

Kevlar™ Fiber-Reinforced Polybenzoxazine Alloys for Ballistic Impact Applications

Sarawut Rimdusit^{1,*}, Somsiri Pathomsap¹, Pornnapa Kasemsiri¹, Chanchira Jubsilp², and Sunan Tiptipakorn³

¹Polymer Engineering Laboratory, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

²Department of Chemical Engineering, Faculty of Engineering, Srinakharinwirot University, Khong 16, Ongkharak, Nakhonnayok 26120, Thailand

³Department of Chemistry, Faculty of Liberal Arts and Science, Kasetsart University, Kamphaeng Saen, Nakhon Pathom 73140, Thailand

E-mail: sarawut.r@chula.ac.th*

Abstract. A light weight ballistic composites from Kevlar™-reinforcing fiber having polybenzoxazine (BA)/urethane prepolymer (PU) alloys as a matrix were investigated in this work. The effect of alloy compositions on the ballistic composite properties was determined. The increase of the elastomeric PU content in the BA/PU alloy resulted in samples with tougher characteristics; the storage modulus of the Kevlar™-reinforced BA/PU composites increased with increasing the mass fraction of polybenzoxazine. A ballistic impact test was also performed on the Kevlar™-reinforced BA/PU composites using a 9 mm handgun and it was found that the optimal composition of BA/PU alloys should be approximately 20wt% of PU. The extent of the delaminated area and interfacial fracture were observed to change with the varied compositions of the matrix alloys. The appropriate thickness of Kevlar™-reinforced 80/20 BA/PU composite panel was 30 plies and 50 plies to resist the penetration from the ballistic impact equivalent to levels II-A and III-A of NIJ standard. The arrangement of composite panels with the higher stiffness panel at the front side also showed the best efficiency ballistic penetration resistance.

Keywords: Polymer alloys, Kevlar™ fiber, ballistic composite, polybenzoxazine, urethane prepolymer.

ENGINEERING JOURNAL Volume 15 Issue 4

Received 23 June 2011

Accepted 3 September 2011

Published 1 October 2011

Online at <http://www.ej.eng.chula.ac.th/eng/>

DOI:10.4186/ej.2011.15.4.23

1. Introduction

In the past, protective armors were traditionally made of metals. With the development of the thermoplastic polymers and synthetic fibers in recent years, hard armor systems with lighter weight have been produced, which combine the use of metals, and/or ceramics with polymeric fabrics as well as fiber-reinforced polymer composites. The development of armor materials has been focused on reducing the weight of the existing armor materials because the reduction of weight could help in saving energy as well as increasing mobility [1, 2]. During the Vietnam War, it was reported that soft armors prepared from fabrics of fiber glass and nylon were used for ballistic protection [3]. Some of the commercial fibers used to manufacture armors include aramids (KevlarTM or TwaronTM) [4], nylon fiber [5], polyethylene fiber (SpectraTM or DyneemaTM) [6, 7], and carbon fiber [8, 9]. The fibers should provide excellent impact resistance required for ballistic armors, and have high sonic velocity and high specific energy absorption as well as the capability to distribute kinetic energy upon ballistic impact [5]. Typical polymeric materials used in ballistic applications are ultra high molecular weight polyethylene (i.e. DyneemaTM) and para-aramid fibers (i.e. Kevlar and Twaron). In general, Kevlar has been introduced as ideal type of base material for ballistic protection due to its outstanding thermal properties and high tensile properties. Its highly crystalline and highly oriented fine structure result in high modulus required for enhanced sonic velocity [3, 6, 10]. Consequently, the fiber is considered as a major reinforcing constituent for ballistic composites in this work. In composite material, even though each parent material (i.e. the fiber and the matrix) cannot provide ballistic resistant properties by itself; the combination of the two components had been found to exhibit an enhanced level of ballistic protection.

In general, an enhanced ballistic performance of light-weight armor requires its ability to deform and/or break-up the projectiles into small fragments and prevent the penetration of the projectile by absorbing projectile's kinetic energy. Absorption of kinetic energy of the composite composes of several mechanisms, including tensile failure of fibers, elastic deformation of composite, interlayer delamination, shear between layers in the composite, and inertia effect. Kinetic energy is absorbed and attributed according to key factors such as fiber mechanical properties, direction of fiber arrangement, matrix properties and interfacial strength [11-15].

Recently, the types of matrix binders for ballistic composites are such as thermoplastic resins [16, 17], thermosetting resin [12, 18, 19], and the alloys between thermoplastics and thermosets [14]. Other binders for KevlarTM-reinforced composites consisted of urethanes [15], epoxy resin [20, 21], polyester [22] styrene-isoprene-styrene [23]. In general, the function of the matrix resin is to hold the fibers firmly together in a three-dimensional array of crossing layers. The selection of a resin for the ballistic composite depends on its required characteristics such as rigidity, environmental resistance to thermal, wear, combustibility, process ability, and shelf-life. The amount of resin necessary to consolidate the fibers has been reported to be approximately 75-80 wt% [24, 25]. If the amount of resin used is substantially increased above the desired amount the matrix, it results in a major part of the armor volume weakening the materials. However, if the resin is less than that required to wet all fibers, this causes the fibers in the composite have not enough properties to consolidate and held in the proper position upon impact; then, the fiber tends to separate relatively easily allowing the projectile to pass through before the fiber absorb force [26]. In general, the resins used as a binder in ballistic armor have an adhesive characteristic with respect to the fiber, while the tensile strength of the resin should be lower than that of the fiber. That is, upon impact, the fiber will function predominantly to transmit impact force along its longitudinal axis. In principle, it is required that the resin should not hold the fiber too rigidly along the surface but allow some small amount of movement of the fiber surface longitudinally within the resin. Obviously, the composite structure resists and provides a limited fiber spreading transversely to the fiber axis upon projectile impact. In some previous works [19, 26], phenolic resins provide a future class of preferred resins for a composite armor. Phenolic resins are inexpensive and easy to handle employing conventional technology. However, they do not bond too firmly to ballistic fiber (especially Kevlar fiber); the moisture is driven from the resins during a curing stage (one additional step in the composite manufacturing process). Polybenzoxazine, a novel class of phenolic resins, has a wide range of mechanical and physical properties that can be tailored to various needs. The polymer can be synthesized by ring-opening polymerization of the aromatic oxazines with no by-products released upon curing, [27]. The property balance of the material renders the polymer

with very low A-stage viscosity, near-zero shrinkage, low water absorption, and fast development of mechanical properties as a function of curing conversion [28-30].

In this study, polybenzoxazine alloying with urethane elastomer used as matrix for ballistic armor composites were evaluated due to one major outstanding property of benzoxazine resin related to an ability to form hybrid network with several other resins for tailor-made behaviors [31-34]. Urethane elastomer was also used to alloy with benzoxazine resin to improve thermal stability and mechanical properties of the resulting polymer hybrids [34]. In this work, the word “alloy” was used in stead of “blend” because there has been evident from some previous works [35-37] that the chemical bonding were generated between polybenzoxazine and urethane elastomer. This makes it possible to fine tune and enhance the properties of the ballistic armor composites.

2. Experimental

2.1. Raw Materials

The materials are benzoxazine resin, urethane prepolymer and Kevlar™ from DuPont. Benzoxazine resin based on bisphenol-A, paraformaldehyde and aniline was synthesized by patented solventless method [27]. The bisphenol-A was supplied by Thai Polycarbonate Co., Ltd (TPCC). Paraformaldehyde and aniline were purchased from Merck Company, and Panreac Quimica SA Company, respectively. The obtained benzoxazine resin is clear-yellowish solid at room temperature. Urethane prepolymer was prepared from isophorone diisocyanate and polyether polyol (diol, MW=2000) using dibutyltin dilaurate as a catalyst. The isophorone diisocyanate was supplied by Degussa-Huls AG and the polyether polyol was available from TPI Polyol Co., Ltd. The urethane prepolymer is clearly viscous liquid at room temperature and it was kept in a refrigerator.

2.2. Composite Processing

The benzoxazine resin was mixed with the urethane prepolymer to provide BA/PU mixtures at the desirable mass fraction. The mixture was heated to about 80°C in an aluminum pan and was thoroughly mixed manually for about 15-30 minutes until it was homogeneous. The weight ratios of binary mixtures at 90/10, 80/20, 70/30, and 60/40 BA/PU resins were evaluated as potentially matrices for Kevlar™-reinforced composites.

The Kevlar™ fabrics were compounded with binary mixture resins using the hand-lay up procedure at 80°C. The weight fraction of fibers was kept constant at 70-80%. The molding compound was compression-molded using a compression molder at 160°C for 2 hours. The samples were then post-cured in an oven at 170°C, 180°C, and 200°C, each step for 2 hours. The fully cured specimens were left at room temperature and used for further characterization.

2.3. Sample Characterization

Dynamic mechanical analyzer (DMA) model DMA242 from NETZSCH was used to investigate the viscoelastic properties of the specimens. The strain at amplitude of 30 μm was applied sinusoidal with a frequency of 1 Hz. The specimen was heated at the rate of 5°C/min from room temperature to 270°C and the specimen dimension was 50mm×10mm×2 mm.

Thermal decomposition characteristic of the cured polymer alloys and the composites were studied using a thermogravimetric analyzer from Perkin Elmer (Diamond TG/DTA). The experiment was measured using a heating rate of 20°C/min under nitrogen atmosphere. The temperature was ramped from 30°C to 880°C using the sample mass of about 15-20 mg.

Instron Universal testing machine, Model-5567 was used to determine flexural properties of composite specimens. The test method used was a three-point bending mode according to ASTM D790-00 (Method I) with a support span of 32 mm with a constant cross head speed of 0.85 mm/min. The specimen dimension was 50mm×25mm×2mm.

The ballistic tests were made using three different ammunitions. The tested composite plate with a dimension of 12.7cm×12.7cm was prepared; each plate was impacted with one projectile. The Kevlar™-reinforced polybenzoxazine alloy plates were 3.2 mm in thickness corresponding to two 10-

ply laminates. The laminates with 20 plies were tested using a 9mm handgun with a standards grains round lead projectiles having a lead outer coating. The first experimental locations chosen for projectile impact were selected so as to evaluate the most suitable composition of the matrix alloys. In addition, the laminates with 20 and 30 plies were tested with standard 124 grains round lead projectile with a copper outer coating (Full Metal Jacket) typically used in the 9mm handgun. The impact velocity used was recommended by the NIJ standard for level II-A protection. The laminates with 40, 50 and 60 plies were tested with a test weapon, meeting the impact velocity according to standard for level III-A. Measured average velocity was determined as 426 m/s for the tests. The velocity of each shot was measured using a triggered timer. The damaged areas on each sample were evaluated.

Interfacial bonding of the composites after they were impacted was evaluated using a scanning electron microscope (JEOL, model JSM-5800LV) at an acceleration voltage of 15 kV. All specimens were coated with thin film of gold using an ion sputtering device (Balzers, model SCD040) for 4 minutes to have a thickness of approximately 30nm. The obtained micrographs were used to evaluate qualitatively the interfacial interaction between the matrix resin and the fiber and to study the mechanisms of ballistic energy absorption.

3. Results and Discussion

3.1. Properties of Cured BA/PU Alloys

The dynamic mechanical properties of the BA/PU polymer alloys are shown in Fig. 1. All specimens, i.e., 100/0 BA/PU, 80/20 BA/PU, 70/30 BA/PU, and 60/40 BA/PU were fully cured to yield highly cross-linked structure. As seen in Fig. 1, the storage moduli (E') in the glassy state of the BA/PU polymer alloys expectedly decreased with increasing the PU fraction due to the incorporation of the more flexible structure of PU in the alloys as already described by Rimdusit et al. [35]. The urethane prepolymer molecule contains a large number of ether linkages in which the internal movement of the molecules is very active compared with the rigid phenolic structure of the polybenzoxazine resulting in the lowering of the stiffness of the alloys. From Fig. 1, the storage moduli at room temperature of the BA/PU polymer alloys were systematically reduced from 5.7 GPa to 1.4 GPa with the addition of the PU from 0 to 40 wt%. On the other hand, the modulus in the rubbery plateau moduli tended to increase with the mass fraction of the PU. This could be implied that the crosslink density of the fully cured specimens increased with increasing the PU content. Theoretically, the relationship between the crosslink density and the rubbery plateau modulus could be exhibited as presented in Eq. (1) [36, 37].

$$E' = 3\nu_e RT \quad (1)$$

where E' is the rubbery plateau modulus at $T_g+50^\circ\text{C}$ in MPa, (ν_e) is crosslink density in mol/m^3 , R is gas constant and T is absolute temperature at $T_g+50^\circ\text{C}$. The calculated values of crosslink density are shown in Table 1.

Table 1. Calculated values of crosslink density of the BA/PU Alloys.

BA/PU alloys	T_g ($^\circ\text{C}$)	Rubbery plateau modulus at $T_g+50^\circ\text{C}$ (MPa)	Calculated Crosslink density (mol/m^3)
100/0	165	92.8	22.4
80/20	175	168.8	39.1
60/40	220	365.2	69.6

When the crosslink density increases with PU content as shown in Table 1, the mobility of the molecular chain in the alloy decreases. This could relate to the glass transition temperature of the alloys. Glass transition temperatures ($T_{g,s}$) of the BA/PU polymer alloys were also detected in the dynamic mechanical thermograms based on the maxima of their loss moduli (E'') as also shown in Fig. 1. The T_g values of the BA/PU polymer alloys showed a synergistic behaviors as $T_{g,s}$ were observed to increase to

the values greater than that of both parent polymers with increasing the amount of the PU fraction. The T_g s of the PU and the polybenzoxazine were reported to be about -70°C and 165°C , respectively [35]. However, the T_g s of the fully cured BA/PU polymer alloys were observed to be 165°C in 90/10 BA/PU, 175°C in 80/20 BA/PU, 217°C in 70/30 BA/PU, and 220°C in 60/40 BA/PU. From Fig. 1, the increase of PU content resulted in the increase in the crosslink density of the polymer alloy. This could be observed from the increase of the storage modulus in the rubbery plateau region and the T_g s as previously reported [35]. The phenomenon was attributed to the additional crosslinking caused by the reaction between an isocyanate group of urethane resin and a hydroxyl group of polybenzoxazine after the phenolic hydroxyl group from the ring opening of benzoxazine resin was produced [38-39].

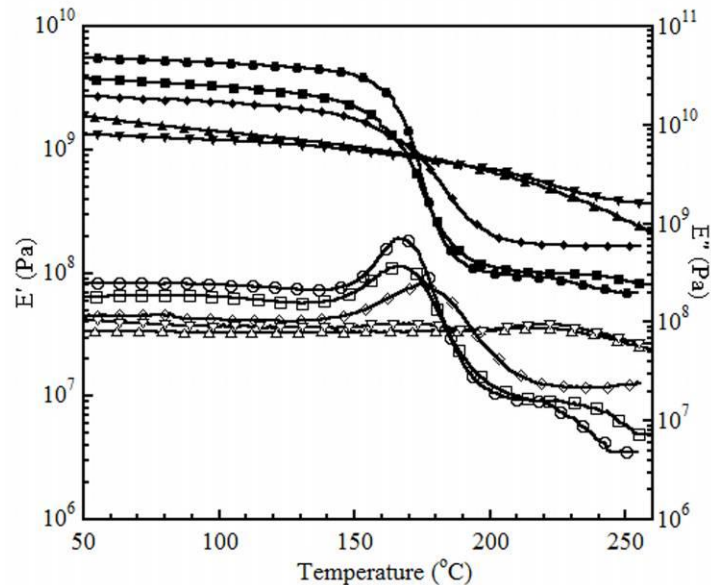


Fig. 1. Viscoelastic properties of the BA/PU alloys at various mass compositions:
 E' (●) 100/0, (■) 90/10, (◆) 80/20, (▲) 70/30, (▼) 60/40;
 E'' (○) 100/0, (□) 90/10, (◇) 80/20, (Δ) 70/30, (▽) 60/40.

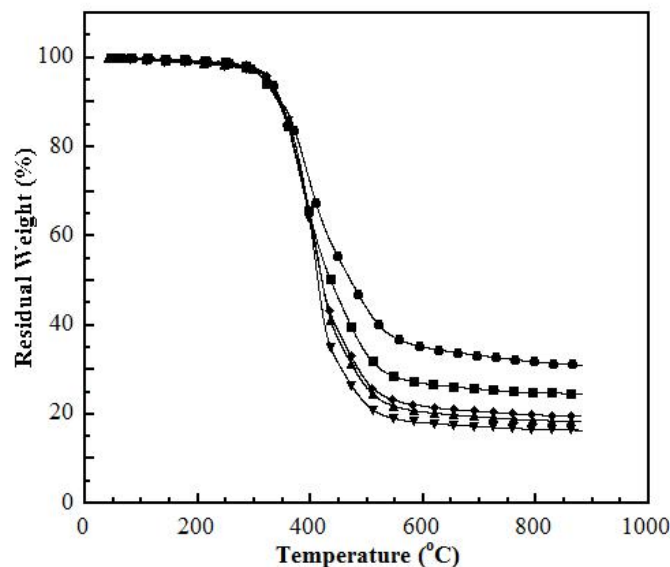


Fig. 2. TGA thermograms of the BA/PU polymer alloys at various compositions:
 (●) 100/0, (■) 90/10, (◆) 80/20, (▲) 70/30, (▼) 60/40.

Figure 2 shows a TGA profile of the polybenzoxazine and BA/PU polymer alloys at investigated compositions. Generally, degradation temperature (T_d) is one of the key parameters needed to be considered for high temperature applications. The results of this study revealed that the T_d of the polymer alloys were significantly higher than that of the polybenzoxazine. The T_d of the

polybenzoxazine at 5% weight loss was determined to be 315°C whereas the T_d values of the BA/PU polymer alloys were approximately 326°C. These results could be due to the reaction of the isocyanate of the PU and the hydroxyl group of the polybenzoxazine helped increase a crosslink density of the polymer alloys as explained earlier. Therefore, one benefit of incorporating the PU into the polybenzoxazine network was to improve the thermal stability of the polybenzoxazine as a result of crosslinking density enhancement. In addition, the residual weight at 800°C of the BA/PU polymer alloys was found to decrease with increasing the PU fraction in the polymer alloys which was consistent with the value previously reported [35]. This can be explained as the structure of the polybenzoxazine contained a more thermally stable benzene rings compared to the mostly aliphatic structure of the diol in the urethane. Consequently, the addition of the PU resulted in the lowering of the char yield in the polymer alloys.

3.2. Properties of KevlarTM-reinforced BA/PU Alloys

3.2.1. Dynamic Mechanical and Mechanical Properties

The dynamic mechanical analysis of the KevlarTM-reinforced alloys is shown in Fig. 3. In the figure, the storage moduli of KevlarTM-reinforced BA/PU alloys at 0- 40 wt% of PU with the fibers kept at 80 wt% were presented. It could be noticed that the storage moduli of the composites systematically decreases with increasing the PU fraction in the polymer alloys as a matrix of the composites, i.e., 16.4 GPa for KevlarTM-reinforced 100/0 BA/PU alloys to 2.8 GPa for KevlarTM-reinforced 60/40 BA/PU alloys. Moreover, the T_{gs} obtained from the maxima of the loss moduli curve of the KevlarTM-reinforced BA/PU alloys were found to increase with increasing the amount of the PU fraction, i.e., 180°C in 90/10 BA/PU, 195°C in 80/20 BA/PU, 218°C in 70/30 BA/PU, and 235°C in 60/40 BA/PU as also shown in Fig. 3. In addition, T_{gs} of Kevlar-reinforced composites were significantly higher than those of the neat BA/PU alloys comparing at the same mass fraction of the PU in the alloys. In general, the T_{gs} of urethane elastomer and polybenzoxazine were reported to be about 70°C and 165°C, respectively [36]. In our study, T_{gs} of the copolymers were also found to increase with the mass fraction of urethane. This enhancement in the T_g could be attributed to the increase in the crosslink density of the binary systems as previously observed in the DMA investigation of the resulting copolymers [36]. Furthermore, this phenomenon could be due to the substantial interfacial adhesion between the fiber and the matrix [40].

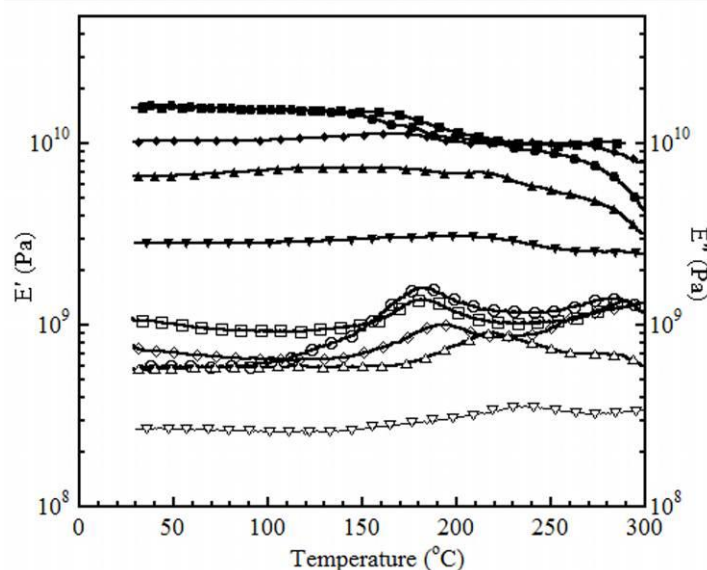


Fig. 3. Viscoelastic properties of KevlarTM-reinforced BA/PU alloys at various mass compositions:
 E' (●) 100/0, (■) 90/10, (◆) 80/20, (▲) 70/30, (▼) 60/40;
 E'' (○) 100/0, (□) 90/10, (◇) 80/20, (Δ) 70/30, (▽) 60/40.

Flexural properties of the KevlarTM-reinforced polybenzoxazine alloys were depicted in Fig. 4. It could be observed that the flexural strength of the alloys was decreased with the PU content from 163 MPa (of pure polybenzoxazine) to 52 MPa (at 40wt% of PU). We also observed the strengths of the

composites decrease in a linear manner with the increase of the PU in the matrix alloys. In addition, flexural moduli of the composites were found to significantly decrease with increasing the amount of the PU in the alloys from 18.3 GPa at 0 wt% of PU to about 7.5 GPa at 40 wt% of PU as illustrated in Fig. 4. The phenomenon was due to the fact that the addition of the rubbery urethane polymer into the rigid polybenzoxazine was able to lower either the strength or the stiffness of the resulting polybenzoxazine alloys.

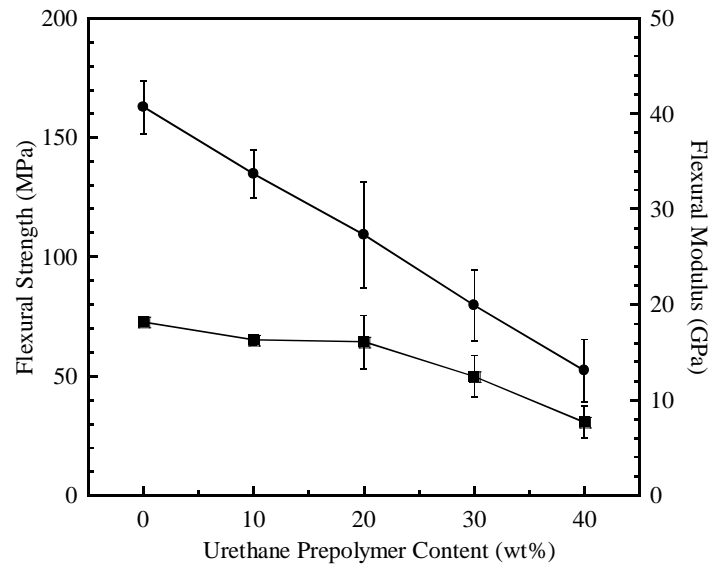


Fig. 4. Flexural properties of the KevlarTM-reinforced BA/PU alloys at various PU contents: (●) Flexural strength; (■) Flexural modulus.

3.2.2. Thermal Stability of the Composites

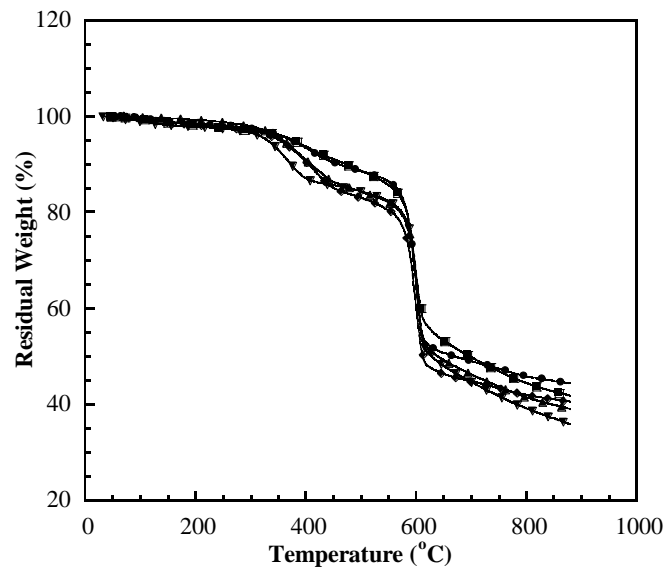


Fig. 5. Thermal degradation behaviors of the KevlarTM-reinforced BA/PU alloys at various mass ratios of BA/PU: (●) 100/0, (■) 90/10, (◆) 80/20, (▲) 70/30, (▼) 60/40.

From Fig. 5, the degradation temperatures (T_d s) at 5% weight loss of KevlarTM-reinforced polybenzoxazine alloys were found to increase systematically with increasing the mass fraction of the polybenzoxazine in the alloys. The T_d at 5% weight loss of the KevlarTM-reinforced polybenzoxazine alloys with the PU compositions of 0 to 40% by weight was ranging from 374°C to 329°C. Another

important feature in the thermograms is the weight residue at 800°C or the char yield of the composites which is related to the flammability of materials and is essential for some ballistic armor applications.

When the armor is penetrated, the heat is generated. The material could first decompose by thermally initiated mechanisms or thermo-oxidative decomposition. It has been reported that char could decrease the diffusion rate of decomposed, flammable gases toward the flame front and decrease the burning of the material [41]. The char yield was found to systematically reduce from 45.8 % to 39.1% with an incorporation of the PU from 0 to 40% by weight. This could be attributed to the fact that urethane contained aliphatic structure, while polybenzoxazine contained benzene rings [42]. Therefore, the increase in urethane content leads to the increase in aliphatic structure having less thermal stability and less char yield [38-39]. However, these values were all greater than those of the matrix alloys comparing at the same PU fraction. This is due to the fact that the char yields of the composites also included the additional residue of the Kevlar™ fiber which possessed a char yield of 44% at 600°C [3].

3.2.3. Firing Tests of the BA/PU Composite Armors

A series of ballistic tests were performed on the composite laminates which were made of Kevlar™ fabric impregnated with BA/PU mixtures and cured using the curing condition as suggested in the experimental section. The Kevlar™ fabric used has the areal density of about 0.016 g/cm². The dimension of the laminated specimens was 25.4mm×25.4mm×1.8mm, corresponding to 10 plies of the Kevlar™ cloth impregnated with about 20% by weight of the BA/PU mixtures. The densities of the composites were determined to be 1.26 g/cm³ at 60/40 BA/PU, 1.28 g/cm³ at 70/30 BA/PU, 1.29 g/cm³ at 80/20 BA/PU, 1.30 g/cm³ at 90/10 BA/PU and 1.31 g/cm³ at 100/0 BA/PU.

3.2.3.1. Low Level Ballistic Impact Test

The composite laminates fabricated with a thickness of 10 plies of the Kevlar™ at various the BA/PU alloy compositions mentioned above were tested using a 9mm handgun with standard lead projectiles having lead outer-coating. From the test results, the composite consisted of only 10 piles of Kevlar™ could not protect ballistic impact from the standard lead projectiles. Therefore the 20 piles of Kevlar™ panels i.e. 10/10 panel arrangement, at all BA/PU alloy compositions were selected for the following tests. Moreover, the bisphenol A-based epoxy-Kevlar™ composites (cured by amine hardener) at the same fiber content were also used to compare its ballistic impact performance with our BA/PU matrix alloys. From the fire test, although both composites with the 10/10 configuration of the composite panels could not resist the projectiles, the polybenzoxazine alloy composite panel exhibited obviously higher energy absorption than the epoxy composites. This could be noticed from the greater delaminated area of the polybenzoxazine composites in Figs. 6(a)-6(d). From Table 2, Figs. 6(c) and 6(d), the firing results also indicated that the 90/10 and the 80/20 mass ratios of the BA/PU matrix alloys exhibited ballistic penetration resistance in comparison with the other compositions of 100/0 BA/PU matrix as well as the epoxy matrix. However, only the composite from the 80/20 BA/PU matrix alloy exhibited 100% ballistic penetration resistance. In Fig. 6(d), the ballistic impact performance of the Kevlar™-reinforced 80/20 BA/PU alloys revealed relatively larger delaminated area than those of the epoxy matrix (Fig. 6(a)) and the polybenzoxazine matrix (Fig. 6(b)). The delaminated area has been known to be one major component of the energy absorption mechanisms in ballistic impact. Further increase the PU mass fractions to 30 wt% and 40 wt% in the composite matrices resulted in a poor ballistic impact resistance. This phenomenon confirms the necessity of identifying optimal fiber-matrix interactions in order to yield a composite system with outstanding ballistic performance. The variation in the BA/PU alloy compositions could allow an optimal interaction between the alloy matrix and its reinforcing fiber, which leads to obtaining the outstanding ballistic performance.

As previously mentioned and reported in the literature [14], the kinetic energy absorption of composite material composes several mechanisms, including tensile failure of fibers, elastic deformation of composites, interlayer delamination, shear between layers in the composite, and inertia effect. Kinetic energy absorption may be attributed to basic factors such as mechanical properties of the composite's constituent direction of fiber arrangement, as well as interfacial strength. Fracture morphology of the composite specimen is sometimes used to qualitatively evaluate the possible kinetic

energy absorption of the material. The fracture surfaces of KevlarTM-reinforced BA/PU alloys at various compositions of PU are depicted in Figs. 7(a)-7(d). The results reveals that the fracture surfaces near the center of ballistic impact of the KevlarTM- reinforced 80/20 BA/PU alloy (Fig. 7(b)) exhibited substantial level of adhesive failure in which the fibers were largely stripped off the matrix materials with only small fragments of the matrix remained adhere to the fibers. This fracture phenomenon could be clearly distinguished from that of the 60/40 BA/PU composites (Fig. 7(d)), which showed much lower degree of interfacial failure. The weaker mechanical properties due to the excessive presence of the soft PU component might be one reason of the observed predominantly cohesive failure in this composite. In other case, too strong adhesion between the KevlarTM fibers and the BA/PU matrix alloy might be attributed to the poor ballistic performance of the matrix resulting in the low degree of composite delamination mechanism. These results also confirmed the effect of the BA/PU alloy compositions on the interaction between the KevlarTM fibers and the alloy matrices and thus the ballistic performance of obtained polymer composites.

Consequently, the selection of a suitable matrix resin that renders the most energy absorption characteristics with particular reinforcing fiber used is crucial to the successful ballistic performance of the composite armor. It could be noted that the BA/PU alloy seemed to render a synergistic behavior in ballistic performance at the composition of 80/20 BA/PU with the most outstanding ballistic performance. Therefore, The 80/20 BA/PU alloy was further used to fabricate the composite armors for higher protection level evaluation.

Table 2. Comparison of resistance to penetration of low level ballistic impact test for different types of matrix with 10 piles/panel and 10/10 arrangement.

Type of Matrix	Resistance to Penetration		Remark
	First panel	Second panel	
Epoxy	No	No	-
Polybenzoxazine	No	No	-
90/10 BA/PU	Yes	Yes	-
80/20 BA/PU	Yes	Yes	100% ballistic penetration resistance

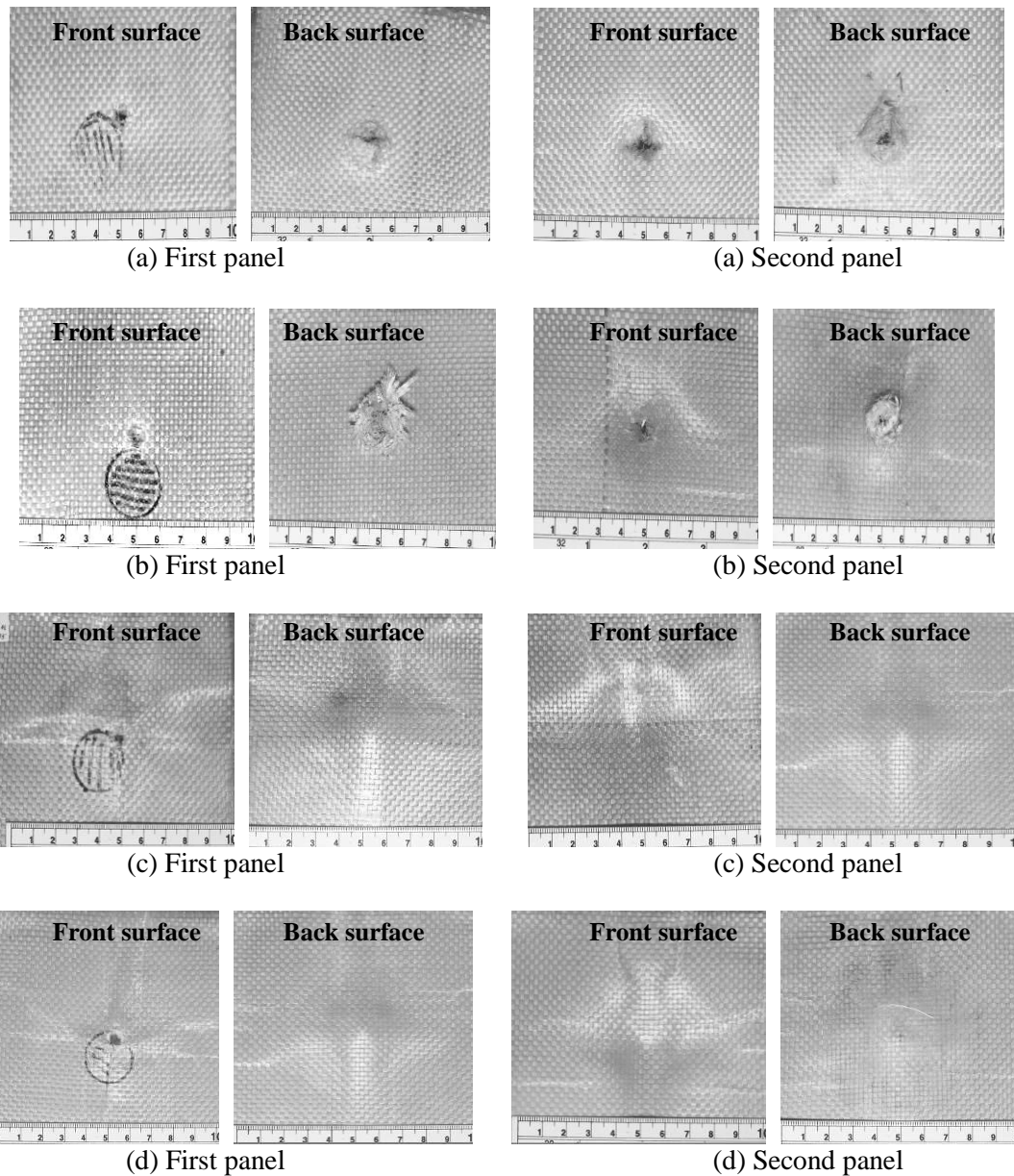


Fig. 6. Damaged and delaminated area of 10 piles/panel with the samples arrangement of 10/10 after impact with standard lead projectiles with lead outer-coating typically used in 9 mm: (a) Kevlar™-reinforced epoxy; (b) Kevlar™-reinforced polybenzoxazine; (c) Kevlar™-reinforced 90/10 BA/PU; (d) Kevlar™-reinforced 80/20 BA/PU.

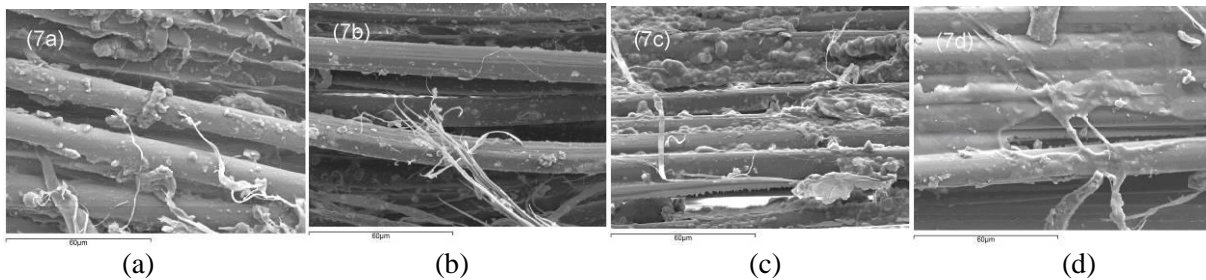


Fig. 7. SEM images of the fracture surface of the composites after impacted with standard lead projectiles (x 1000 magnification): (a) Kevlar™-reinforced polybenzoxazine; (b) Kevlar™-reinforced 80/20 BA/PU; (c) Kevlar™-reinforced 70/30 BA/PU; (d) Kevlar™-reinforced 60/40 BA/PU.

3.2.3.2. Ballistic Impact Test of NIJ Level II-A

The ballistic impact velocities required by NIJ standard for level II-A was used to study the effect of the composite panel thickness and arrangement based on the Kevlar™-reinforced 80/20 BA/PU alloys. The samples were prepared approximate thicknesses of 1.8mm, 3.5mm, and 5.0mm for panel manufactured 10, 20, and 30 pile composites, respectively. The areal densities were 0.48 g/cm^2 for the 10 piles, 0.48 g/cm^2 for the 20 piles, and 0.70 g/cm^2 for the 30 piles panel composites. The Kevlar™-reinforced 80/20 BA/PU composite samples with 20 piles, and 30 piles were tested in the NIJ standard. The 20-ply composites were arranged in 2 patterns, i.e., 10/10 and 20/0 configurations. In case of the 30-ply composites, they were arranged in 3 patterns, i.e., 10/10/10, 20/10/0, and 30/0/0 configurations.

The penetration resistance results of the composite after impact with projectile velocities for the NIJ level II-A ballistic test are shown in Table 3. All samples were fired with a 9 mm handgun, which is known to have a greater impact velocity than that required by the NIJ standard of level II-A. The individual value for the deformed depth as well as the averaged diameter of the damaged area of the BA/PU composites after impacted with the projectiles was reported. From the table, all composite laminates assembled to have a combined thickness of 20 plies of the Kevlar™ did not pass this level of the NIJ standard for ballistic protection. Eventually in the 30-ply composite arrangements, none of these samples was perforated by the level II-A projectiles as seen in Table 3 and Fig. 8. From the delaminated area measurement, it is apparent that a sample with an arrangement of the 20-ply panel in front of the 10-ply panel (20/10 configuration) (Fig. 8(b)) exhibited the best ballistic performance. The damaged area of this sample arrangement was significantly smaller than those of the other two arrangements, i.e., the 10/10/10 (Fig. 8(a)) and 30/0/0 (Fig. 8(c)) configurations. Therefore, the arrangement of composite panel in the firing test was found to be one important factor on the ballistic performance of the composites. The front panel with at least 20 plies of Kevlar™ cloth was thus necessary for the level II-A resistance of perforation and was supposed to possess sufficient properties to destroy or deform this type of projectile. As a result, the kinetic energy was substantially reduced before piecing through the rear plate of 10 piles thickness. Moreover, the energy might also be dissipated via the inertia effect when the projectile passed through the gap between the two plates. However, the front plate of the 10/10/10 (Fig. 8(a)) configuration composite was found to possess insufficient mechanical integrity to destroy the projectiles. Consequently, a relatively large portion of the impact energy could still be transferred to the adjacent plate and caused relatively large damaged area to the rear plate. In the other hand, although, the 30/0/0 (Fig. 8(c)) configuration composite possessed relatively high stiffness enough to substantially deform the projectile, this sample lacked the energy dissipation by an inertia effect as likely to occur in the 20/10 (Fig. 8(b)) configuration. As a result, a larger damaged area comparing with the 20/10/0 configuration composite was observed. The cross-sections of the front plate of the tested composites with 20/10/0 and 30/0/0 arrangements are also illustrated in Fig. 9(a) and Fig. 9(b), respectively, revealing the macroscopic delamination of the Kevlar™'s cloth in the 20 plies and 30 plies thick composites.

Table 3. Effect of number of piles and panel arrangement of KevlarTM-reinforced 80/20 BA/PU composites after ballistic impact at projectiles velocities required by NIJ standard level II-A.

Configuration	Penetration resistance	Damage dimension of the rear plate	
		Depth (mm)	Diameter (mm)
10/10	No	-	-
20/0	No	-	-
10/10/10	Yes	10.8	69.5
20/10/0	Yes	7.8	44.5
30/0/0	Yes	8.7	66.6

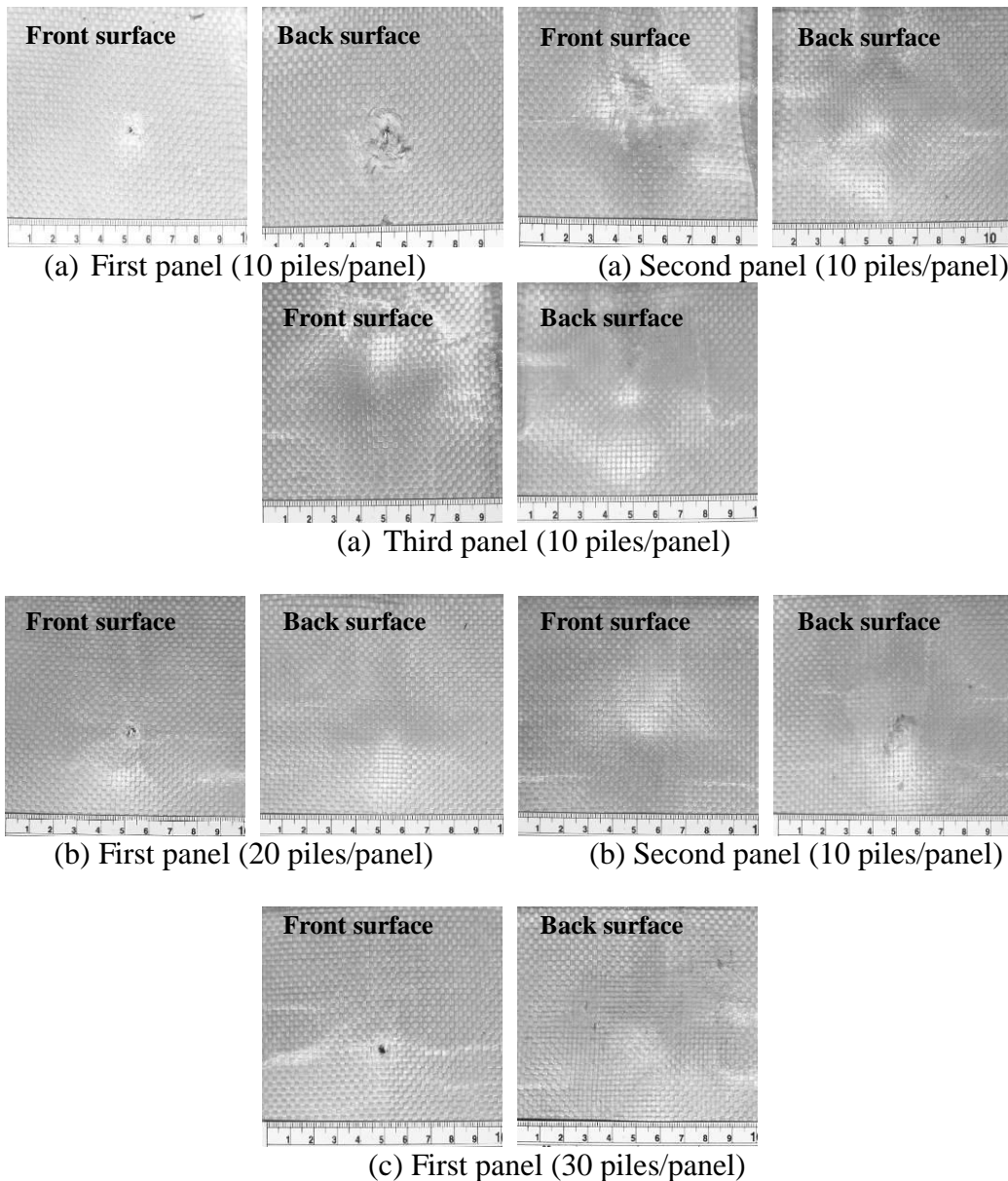


Fig. 8. Damaged and delaminated area of sample after impact with projectiles velocities required by NIJ standard for level II-A with the sample arrangement of: (a) 10/10/10, (b) 20/10/0, and (c) 30/0/0.

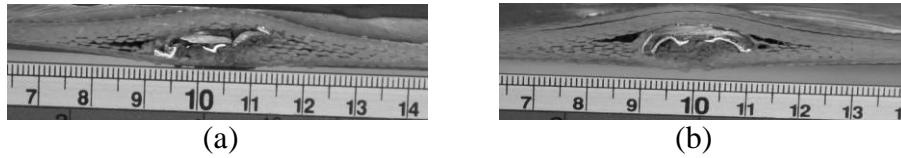


Fig. 9. Damaged panel cross-sections of specimen that could stop projectiles at velocities required by NIJ standard for level II-A: (a) first panel of sample having arrangement of 20/10/0; (b) first panel of sample having arrangement of 30/0/0.

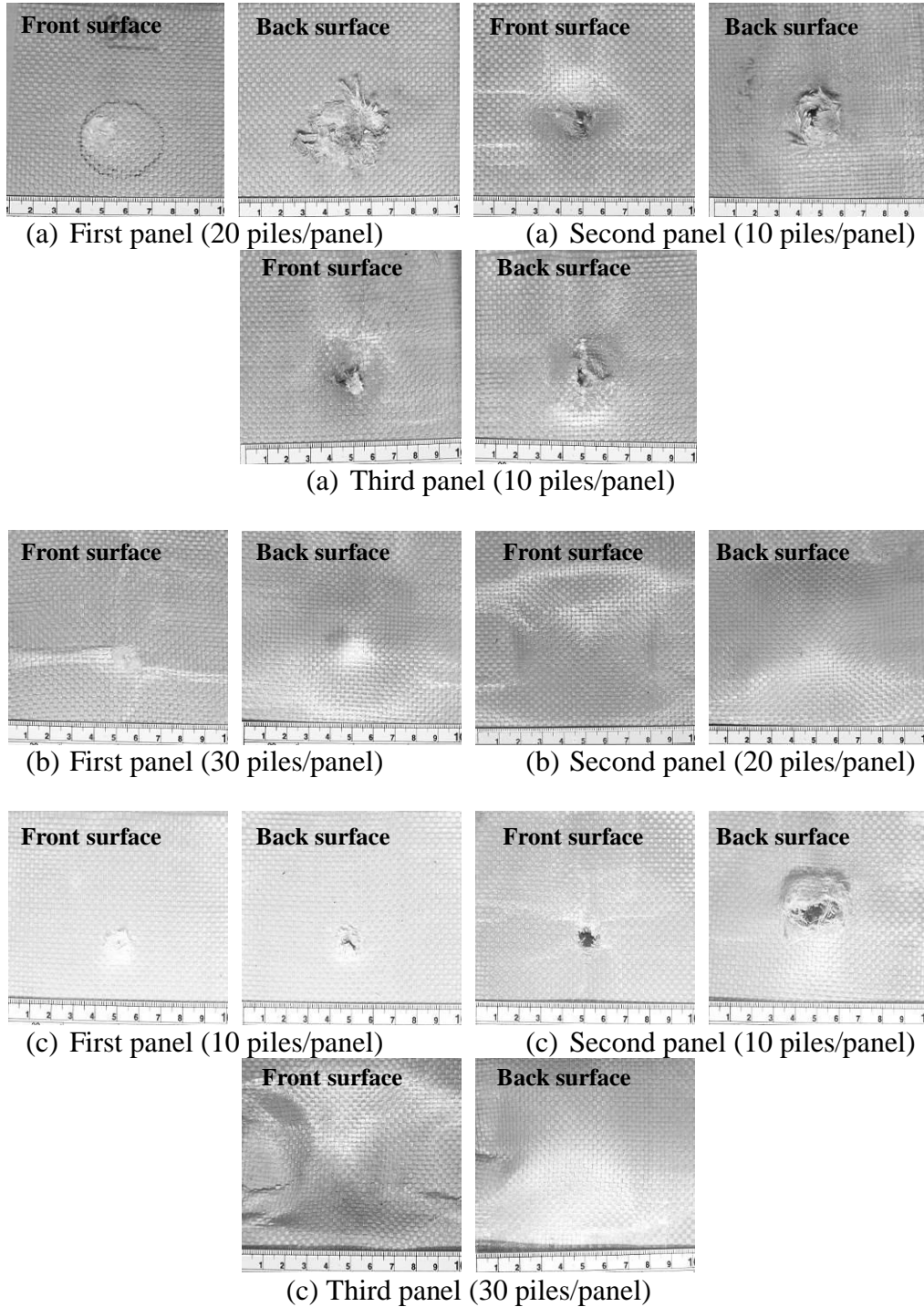


Fig. 10. Damaged and delaminated area of sample after impact with projectiles velocities required by NIJ standard for level III-A with the sample arrangement of: (a) 20/10/10, (b) 30/20/0, and (c) 10/10/30.

Table 4. Effect of number of piles and panel arrangement of KevlarTM reinforced 80/20 BA/PU composites after ballistic impact at projectiles velocities required by NIJ standard level III-A.

Configuration	Impact velocity (m/s)	Penetration resistance	Damage dimension of the rear plate	
			Depth (mm)	Diameter (mm)
10/10	426	No	-	-
20/0	430	Yes	13.6	93.3
10/10/10	429	Yes	19.5	119.1
20/10/0	429	Yes	11.0	90.3
30/0/0	431	Yes	10.1	66.1

3.2.3.3. Ballistic Impact Test of NIJ Level III-A

In this investigation, the KevlarTM-reinforced 80/20 BA/PU composite with the combined thickness of 40, 50, and 60 plies were subjected to a ballistic impact evaluation at a projectile velocity required by NIJ standard for level III-A. This III-A level test is currently the reported maximum level of protection based on polymer composites. The composites with the combined thickness of 40 plies had one type of arrangement, i.e. 20/10/10 configuration whereas that of 50 plies had two types of arrangements, i.e. 30/20/0, and 10/10/30 configurations. In the case of the samples of 60 plies, the arrangements were set to be 30/20/10/0, and 30/10/10/10 configurations. The test outcomes are listed in Table 4. In addition, Fig. 10 also shows of the photographs of some composites tested in this protection level revealing damaged or delaminated areas of the composites.

From Table 4, it is apparent that the test weapon with standard 124 grains round lead projectile with a copper outer coating (Full Metal Jacket) typically used in the 9mm handgun having a speed required by level III-A could be stopped with at least 50 plies of the composites. The damage area evaluation confirmed that the arrangement of composite panels had an important effect on their ballistic protection. It can be seen that the composite with 30/20/0 arrangement rendered the damaged depths and diameters smaller than those of the composite with the 10/10/30 arrangement. This result implied that the composite arrangement for level III-A protection needed at least 30-ply composite panel as a front plate in the impact direction. The sufficiently stiff panel seemed to play a crucial role as to deform the shape of the projectile as discussed previously.

In the combined 60-ply thick composite panels, the arrangement was set to be 30/20/10, and 30/10/10/10 configurations. These two types of arrangements were again found to lead to different damaged areas and deformed depths. The composite with 30/10/10/10 configuration rendered less damaged area than that of composite with 30/20/10 configuration. Since the number of the KevlarTM plies combined was the same in each tested sample, the sample arrangement with the thicker panel of 30 plies for level III-A to be on the front and was found to be essential in the successful ballistic impact resistance of the composites with lower degree of sample deformations.

4. Conclusions

In this study, the suitable matrix alloy based on benzoxazine, and urethane resins for Kevlar™ fiber-reinforced composite armor was determined. The synergism in the T_g can be observed in Kevlar™-reinforced BA/PU alloys. This phenomenon was due to the addition of urethane prepolymer is attributed to improve crosslinked density of the matrix alloys. However, the increase of the PU fraction significantly lowered the stiffness and degradation behavior of the composites. The results of low level ballistic impact test of the 20-ply Kevlar™-reinforced composites revealed that only the composite from the 80/20 BA/PU matrix alloy exhibited 100% ballistic penetration resistance. The studies of specimen's thickness and the arrangement of the composite panels indicated that the suitable thickness having 30 piles of the Kevlar™ cloth can protect the ballistic impact at level II-A, whereas the 50 ply-thick composite was able to protect the ballistic impact of NIJ level III-A. Furthermore, the arrangement of composite panels was also found to significantly affect the ballistic performance of our composites with the thicker and stiffer panel should be placed in the front face of the composite panel assembly to yield best ballistic resistance.

Acknowledgments

This research receives financial supports from the National Metal and Materials Technology Center (Thailand), the Research Grant for Research Scholar of the Thailand Research Fund, and from the National Research University Project (AM1076A) of the Ministry of Education, Thailand. Bisphenol-A, isophorone diisocyanate, and diols were kindly provided by Thai Polycarbonate Co. Ltd. (Thailand), Degussa- Huls AG (Thailand), and TPI Polyol Co., Ltd. (Thailand), respectively.

References

- [1] A. R. Sabet, M. H. Beheshty, and H. Rahimi, "High velocity impact behavior of GRP panels containing coarse-sized sand filler," *Polym. Compos.*, vol. 29, no. 8, pp. 932-938, 2008.
- [2] W. J. Cantwell and J. Morton, "The impact resistance of composite materials - a review," *Composites*, vol. 22, no. 5, pp. 347-362, 1991.
- [3] H. H. Yang, *Kevlar Aramid Fiber*, Chichester, England: John Wiley&Sons, 1993.
- [4] R. H. Zee and C. Y. Hsieh, "Energy loss partitioning during ballistic impact of polymer composites," *Polym. Compos.*, vol. 14, no. 3, pp. 265-271, Jun, 1993.
- [5] B. Z. Jang, L. C. Chen, L. R. Hwang, J. E. Hawkes, and R. H. Zee, "The response of fibrous composites to impact loading," *Polym. Compos.*, vol.11, no. 3, pp. 144-157, Jun, 1990.
- [6] M. J. N. Jacobs and J. L. J. Van Dingenen, "Ballistic Protection Mechanisms in Personal Armour," *J Mater Sci*, vol. 36, no. 13, pp. 3137-3142, Jul, 2001.
- [7] R. H. Zee, C. J. Wang, A. Mount, B. Z. Jang, and C. Y. Hsieh, "Ballistic response of polymer composites," *Polym. Compos.*, vol. 12, no. 3, pp.196-202, Aug, 2004.
- [8] H. Ishida and T. Chaisuwan, "Mechanical property improvement of carbon fiber reinforced polybenzoxazine by rubber interlayer," *Polym. Compos.*, vol. 24, no. 5, pp.597-607, Oct, 2003.
- [9] S. B. Shen and H. Ishida, "Development and characterization of high-performance polybenzoxazine composites," *Polym. Compos.*, vol. 17, no. 5, pp.710-719, Oct, 1996.
- [10] S. Chabba, M. van Es, E. J. van Klinken, M. J. Jongedijk, D. Vanek, P. Gijsman, and A. C. L. M. van der Waals, "Accelerated aging study of ultra high molecular weight polyethylene yarn and unidirectional composites for ballistic applications," *J. Mater. Sci.*, vol. 42, no. 8, pp. 2891-2893, Apr, 2007.
- [11] N. K. Naik, P. Shrirao, and B. C. K. Reddy, "Ballistic impact behaviour of woven fabric composites: Parametric studies," *Mater. Sci. Eng.*, vol. A412, pp.104-116, Dec, 2005.
- [12] C. Ulven, U. K. Vaidya, and M. V. Hosur, "Effect of projectile shape during ballistic perforation of VARTM carbon/epoxy composite panels," *Compos. Struct.*, vol. 61, no. 1-2, pp. 143-150, Jul, 2003.

- [13] M. V. Hosur, S. M. W. Islam, U. K. Vaidya, A. Kumar, P. K. Dutta, and S. Jeelani, "Dynamic punch shear characterization of plain weave graphite/epoxy composites at room and elevated temperatures" *Compos. Struct.*, vol. 70, no. 3, pp. 295-307, Sep, 2005.
- [14] S. S. Morye, P. J. Hine, R. A. Duckett, D. J. Carr, and I. M. Ward, "Modelling of the energy absorption by polymer composites upon ballistic impact," *Compos. Sci. Technol.*, vol. 60, no. 14, pp. 2631-2642, Nov, 2000.
- [15] M. Grujicic, B. Pandurangan, K. L. Koudela, and B. A. Cheeseman, "A computational analysis of the ballistic performance of light-weight hybrid composite armors," *Appl. Surf. Sci.*, vol. 253, no. 2, pp.730-745, Nov, 2006.
- [16] J. N. Epel, "Fibrous armor material," U.S. Patent, 4,639,387 (1987).
- [17] W. N. Smith, Jr., "Light weight armor," U.S. Patent, 4,732,803 (1988).
- [18] X. F. Wu, G. Ghoshal, M. Kartashov, Z. Aslan, J. A. Turner, and Y. A. Dzenis, "Experimental characterization of the impact-damage tolerance of a cross-ply graphite-fiber/epoxy laminate," *Polym. Compos.*, vol. 29, no. 5, pp. 534-543, May, 2008.
- [19] L. A. Pilato, "Ballistic resistant laminate," U.S. Patent, 5,190,802 (1993).
- [20] D. R. Denomme, "Method of making deep drawn, laminated articles," U.S. Patent, 3,956,447 (1976).
- [21] N. John, "Structural sandwich panel with energy-absorbing material pierced by rigid rods," U.S. Patent, 5,102,723 (1992).
- [22] I. Rosenberg and W. K. Ansite, "Ballistic resistant armor panel and method of constructing the same," U.S. Patent, 4,550,044 (1985).
- [23] L. H. Li, Y. D. Kwon, and D. C. Prevorsek, "Sulfamoyl hydrogen bond donating groups on thermal solvents for image separation systems," U.S. Patent, 5,480,760 (1996).
- [24] A. D. Park, "Thin film color filter for liquid crystal display," U.S. Patent, 5,395,678 (1996).
- [25] A. D. Park, "Method for fabricating a ballistic laminate structure," U.S. Patent, 5,547,536 (1999).
- [26] G. A. Harpell, I. Palley, S. Kavesh, and D. C. Prevorsek, "Ballistic-resistant composite article," U.S. Patent, 4,748,064 (1988).
- [27] H. Ishida, "Process for preparation of benzoxazine compounds in solventless systems," U.S. Patent, 5,543,516 (1996).
- [28] H. Ishida and D. J. Allen, "Physical and mechanical characterization of near-zero shrinkage polybenzoxazines," *J. Polym. Sci. Pol. Phys.*, vol. 34, no. 6, pp. 1019-1030, Apr, 1996.
- [29] N. N. Ghosh, B. Kiskan, and Y. Yagci, "Polybenzoxazines—New high performance thermosetting resins: Synthesis and properties," *Prog. Polym. Sci.*, vol. 32, no. 11, pp. 1344-1391, Nov, 2007.
- [30] C. P. R. Nair, "Advances in addition-cure phenolic resins," *Prog. Polym. Sci.*, vol. 29, no. 5, pp. 401-498, May, 2004.
- [31] H. Ishida and D. J. Allen, "Mechanical characterization of copolymers based on benzoxazine and epoxy," *Polymer*, vol. 37, no. 10, pp.4487-4495, Sep, 1996.
- [32] S. Rimdusit and H. Ishida, "Synergism and multiple mechanical relaxations observed in ternary systems based on benzoxazine, epoxy, and phenolic resins," *J. Polym. Sci. Polym. Phys.*, vol. 38, no. 13, pp.1687-1698, Jul, 2000.
- [33] C. Jubsilp, T. Takeichi, and S. Rimdusit, "Effect of novel benzoxazine reactive diluent on processability and thermomechanical characteristics of Bi-functional polybenzoxazine," *J. Appl. Polym. Sci.*, vol. 104, no. 5, pp. 2928-2938, Jun, 2007.
- [34] T. Takeichi, Y. Guo, and S. Rimdusit, "Performance improvement of polybenzoxazine by alloying with polyimide: effect of preparation method on the properties," *Polymer*, vol. 46, no. 13, 4909-4916, Jun, 2005.
- [35] S. Rimdusit, C. Liengvachiranon, S. Tiptipakorn, and C. Jubsilp, "Thermomechanical characteristics of benzoxazine-urethane copolymers and their carbon fiber-reinforced composites," *J. Appl. Polym. Sci.*, vol. 113, pp. 3823-3830, Feb, 2009.
- [36] P. J. Flory, *Principles of Polymer Chemistry*, Ithaca: Cornell University Press, 1953.
- [37] I. M. Ward, *Mechanical Properties of Solid Polymers*, New York: Wiley Interscience, 1971.

- [38] T. Takeichi, Y. Guo, and T. Agag, "Synthesis and characterization of poly(urethane-benzoxazine) films as novel type of polyurethane/phenolic resin composites", *J. Polym. Sci.: Part A: Polym. Chem.*, vol. 38, no. 22, pp. 4165-4176, 2000.
- [39] T. Takeichi and Y. Guo, "Preparation and Properties of Poly(urethane-benzoxazine)s Based on Monofunctional Benzoxazine Monomer", *Polymer J.*, vol. 33, no. 5, pp. 437-443, 2001.
- [40] X-L. Xie, C. Y. Tang, X. P. Zhou, R. K. Y. Li, Z. Z. Yu, Q. X. Zhang, and Y. W. Mai. "Enhanced Interfacial Adhesion between PPO and Glass Beads in Composites by Surface Modification of Glass Beads via In Situ Polymerization and Copolymerization", *Chem. Mater.*, vol. 16, pp. 133-138, 2004.
- [41] H. Ishida and T. Agag, *Handbook of Benzoxazine Resins*, 2011, pp. 12.
- [42] S. Tiptipakorn, S. Damrongsakkul, S. Ando, K. Hemvichian, and S. Rimdusit, "Thermal degradation behaviors of polybenzoxazine and silicon-containing polyimide blends", *Polym. Degrad. Stabil.*, vol. 92, no. 7, pp. 1265-1278, 2007.

