive	Open Time (min)	Handling Time (min)	Peak Exotherm
4th Gen – LORD 7800 A/D	5-7	25	5:40; 63 °C
3rd Gen	6-8	60	6:20; 59 °C
2nd Gen	4-7	60-120	9:24; 68 °C

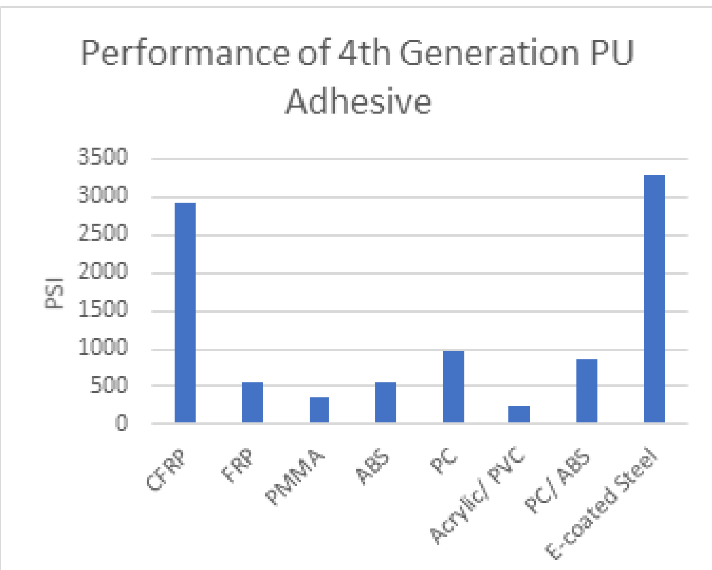
Mechanical Performance on Various Substrates

The surest way to determine the handling and processing strengths of a given adhesive is to measure the rate of bond strength development using the substrates from a given process, mimicking the processing conditions under which the adhesive will be used. A good supplier will offer testing to confirm the desired processing times and/or assist in the development of manufacturing processes which achieve the OEM's desired cycle times.

Figure 7 presents the results of shear strength testing performed on lap shear according to ASTM D1002 or ASTM D3165 on various substrates using LORD 7800 fourth-generation polyurethane adhesive. The substrates tested include CFRP (epoxy resin continuous phase; 2x2 twill); FRP (Fiberglass; Polyester Resin continuous phase); PMMA; ABS, PC; Acrylic/PVC (Kydex™ *; fire-rated); PC/ABS (Bayblend™ **); and E-Coated Steel (PPG E-coat ED 6060). (*Kydex is a trademark of Sekisui-SPI.) (**Bayblend is a trademark of Covestro.)

All of the thermoplastics and the FRP yielded stock failure, with the CFRP and E-coated yielding cohesive failure. The combination of excellent adhesion of a variety of substrates, low exothermic temperature (which prevents softening of thermoplastics and potential read-through) and the short timespan needed to achieve processing strength highlight the potential advantages of the fourth-generation polyurethane adhesives.

Figure 7: Shear strength performed on various substrates for LORD 7800 adhesive (as per lap shear tests specified in ASTM D1002).



Opportunities for Increased Manufacturing Throughput

The following examples illustrate the time savings and increased throughput offered by fourth-generation polyurethane adhesives.

Heavy-Duty Truck Manufacturing OEMs

In the first example, a heavy-duty truck OEM was using a two component, heat-cured adhesive for their assembly operations on SMC truck cabs and FRP truck hoods. Existing assembly methods required that the SMC be cured in a heated fixture for six minutes at 143 °C (290 °F). The FRP assembly method used a lower temperature of 102 °C (215 °F) for nine minutes. (The lower temperature and longer time in the fixture were needed to prevent degradation of the gelcoat surface.) Tests were conducted comparing LORD 7800 A/D to the existing adhesive solution.

Table 5 demonstrates equivalent or better performance from fourth-generation polyurethanes over the heat-cured polyurethane adhesive, while improving the cycle time by two minutes in the heated fixtures. Furthermore, the SMC processing temperature was lowered to 104 °C (220 °F). This allowed for better in-process quality, as the tooling may have cold spots during start-up operations. (Temperatures may be unacceptably low for curing the competitor's adhesive.) The heated tooling process was kept in place, though not required by LORD 7800, which cures at room temperature. Therefore, there was no need to propose changes in the manufacturing cell.

Table 5: Tooling temperature and cycle time reduction*

Test Exposure / Condition	LORD 7800 A/D	Competitive 2K Heat-cured PU
SMC - IPA Wipe	4 min @ 104 °C (220 °F)	6 min @ 143 °C (290 °F)
RT Lap Shear	809 (Sub)	764 (Sub)
60C Lap Shear	633 (Sub)	522 (ADH)
(-40C) Lap Shear	744 (Sub)	756 (Sub)
FRP 220 Grit + IPA Wipe	7 min @ 102 °C (215 °F)	9 min @ 102 °C (215 °F)
RT Lap Shear	1556 (Sub/ FT)	1036 (FT)
60C Lap Shear	1447 (Sub)	529 (ADH)
(-40C) Lap Shear	1186 (Sub)	971 (FT)

*All samples tested via ASTM D3163 at 2 in/min. (FT=Fiber tearing; ADH=Adhesive failure; Sub= substrate failure).

Automotive Lightweighting

Automotive manufacturers continue their efforts to achieve better fuel efficiency in vehicles by using lighter-weight materials—which require less energy to move-in body construction. One new material that is gaining acceptance and usage is glass-filled polypropylene thermoplastic composite. Although the material is low surface energy, LORD 7800 offers excellent adhesion once the surface has been treated either with a flame or plasma surface treatment. Table 6 shows the performance of the new fourth-generation polyurethane adhesive on 40 percent long glass fiber-filled polypropylene.

In this example, the OEM was implementing the new material to replace SMC. The cycle time for this portion of the assembly operation of a rear hatch back was a mere 90 seconds within a heated fixture. LORD 7800 A/C, which has a two- to four-minute open time, was able to achieve sufficient handling strength within the 90 second cycle time, while providing enough open time that the adhesive did not cure in the static mixer. This balance of open time and rapid strength development keeps the robotic assembly operation moving without having to shut down the line while static mixers are changed out. Table 6 highlights the performance after surface treatment on long glass fiber polypropylene (40 percent filled).

Table 6: Performance of the fourth-generation polyurethane adhesive on 40 percent long glass fiber-filled polypropylene*

Condition		40 % LGF PP
		LORD 7800
Alcohol wipe only	Strength	0.469 MPa (68 psi)
	Failure mode	100 ADH
IPA + flame treatment (40-50 dyne)	Strength	3.654 MPa (530 psi)
	Failure mode	100 Sub
IPA + flame treatment + 30 min post bake @ 121 °C (250 °F)	Strength	2.834 MPa (411 psi)
	Failure mode	100 Sub
Flame treatment only (40-50 dyne)	Strength	2.806 MPa (407 psi)
	Failure mode	100 Sub
Plasma treatment only (40-50 dyne)	Strength	2.944 MPa (427 psi)
	Failure Mode	100 Sub
Plasma treatment only (>50 dyne)	Strength	3.440 MPa (499 psi)
	Failure Mode	100 Sub

*All samples tested via ASTM D3163 at 2 in/min. (FT=Fiber tearing; ADH=Adhesive failure; Sub= substrate failure).

Automotive Headlamp Assemblies

Automotive headlamps are typically a polycarbonate lens bonded to a rear glass- or talc-filled housing. Tier 1 suppliers to automotive OEMs have long used either a one-component reactive, hot-melt polyurethane (PUR) or a two-component polyurethane adhesive for headlamp assembly. Critical to the operation is a 100 percent leak check on all assemblies. The leak check is performed using between 0.007 and 0.034 MPa (1 and 5 psi) air pressure to ensure moisture won't penetrate the headlamp and lead to fogging of the lamps after assembly. When manufacturers use one-component PURs, they typically build into their assembly lines a time or waiting queue so that the PURs can cool and re-crystallize. This time queue may be from 10 to 60 minutes and it delays the next critical quality check. LORD 7800 A/D, which has a five- to seven-minute open time, affords sufficient time to reduce waste from purging the static mixers when the robot is at the home station during the manufacturing cycle. Furthermore, the critical pressure test for quality can be accomplished after 20 minutes of room temperature curing (or on a shortened timeline of as little as five minutes if using IR heaters to accelerate cure).

LORD 7800 A/D is now an approved material for General Motor's worldwide headlamp standard, GMW 16506.

Table 7: Dwell time needed prior to pressure testing

LORD 7800 A/D	Circular Headlamp, 225 mm in diameter	
MPa / psi	0.014 MPa (2 psi)	0.007 MPa (1 psi)
RT cure	20 min.	18 min.
Heated cure*	5 min.	5 min.

*Heated cure provided by IR lamp.

Conclusion

When OEMs can reduce steps and cycle times in their manufacturing processes, they improve throughput. Using fourth-generation polyurethane adhesives to replace acrylic adhesives has been demonstrated to result in such efficiencies. These fourth-generation polyurethane adhesives are penetrating the market, as shown by the examples above. As automakers escalate adoption of new materials in their quest for lighter-weight vehicle designs, use of next-generation adhesives is expected to increase.

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