INTER Materials
Product Development & Technologies

ADVANCED ALIPHATIC POLYURETHANE RESINS FOR HIGH DURABILITY AND SUPERIOR BALLISTIC PERFORMANCE LAMINATED GLASS

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SUMMARY

Advanced aliphatic polyurethane (PU) resins have been developed for manufacturing laminated ballistic resistant glass that are lighter and more durable than commercially available glass. The newly developed aliphatic PU resins have very high adhesion strength to glass, polycarbonate and polymethyl metacrylate (PMMA). They also have an excellent optical quality and generate lower thermal stresses by using low processing temperatures during glass lamination. This paper discusses the adhesion, high temperature creep, and aging properties of the new optical aliphatic PU that offer the potential for reducing delamination failures, increasing the ballistic performance, and reducing the weight of future laminated transparent armor designs.

INTRODUCTION

The US Army has been investigating advanced single-crystal and polycrystalline ceramics as transparent armor candidates, including single-crystal sapphire, magnesium aluminate spinel, aluminum oxinitride (ALON), and high-hardness glass. These new materials exhibit excellent ballistic resistance, but they are currently very expensive to fabricate. The US Army objectives are to reduce the weight and thickness of transparent armor by 30-40%.

Since scientists and engineers recognize that transparent armor systems will require multilayer designs, adhesive interlayer materials are also being investigated. To address these challenges, INTER Materials is introducing advanced optical aliphatic PU films with a wide range of properties suitable for laminated transparent armor designs.

The light vehicle armoring civilian market has also identified the needs for reducing weight and thickness of transparent armor. In the US the officially recognized standard for non-transparent ballistic resistant materials (armor) is the National Institute of Justice (NIJ) protocol 0108.01 that includes a classification of six levels of ballistic protection, Table I, and a test method to certify an armor system [1].

TABLE I. NIJ STANDARD 0108.01 FOR BALLISTIC RESISTANT MATERIALS

Level of Threat	Caliber Ammunition	Weight Grains (grams)	Velocity ft/s	Velocity m/s
I	22 LRHV lead 38 RN Lead	40 (2.6) 158 (10.2)	1050 ± 40 850 ± 50	320 ± 12 259 ± 15
IIA	9 mm, FMJ .357 Magnum, JSP	124 (8.0) 158 (10.2)	1090 ± 40 1250 ± 50	332 ± 12 381 ± 15
II	9 mm, FMJ .357 Magnum, JSP	124 (8.0) 158 (10.0)	1175 ± 40 1395 ± 50	358 ± 12 425 ± 15
IIIA	9 mm, FMJ .44 Magnum, SWC	124 (8.0) 240 (15.6)	1400 ± 50 1400 ± 50	426 ± 15 426 ± 15
III	7.62 x 51mm, FMJ 308 Winchester	150 (9.7)	2750 ± 50	838 ± 15
IV	30-06 AP M2	166 (10.8)	2850 ± 50	868 ± 15

Once the threat level has been selected, the ammunition and impact velocities are defined. The ballistic test procedure is a simple pass/fail test which requires five fair hits per panel, except Level IV that requires only one hit. The test specimen must be 5 m from the muzzle and all shots must hit at least 7.6 cm from any edge and at least 5 cm from each other. To be certified, no complete penetrations are allowed at the specified impact velocities. However, for rating bullet resistant glass (glazing) in the US, the Underwriters Laboratories (UL) Standard for Safety for Bullet-Resistant Equipment, UL 752, is the most popular standard [2], Table II.

Upon a bullet striking, the glass is broken by the projectile impact and by the compressive and reflective pressure waves that travel across the thickness. The PC layer in the back, a high tenacity thermoplastic, absorbs the energy by its plastic deformation and catches all the glass fragments as a spall liner.

The major issues of concerns in vehicle armoring are the weight and durability of the laminated ballistic glass. The ballistic glass represents 60-70% of the total added armoring weight. The approximated thickness and weight of commercially available laminated glass in this market are shown in TABLE III. The delamination failures also represent a large expense for laminated glass manufacturers when replacing glass that is within a two years replacement warranty.

The challenges of weight reduction and durability of laminated glass for military vehicles would be even greater. The ballistic threats for military vehicles in a battle field are not only from fragments of all sizes; but also, from high energy rifle fire. The environment for military vehicles is also harsher and more demanding, such as the extreme high temperatures and blasting sand in a desert.

TABLE II. UL STANDARD FOR SAFETY FOR BULLET-RESISTANT EQUIPMENT, UL 752

Rating	Ammunition	Weight Grains (grams)	Velocity f/s (m/s)	Number of Shots
Level 1	9 mm FMJ	124 (8.0)	1,175 (358)	3
Level 2	.357 Magnum, JSP	158 (10.2)	1,250 (381)	3
Level 3	.44 Magnum, SWC	240 (15.6)	1,350 (411)	3
Level 4	.30 Caliber, JSP	180 (11.7)	2,540 (774)	1
Level 5	7.62 x 51mm, FMJ M80 Military Ball	150 (9.7)	2,750 (838)	1
Level 6	9 mm, FMJ	124 (8.0)	1,400 (427)	5
Level 7	5.56 x 45mm, FMJ	55 (3.56)	3,080 (939)	5
Level 8	7.62 x 51mm, FMJ M80 Military Ball	150 (9.7)	2,750 (838)	5
Supplementary Shotgun	12-Gauge Rifle Lead 12-Gauge 00 Lead Buckshot (12 pellets)	437 (28.3) 650 (42)	1,585 (483) 1,200 (366)	3 3

TABLE III. COMMERCIAL LAMINATED BALLISTIC GLASS FOR VEHICLE ARMORING

Ammunition	**9 mm FMJ, .357 Magnum, JSP & .44 Magnum, SWC**	**7.62 x 39mm Soviet SP Ball (M1943)**	**7.62 x 51mm M80 NATO**
Glass Thickness mm	20-22	32	40-42
Glass Weight Kg/m2 (psf)	50 (10.2)	75 (15.3)	100 (20.4)

LAMINATED BALLISTIC GLASS DESIGNS

The most common ballistic resistant glass in the vehicle armoring market is made out of layers of float glass bonded with Polyvinyl Butyral (PVB) plus one layer of polycarbonate (PC) in the back bonded to the glass with PU. The manufacturing process often involves vacuum bagging the whole glass-PC composite and laminating under temperature and pressure in an autoclave.

A popular glass-PC composite in the automotive market today that meets the ballistic NIJ (Level IIIA) is 21 mm thick and weighs 49.8 kg/m^2 as shown in Figure 1. The construction is often comprised by three layers of glass, each 6 mm thick plus a 3 mm thick layer of PC in the back [3].

To design a lighter and more durable ballistic laminated glass, not only stronger transparent materials are needed; but also, a more compliant interlayer with excellent adhesion characteristics to those new materials. Chemically strengthened glass, transparent alumina glass, and ALON are just a few examples of materials being developed stronger than float glass.

Regardless of the strength of those new transparent ceramics and chemically strengthened glasses, there still exists a great need for more compliant adhesive interlayers. These interlayers need to strongly bond those new materials during lamination, have excellent optical properties, and withstand the thermal stresses generated by the lamination process and extreme weather conditions. At present, the use of PVB is one major limiting factor to design lighter and more durable transparent armor.

In a glass-PC laminate, PU is used to bond glass and PC because PVB does not bond to PC. As a result, when a laminated glass-PC part is made in an autoclave at high temperatures, very high thermal stresses at the glass-PC interface are generated during cooling. Those thermal stresses are responsible for most of the delamination failures. Failures often start at the edges of the laminated glass and are aided by plasticizers and additives from the PVB resin that migrate to the edges and attack the PC.

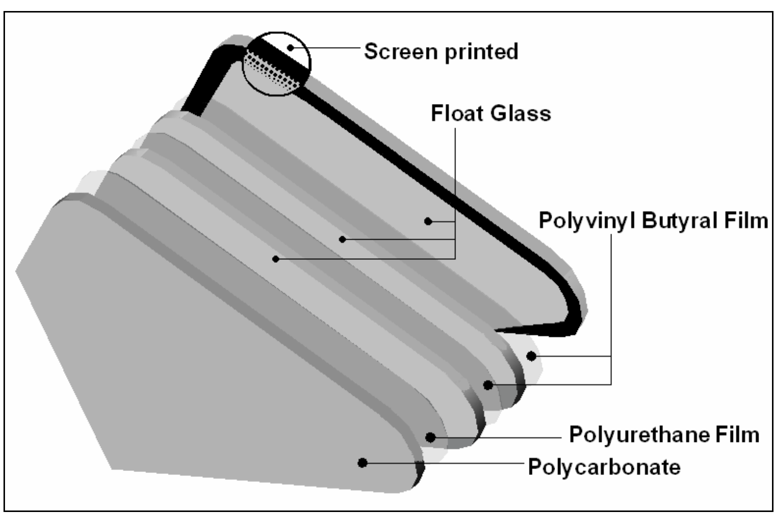

FIGURE 1. Commercial Ballistic Resistant Glass-Polycarbonate Laminate

OPTICAL ALIPHATIC POLYURETHANES

Aliphatic PUs represent a special class of thermoplastic polyurethane (TPU) elastomers where long-term solar exposure demands non-yellowing behavior and no degradation in performance. TPUs are typically produced by reacting diisocyanate with a high-molecular-weight linear polyether or polyester polyol and with a low-molecular-weight diol or amine chain extender in a one- or two-step reaction process.

Aromatic diisocyantes such as MDI, TDI, or NDI are the largest segment of the PU business, but during the last decade aliphatic diisocyanates such as H_{12}MDI, IPDI, HDI, XDI, and TMXDI have been increasingly used where transparency and UV-light stability are important properties. A very good insight on PU chemistry and technology is given by Hepburn [4], and by Randall and Lee [5].

The final resin consists of linear polymeric chains having alternating hard and soft segments. The diisocyanate and the chain extender react to form a high polarity rigid segment referred as the hard block linked through the polyol low polarity soft blocks to form the final polymer structures often described as segmented block copolymers. These alternating hard and soft segments are the primary reason that the PU elastomers have such good mechanical properties over a wide range of temperatures.

TPUs are one product class within the PU family that is supplied as a fully-reacted product, in contrast to all other PUs, with the exception of powder coatings which are supplied as reactive liquids. TPUs can be made into film or sheet materials with a variety of thicknesses using either a blown film or casting process with hardness between 70 to 95 Shore A.

Optical aliphatic PUs offer high optical clarity in bullet resistant glazing, provide excellent adhesion properties to glass, PC, and acrylic. They also offer excellent resistance to hydrocarbons, chemicals, ozone, fungus, and moisture. The combination of these characteristics enables the laminated glass designer to select the right optical aliphatic PU adhesive interlayer to achieve the required engineering properties.

The physical properties of four new optical aliphatic PU films (IM-2500, IM-1600, IM-800A, and IM-800B) are listed in Table IV. Comparing their film properties, IM-2500 has a much higher Short Hardness A, Tensile Strength, Tensile Modulus, Tear Strength, and TMA Peak temperature than both IM-800A and IM-800B. IM-1600 properties are in between IM-2500 and the 800 series.

The wide range and combination of available Tensile Strength, Tensile Modulus and Tear Strength provide design flexibility to use a different PU interlayer to bond glass-glass, glass-PC and glass-acrylic. To apply this design flexibility concept, test data for the adhesion strength to glass and acrylics of the new optical aliphatic films has also been generated.

TABLE IV. OPTICAL ALIPHATIC POLYURETHANE FILM PROPERTIES

Properties	Test Method	IM-2500	IM-1600	IM-800A	IM-800B
Short Hardness A	ASTM D-2240	95	80	70	70
Tensile Strength @ break, psi	ASTM D-412	6500	6500	4100	4000
Ultimate Elongation, %	ASTM D-412	350	500	510	440
100% Tensile Modulus, psi	ASTM D-412	1800	300	300	280
300% Tensile Modulus, psi	ASTM D-412	5300	1000	1000	1200
Tear Strength, pli	ASTM D-624	580	210	200	165
Specific Gravity, g/cm^3	ASTM D-792	1.07	1.07	1.04	1.04
TMA Peak, ^{o}C	TMA	144	125	88	88
TMA Range, ^{o}C	TMA	109-175	80-180	65-125	65-125

To test for adhesion to glass and to acrylics, the ASTM D-3167 standard is followed using 12” x ½” samples. The samples are made by placing the PU film in between a 0.25” glass or acrylic and a 0.016” PC strip. The ½” samples are cut from 12”x12” plates made by autoclave under an ultimate temperature of 250 ^{o}F and ultimate pressure of 150 psi. The holding time is 60 minutes and the temperature heating and cooling rates are 5 ^{o}F per minute. The 12”x12” plates are in the autoclave inside vacuum bags at 24 in.Hg during the whole autoclave cycle.

The adhesion levels to glass of those new PU films are shown in Table V. We can observe that the 800 series of PU films have developed adhesion levels higher than 130 pound per linear inch (pli) at temperatures as low as 90 ^{o}C, while the IM-2500 has to be laminated at temperatures higher than 120 ^{o}C to reach adhesion levels higher than 100 pli. The adhesion to glass of film IM-1600 is in between the level of adhesion of the 2500 and 800 series.

A high level of adhesion to acrylic might be of interest to design a lighter laminated ballistic glass by replacing some glass layers with acrylic. In this case, a low modulus IM-800A interlayer with unusually high 63 pli of adhesion to acrylic can be selected. TABLE VI shows a range of adhesion strength that has been achieved when bonding the new optical aliphatic PU to acrylic.

TABLE V. OPTICAL ALIPHATIC ADHESION TO GLASS, pli

Temperature ^{o}C	IM-2500	IM-1600	IM-800A	IM-800B	IM-800C
80			144	81	128
85		16			
90			155	138	140
100		57	160	140	152
115	79	120			
120		125	138		
125	103	140			

TABLE VI. OPTICAL ALIPHATIC PU ADHESION TO ACRYLIC

Polyurethane Film	Thickness	Ultimate Temp.		Adhesion to Acrylic		
	(mils)	°F	°C	(pli)	(N/mm)	(kg/cm)
IM-2500	25	250	121	**20**	3.5	3.57
IM-1600	50	250	121	**25**	4.38	4.46
IM-800A	50	250	121	**63**	11.00	11.25
IM-800B	25	250	121	**38.5**	6.74	6.88

For high temperature adhesion properties, 12”x12” plates are prepared for the Creep Peel Test in the same fashion as described for the adhesion test, inside a vacuum bag in an autoclave at an ultimate temperature of 121 °C and an ultimate pressure of 150 psi. Except that the samples are cut at 1” width.

During the Creep Peel Test, a 6 lbs weight is hanged from the PC strip and the peeling displacement or de-bonding length is measured in millimeters after the sample has been in the oven for one hour at each temperature. When the failure is due to adhesion between the PU and the substrate, the surface upon peeling is shiny and clean. Otherwise, the failure is classified as cohesive failure.

In the case of cohesive failure, the fracture takes place inside the PU interlayer or substrates displaying a very rough surface during peeling. Meaning that, at the temperature when cohesive failure is observed, the strength of the PU interlayer is lower than the strength of the bonding between the PU and the acrylic or glass substrate. The test stops when the measured de-bonding rate reaches 2” per hour.

For durability, high temperature adhesion properties as measured by the Creep Peel Test are important because military vehicles are often exposed to climate conditions where the vehicle can reach temperatures within a 70-80 °C range under the sun during hot summer days or desert regions.

Both Tables VII and VIII show that the optical aliphatic PU IM-800A and IM-800B, which have low modulus and very high adhesion strength to acrylic, have displayed cohesive failures around 70-80 °C. These PUs are low temperature processing interlayers.

However, IM-2500 and IM-1600 with higher modulus and lower adhesion strength than the 800 series, have displayed very high bonding strength to both glass and acrylic at temperatures between 70 °C and 80 °C and they process during lamination at higher temperatures than the IM-800 series PUs.

TABLE VII. CREEP PEEL TEST TO ACRYLIC-ADHESIVE PEEL AND COHESIVE PEELING

Polyurethane Film	Thickness (mils)	50 °C	60 °C	70 °C	80 °C	90 °C
IM-2500	25	1 mm	1 mm	1 mm	12 mm	n/a
IM-1600	50	1 mm	1 mm	1 mm	16.5 mm	n/a
IM-800A	50	6 mm	67 mm	Cohesive		
IM-800B	50	1 mm	8 mm	73 mm	Cohesive	

TABLE VIII. CREEP PEEL TEST TO GLASS-ADHESIVE PEEL AND COHESIVE PEELING

Polyurethane Film	Thickness (mils)	50 °C	60 °C	70 °C	80 °C	90 °C
IM-2500	25	0 mm	0 mm	1 mm	23 mm	86 mm
IM-1600	50	0 mm	0 mm	1.5 mm	25.5 mm	Cohesive
IM-800A	50	3 mm	52 mm	Cohesive		
IM-800B	50	2 mm	27.5 mm	Cohesive		

A summary of the optical aliphatic PU film properties tested so far is provided in Table IX. The wide range of tear strength, tensile modulus, short hardness A, and adhesion levels at room and high temperatures will allow the designer flexibility to select the right PU as adhesive interlayer to bond two materials.

IM-2500 is a tough film with high modulus, very high tensile strength and tear strength, designed to autoclave at high temperature when combined with PVB. Suitable for glass/glass impact laminates such as storm windows and security glazing. IM-800A and IM-800B are low modulus, low processing temperature and exceptional adhesion to acrylic adhesive interlayers. In addition, IM-800B high shear resistance and great cold temperature impact makes it suitable for aircraft applications where bridging the coefficient of thermal expansion of two different materials and absorption of thermal and mechanical shock are important characteristics.

IM-1600 is a mid range modulus and processing temperature adhesive interlayer designed for a broad range of glass/polycarbonate laminated glazing and suitable for down-line processing.

Further studies are underway to understand and measure the long term effects of solar radiation, UV energy, heat and humidity on the properties of the optical aliphatic PU films. Table X and XI show the little impact that QUV conditions has on IM-1600 and IM-2500 film properties after so many hours of exposure. For example, tensile strength and tear strength change very little after 1500 and 2000 hours of exposure.

TABLE IX. SUMMARY OF OPTICAL ALIPHATIC POLYURETHANE FILM PROPERTIES

Properties	Test Method	IM-2500	IM-1600	IM-800A	IM-800B
Short Hardness A	ASTM D-2240	95	80	70	70
Tensile Strength @ break, psi	ASTM D-412	6500	6500	4100	4000
Ultimate Elongation, %	ASTM D-412	350	500	510	440
100% Tensile Modulus, psi	ASTM D-412	1800	300	300	280
TMA Peak, °C	TMA	144	125	88	88
Temperature, °C **Adhesion to Glass @ >100 pli**		125	115	90	90
Adhesion to Acrylic, pli **at 250 °C**		20	25	65	38.5
Creep Peel Test to Acrylic, mm **70 °C** **80 °C**		1 12	1 16.5	Cohesive n/a	8 Cohesive
Creep Peel Test to Glass, mm **70 °C** **80 °C**		1 23	1.5 25.5	Cohesive n/a	Cohesive n/a

TABLE X. ACCELERATED WEATHERING QUV EXPSURE HOURS FOR IM-1600

Properties	0	500	1000	1500	2000
Tensile Strength @ break, psi	4000	4000	3900	3500	4300
100% Tensile Modulus, psi	400	380	440	420	370
300% Tensile Modulus, psi	3500	2800	2500	2400	2000
Ultimate Elongation, %	300	300	280	280	360
Tear Strength, pli	140	125	125	125	170
Yellowness Index	0.42	1.73	2.08	1.86	2.52

TABLE XI. ACCELERATED WEATHERING QUV EXPSURE HOURS FOR IM-2500

Properties	0	500	1000	1500	2000
Tensile Strength @ break, psi	6900	5700	6600	6800	6900
100% Tensile Modulus, psi	1400	1200	1300	1400	1200
300% Tensile Modulus, psi	4800	4500	5900	4900	4000
Ultimate Elongation, %	300	300	300	360	410
Tear Strength, pli	470	400	420	470	440
Yellowness Index	1.60	1.74	1.85	2.01	2.24

So far we have found that, once the IM-1600 film is laminated to glass, the adhesion values are higher than 130 pli. An absolute value has been difficult to measure, since the 0.016” polycarbonate film used to reinforce the PU, keeps breaking before the PU delaminates.

Data will soon be available from testing full size laminated glass parts in a weathering/aging chamber where we can adjust temperature by convective and infrared heat, humidity, UV radiation, and vibration. Five pieces of laminated glass windshield size can be tested at a time. Each glass piece can also be mounted in a frame assembly to simulate the installation in a particular vehicle.

In summary, optical aliphatic PUs are the most cost-effective solution and the material of choice for high performance bullet resistant glazing including side windows and windshields for cars and military vehicles, aircraft and trains, security windows for prisons, banks, and buildings.

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