CHAPTER IV

EXPERIMENT

4.1 Materials

The materials used in this research are benzoxazine resin, urethane resin and Kevlar™ fiber from DuPont. Benzoxazine resin is based on bisphenol, aniline and paraformaldehyde. The bisphenol A was supplied by Thaipolycarbonate Co.,Ltd (TPCC). Para-formaldehyde was purchased from Merck Company, and aniline was purchased from Panreac Quimica SA Company. Urethane prepolymer was prepared from isophorone diisocyanate and polyether polyol. The isophorone diisocyanate was obtained from Degussa-Huls AG and the polyether polyol was supported by TPI Polyol CO., LTD.

4.2 Preparation of Resins

4.2.1 Benzoxazine resin preparation

Benzoxazine monomer was synthesized using bisphenol A, aniline and paraformaldehyde at a 1:2:4 molar ratio. The reactant mixture was constantly stirred at 110°C for approximately 30 minutes. This resin was prepared based on a patented solventless method (Ishida, 1996). The benzoxazine monomer was obtained as clear-yellowish solid powder at room temperature. The product was then ground into fine powder and can be kept in a refrigerator for future-use.

4.2.2 Urethane resin preparation

The urethane prepolymer was prepared using isophorone diisocyanate with diol of MW 2000 at a 1:2 molar ratio. Isophorone diisocyanate and diol were mixed in a distillation flask and the mixture was stirred under nitrogen stream at 90°C for two

hours. In the reaction, 0.4 g of dibutyltin dilaurate was used as a catalyst. After that, the mixture (urethane prepolymer) was cooled to room temperature and was kept in a refrigerator.

4.3 Benzoxazine/Urethane Binary Mixture Preparation

The benzoxazine monomer was mixed with the urethane prepolymer to provide Ba/PU mixture at the desirable mass fraction. The mixture was heated to about 80°C in an aluminum container and was thoroughly mixed by hand for about 15-30 minutes until a homogeneous mixture was obtained. The weight ratios of the benzoxazine (BA) and urethane (PU) binary mixtures at 90/10 (BA/PU 90/10), 80/20 (BA/PU 80/20), 70/30 (BA/PU 70/30) and 60/40 (BA/PU 60/40), were evaluated as potential matrices for Kelar™-reinforced composites for a ballistic armor.

4.4 Processing Method of Composites

The Kevlar™ fabrics were pre-impregnated with the binary mixture resins using the hand-lay up procedure at 80°C. The weight fraction of the fiber was kept constant at approximately 70-80% by weight. The molding compound was compression-molded using a compression molder at 160°C and at a hydraulic pressure of 150 kg/cm^2 for 120 minutes. The samples were then removed from the compression molder to an oven for post-curing at 170°C, 180°C, and 200°C for 120 minutes. The specimens were finally left to cool down to room temperature and were ready for characterizations.

4.5 Characterization Methods

4.5.1 Polymerization conditions and thermal property assessment

The polymerization behaviors of the benzoxazine resin/urethane prepolymer, mixtures and their prepregs were examined using a differential scanning calorimeter (DSC) model 2910 from TA Instruments. All samples were placed in a non-hermetic aluminum pan with lid. The mass of the sample is in range of 3-5 mg. The experiment was performed at a heating rate of 10°C/min under nitrogen purging. The glass transition of the alloys and their composites were obtained using the DSC scan in the range of 50-300°C using heating rate of 10°C/min under N_2 purging.

4.5.2 Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of all samples under various curing methods were acquired by using a Spectrum GX FT-IR spectometer from Perkin Elmer. The apparatus is equipped with a KBr beam splitter and a deuterated triglycine sulfate (DTGS) detector. A small amount of a solid sample, preferably 0.5-1.0 mg, was ground and casted on a potassium bromide (KBr) disk. The sample was sufficiently thin with optical thickness of a fraction of a millimeter in compliance with the thickness specified under the Beer-Lambert's law. The sample was then mounted on a sample holder. All spectra were taken with 32 scans at a resolution of 4 cm^{-1} and a spectral range of 4000-400 cm^{-1}.

4.5.3Thermal degradation evaluation

Thermal stability and thermal decomposition of the cured polymer alloys were studied using a Perkin Elmer's TG/DTA thermogravimetric analyzer model SII Diamond. The experiment was done using a heating rate of 20°C/min under nitrogen atmosphere. The temperature was ramped from 30°C to 900°C using a sample mass of about 15-20 mg. The degradation temperature at 5% weight loss and the char yield at 900°C were recorded for each specimen.

4.5.4 Density measurement

The density of the polymer alloys and the Kevlar^{TM} fiber composites were measured by water displacement method according to ASTM D792-91 (Method A). All specimens were prepared in a rectangular shape of 50 mm×25 mm×1 mm and weighted both in air and in water.

The density was calculated using the following equation:

$$\rho = \left(\frac{A}{A - B}\right) \times \rho_o \qquad (4.2)$$

where ρ = Density of the specimen (g/cm^3)

A = Weight of the specimen in air (g)

B = Weight of the specimen in liquid (g)

ρ_o = Density of the liquid at the given temperature (g/cm^3)

4.5.5 Flexural property measurement

A universal testing machine (model 5567) from Instron Co., Ltd. was used to determine flexural properties of composite specimens. The test method used was a three-point bending mode with a support span of 32 mm at a constant cross head speed of 0.85 mm/min. The dimension was 25 mm in width, 50 mm in length, and 2 mm in thickness. The flexural properties were determined using ASTM D 790M-93 according to the following equations:

$$E_B = \frac{L^3 m}{4bd^3} \qquad (4.3)$$

$$S = \frac{3PL}{2bd^2} \qquad (4.4)$$

where E_B = Flexural modulus (MPa)

S = Flexural strength (MPa)

P = Load at a given point on the load-deflection curve (N)

L = Support span (mm)

b = Width of beam tested (mm)

d = Depth of beam tested (mm)

m = Slope of the tangent to the initial straight-line portion of the load-deflection curve (N/mm)

4.5.6 Dynamic mechanical analysis

A dynamic mechanical analyzer (DMA) model DMA242 from NETZSCH was used to investigate specimens' dynamic mechanical properties. The dimension of each specimen was 50 mm×10 mm×2 mm. The strain was applied sinusoidally with a frequency of 1 Hz and the specimen was heated at a rate of 5°C/min from room temperature to 270°C. The storage modulus (G'), loss modulus (G''), and loss tangent (tan δ) were then obtained. The glass transition temperature was taken as the maximum point on the loss modulus curve in the temperature sweep test.

4.5.7 Fire test

The ballistic tests were made using 3 different classes of ammunitions. The tested composite panel was approximately 12.5 cm×12.5 cm with varied thickness depending on the number of layers of Kevlar™ cloth used. Each plate was impacted with only one projectile. The Kevlar™–reinforced polybenzoxazine alloy plates were about 1.5 mm thick corresponding to 10-plies of the laminated composite. The laminates were tested using a 9 mm handgun as shown in Figure 4.2 and were impacted by a standard grain of a round lead projectile with lead outer coating. The first experiment was aimed to evaluate the most suitable composition of the matric alloys for ballistic protection.

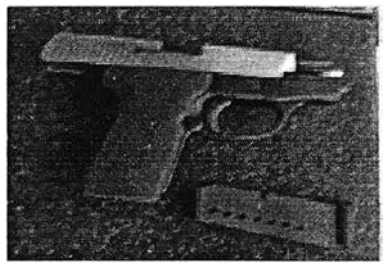

Figure 4.1 The 9 mm handgun for the fire test

The laminates with a combined thickness of 20 and 30 plies were tested with a standard 124 grain of a round lead projectile with copper outer coating (i.e. full metal jacket ammunition) as shown in Figure 4.1. The impact velocity obtained from this projectile was complied by the NIJ standard of level II-A.

The laminates with a combined thickness of 40, 50 and 60 plies were tested with a test weapon having an impact velocity following NIJ standard of level III-A. The velocity of each shot was recorded using a triggered timer system, as shown in Figure 4.2. For these laminates, the average velocity measured was 426 m/s.

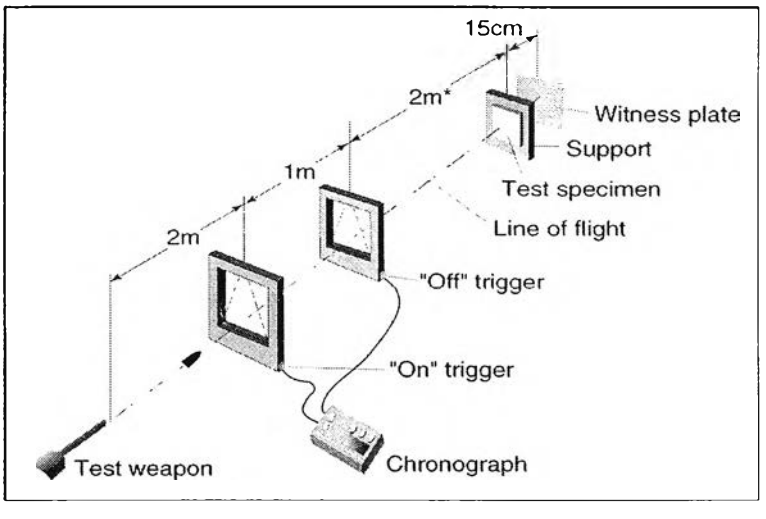

Figure 4.2 Testing scheme used for the NIJ standard ballistic test

Table 4.1: Complete descriptions of all composite laminates used in the fire tests

Fire test	Number	Type of matrix	Number of piles
I	1a	epoxy	10+10
	1b	100/0 BA/PU	10+10
	1c	90/10 BA/PU	10+10
	1d	80/20 BA/PU	10+10
	1e	70/30 BA/PU	10+10
	1f	60/40 BA/PU	10+10
2	2a	80/20 BA/PU	10+10
II-A	2b	80/20 BA/PU	20
	2c	80/20 BA/PU	10+10+10
	2d	80/20 BA/PU	20+10
	2e	80/20 BA/PU	30
3	3a	80/20 BA/PU	20+10+10
III-A	3b	80/20 BA/PU	30+20
	3c	80/20 BA/PU	10+10+30
	3d	80/20 BA/PU	30+20+10
	3e	80/20 BA/PU	30+10+10+10

4.5.8 Interfacial bonding examination

Interfacial bonding of the ballistic composite was investigated using a scanning electron microscope (SEM) at an acceleration voltage of 15 kV. All specimens were coated with thin gold film using a JEOL ion sputtering device (model JFC-1100E) for 4 min to obtain a thickness of approximately 30Å and the micrographs of the specimen's fracture surface were taken. The obtained micrographs were used to qualitatively evaluate the interfacial interaction between the BA/PU matrix resin and the Kevlar^{TM} fiber.