

CHAPTER III

LITERATURE REVIEWS

Protective armors were traditionally made of metals in the old day. With the development of the thermoplastic polymers and synthetic fibers in recent years, hard armor systems of lighter weight have been produced that combine the use of metals, and/or ceramics with polymeric fabrics as well as fiber-reinforced polymer composites. Soft armors prepared from fabrics of fiber glass and Nylon and used for ballistic protection during the Vietnam War had been reported. (Yang, 1993)

Jacobs and Dingenen in 2001 suggested high performance fibers used in ballistic products as being characterized by: their low density, high strength, high energy absorption and high sonic velocity because of its distribution of kinetic energy upon ballistic impact. In ballistic products, the major fibers used include glass fibers, aramid (KevlarTM), high performance polyethylene (UHMPE) fibers. Recently ballistic products based on PBO fiber have been introduced in the market.

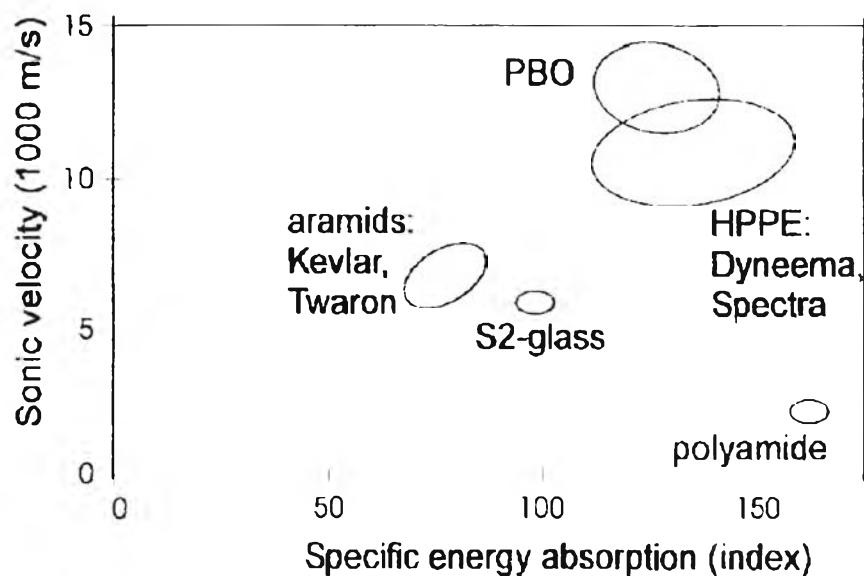


Figure 3.1: Primary ballistic figures of merit for various fibers (Jacobs and Dingenen, 2001)

KevlarTM was reported to be well suited to ballistic armor applications because it combines a high specific strength and modulus with high thermal resistance and fire resistance. In the early 1970s, ballistic standards for body armor of aramid fiber have been established and improved over the years (Yang, 1993). In addition Park, 2003 patented a light weight soft armor product comprising at least one ballistic panel including of an assembly of 50 piles woven aramid fabric, weighing between 600 and 850 deniers. Its areal density was no greater than 0.66 g/cm^2 and can protect a .22 caliber, 17 grains FSP (NIJ Level I)

The development of composite technology has improved armor structure and properties because it can decrease or absorb kinetic energy more than the unimpregnated one. Gerard, 1980 proposed that the fibers encapsulated in relatively rigid matrix provided ballistic protection higher than unimpregnated fabrics of equal weight. The selection of resin for ballistic composite depends on its required characteristics. Some important parameters needed to be considered include rigidity, process ability, its viscosity, curing temperature, and shelf-life.

In the Tables 3.1, the types of resins used as matrices for ballistic resistance have been summarized. Matrix polymers that have high modulus and strength will be more brittle and crack notch sensitive. These properties lead to decreasing of energy absorption capability. On the other hand, elastomeric matrices will decrease penetration resistance per unit area of the composite armor but with great potential of energy absorption capacity. Therefore, the appropriate ductile matrix should be chosen and reinforced with strong fibers to achieve the effective composite armor.

Table 3.1: Review on United States patents of polymer composite ballistic armor

Fiber	Matrix	Matrix Properties	Reference
1. Spectra™	Thermosetting <ul style="list-style-type: none"> - epoxy 	<ul style="list-style-type: none"> - elastomer - modulus 500,000 psi - strength 3,000 psi at high temp. - below the melting point of fiber 	Patent No. 4,748,064 Date: May 31, 1988 Patent No. 4,403,102 Date: Sep 6, 1983
	Thermoplastic elastomer <ul style="list-style-type: none"> - thermoplastic elastomer - urethanes - styrene-isoprene-styrene (SIS) dissolved in methylene chloride 	<ul style="list-style-type: none"> - areal density 4.5 oz/yd. - $T_g = -70$ to 0°C - low modulus - below the melting point of fiber - $T_g = -55^\circ\text{C}$ - melt index = 9 g/min using - modulus 100 psi at 300% elongation 	Patent No. 5,724,670 Date: Mar 10, 1998 Patent No. 5,534,343 Date: Jul 9, 1996 Patent No. 4,403,102 Date: Sep 6, 1983 Patent No. 5,480,706 Date: Jan 2, 1996 Patent No. 5,093,158 Date: Mar 3, 1992 Patent No. 4,748,064 Date: May 31, 1988
2. Kevlar™	Thermosetting <ul style="list-style-type: none"> - phenolic resin - polyester - epoxy 	<ul style="list-style-type: none"> - impact strength 17 J/m, 32 mm thick - $T_g = 170^\circ\text{C}$ - elastomer - modulus 500,000 psi - strength 3,000 psi at high temp 	Patent No. 5,190,802 Date: Mar 2, 1993 Patent No. 4,748,064 Date: May 31, 1988 Patent No. 4,639,387 Date: Jan 27, 1987 Patent No. 4,550,044 Date: Oct 29, 1985 Patent No. 5,102,723 Date: Apr 7, 1992 Patent No. 3,956,447 Date: May 11, 1976
	Thermoplastic <ul style="list-style-type: none"> - urethanes - styrene-isoprene-styrene (SIS) 	<ul style="list-style-type: none"> - $T_g = -70$ to 0°C - low modulus - $T_g = -55^\circ\text{C}$ - melt index = 9 g/min using - modulus 100 psi at 300% elongation 	Patent No. 4,639,387 Date: Jan 27, 1987 Patent No. 5,480,706 Date: Jan 2, 1996

Fiber	Matrix	Matrix Properties	Reference
3. Glass Fiber	Thermosetting <ul style="list-style-type: none"> - phenolic - polyester 	<ul style="list-style-type: none"> - moldable - MW. Range 800 to 5.000 or more 	Patent No. 5.215.813 Date: Jan 1. 1993 Patent No. 4.639.387 Date: Jan 27. 1987 Patent No. 4.550.044 Date: Oct 29. 1985
	Thermoplastic <ul style="list-style-type: none"> - urethane - styrene-isoprene-styrene (SIS) 	<ul style="list-style-type: none"> - flexibility - resistance to degradation - $T_g = -55\text{ C}$ - melt index = 9 g/min using - modulus 100 psi at 300% elongation 	Patent No. 4.639.387 Date: Jan 27. 1987 Patent No. 4.822.439 Date: Apr 18. 1989
4. Polybenzoxazole and Polybenzothiazoe	<ul style="list-style-type: none"> - are not limited to thermoplastic or thermosetting 		Patent No. 6,268.301 B1 Date: Jul 31. 2001
	Thermoplastics <ul style="list-style-type: none"> - polybenzoxazole or polybenzothiazoe 	<ul style="list-style-type: none"> - low flammability - low smoke - high temperature stability - high chemical and solvent resistance - high strength and modulus 	Patent No. 5.196.259 Date: Mar 23. 1993
5. Mixed Fibers -aramid and carbon - aramid and glass - carbon and glass - carbon, glass and spectra	<ul style="list-style-type: none"> - ethylene-acrylate, methacrylate copolymer, vinyl ester phenilic polyimide, polycarbonate or the like 	<ul style="list-style-type: none"> - high modulus - higher in impact resistance 	Patent No. 4.732.803 Date: Mar 22. 1988

The resin content is needed to be carefully controlled to achieve a balance of structure and ballistic properties. Such a fabric is impregnated with resin applied to extent of about 20-25 percent by weight having been reported (Denommee et al., 1976; Epel, 1987; Park, 1996, 1999). Park, 1996, 1999 reported, if the amount of resin substantially increased above the desired amount the matrix, it would become a major part of the armor volume and weaken the materials. However if the resin amounts substantially less than that required to wet all fibers, this will result in the material composition wherein the fibers are not properly consolidated and held in the proper position so that upon impact, the fiber tends to separate relatively easily, allowing the projectile to pass through before the fiber absorbs impact forces.

Some binders have been reported to be used with KevlarTM fiber to produce ballistic composites such as 50:50 mixture of phenol formaldehyde resin and polyvinyl butyral resin (Morye et al., 2000). The KevlarTM composites of this resin mixture were 27 layers of Kevlar yielding 5.9 mm in thickness. It was capable to protect a projectile of 0.68 g steel sphere at 612 m/s strike velocity.

Coppage et al., 2000 patented composite fabric comprised of aramid fiber combined with PBO fiber and at least one flexible, rubbery resin used in making ballistic armor. Its composite was able to pass the NIJ III-A (.44 magnum). The products possessed an area density of 0.48 g/cm².

Phenolic resins provide a future class of preferred resins for a composite armor (Denommee et al., 1976; Pilato, 1993; Hartran et al., 1993). Phenolic resins are inexpensive, can be handled using conventional technology, and do not bond too firmly to ballistic fiber especially KevlarTM. However, phenolics do require that moisture be driven from the resins during curing stage which is one additional step in the composite fabrication process thus the processing cost.

In this work, polybenzoxazine alloys as a ballistic composite will be selected. It is a new class of phenolic resins designed molecularly to overcome most problems encountered in traditional phenolics. Ning and Ishida, 1994 investigated the synthesis of bifunctional benzoxazine precursors. These polyfunctional benzoxazine were found to exhibit excellent mechanical and thermal properties with good handling capability for material processing and composite manufacturing, e.g., the glass transition temperature of 190°C, tensile modulus of 3.2 GPa, and tensile strength of 58 MPa. In addition, they offered greater flexibility than conventional phenolic resins in terms of molecular design. They do not release by-product during reactions and there are no solvent other than for the solvency which the reactants may have for each other. The other outstanding property of benzoxazine resin is its ability to undergo hybrid network formation with several other resins for tailor-made properties (Ishida and Allen, 1996; Takeichi et al., 2000; Rimdusit et al., 2000, 2005). This makes it possible to fine tune and enhance the properties of the ballistic armour.

Ishida and Allen, 1996 reported that hybrids of benzoxazine resin (BA-a) and bisphenol a-typed epoxy exhibited a substantial increase in their cross-linked density, thus raising their glass transition temperature, flexural stress, and flexural strain at break over those of the BA-a homopolymer. Takeichi et al., 2000 had successfully developed clear poly(urethane benzoxazine) films based on BA-a resin and TDI/polyethylene adipate polyol-typed urethane resin. The obtained films showed a single glass transition temperature, implying no phase separation occurred in the resulting alloys. The properties of the films ranged from elastomers to plastic, depending on the content of the benzoxazine fraction in the alloys.

Recently, Rimdusit et al., 2005 improved the toughness of polybenzoxazine by alloying with isophorone diisocyanate (IPDI) based urethane prepolymers (PU) or with flexible epoxy. The toughness of alloys of rigid polybenzoxazine and the PU or epoxy systematically increases with the amount of either tougheners due to the addition of more flexible molecular segments in the polymer alloys, Interestingly glass transition temperatures (T_g) of BA-a/PU alloys was found to be higher than those of the parent resins, i.e. 165°C for BA-a and -70°C for PU while T_g of the BA-a/PU alloys at 70/30 mass ratio was found to be 220°C. However, this characteristics was not observed in the BA-a/flexible epoxy alloys systems. BA-a/PU alloys thus may be suitable for an application as a composite matrix to produce a ballistic armor due to the above observed thermal stability as well as the broad range of the modulus of the resulting alloys. In this study, the suitable composition ratios of the polymeric alloys between benzoxazine and urethane resins and the number of the layers of the Kevlar cloth to produce ballistic composite of level IIA or higher will be explored.