# 論文

## 우레탄 수지 첨가에 의한 다이니마/비닐에스터 복합재료의 방탄효과 향상 연구

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## Effect of Urethane Modification on the Anti-Bullet Property of Dyneema/vinylester Composites

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## ABSTRACT

Polyurethane oligomers (PUOs) such as UA8297, UP127 and EB8200 were utilized to enhance the anti-bullet property of Dyneema[®]/vinylester composites. First, prepregs of PUO and vinylester (XSR10) were prepared via spray coating on Dyneema[®] fabric at 21 % resin content (by volume). In addition, spray coating and film lamination were also carried out with a mixture of XSR10/PUO for selected PUOs. Next, the prepregs were dried at RT for 1-2 h and then at 100 °C for 30 min to remove the solvent and to provide partial cure when necessary. The prepregs were stacked in 24 layers and cured at 120 °C for 5 min under the contact pressure and for additional 25 min at 150 kg/cm$^2$. Finally, the anti-bullet properties of composite samples were evaluated by measuring $V_{50}$ with simulated fragment projectile (SFP, 17 gr). The results showed a 6.5 and 9.0 % increase of $V_{50}$ with UP127 and EB8200, respectively.

## 초 록

우레탄 수지 첨가에 의한 다이니마/비닐에스터 복합재료의 방탄효과 향상을 고찰하였다. 첫째로 우레탄 수지와 비닐에스터 수지를 스프레이 코팅하여 프리프레그를 제조하였으며, 수지함량을 21%로 조절하였다. 또한 혼합수지를 스프레이 코팅과 필름코팅으로 비교를 위한 프리프레그를 제조하였다. 그 다음 이들을 상온에서 1-2시간, 그리고 필요 시 100 °C 에서 30분 정도 건조시켰다. 이들 프리프레그를 24층 적층한 다음 120 °C에서 5분 동안 정치 시킨 후 25분 동안 150 kg/cm$^2$ 압력하에서 경화 시켰다. 모의 파편탄(17 gr)을 이용하여 이들 복합재료의 방탄성능($V_{50}$)를 측정하였으며, UP127 및 EB8200으로 제조된 시편은 XSR10으로 제조된 시편에 비하여 각각 6.5 및 9.0 % 향상된 값을 보였다.

Key Words : 우레탄 수지(polyurethane oligomer (PUO)), 다이니마(Dyneema), 비닐에스터(vinylester), 방탄시험(anti-bullet test), 굴곡강도(flexural strength), 충격강도(impact strength)

### 1. Introduction

Ever since fiber-based personal armor systems utilizing cotton fibers were introduced in Korea in the late 19th century[1], considerable research have been conducted on fiber-based personal armors and fiber-composite-based armors using high performance fibers[2], such as aramid and ultra high molecular weight polyethylene (UHMWPE) fibers, which possess very high-specific strength and stiffness[3,4]. Currently, composite-based armors using these fibers dominate

the field[5,6].

Unfortunately, early composite-based armors including helmets[7] failed to provide complete protection from bullets, which resulted in research efforts being focused on the improvement of ballistic resistance of composite materials. As expected, properties such as specific modulus, specific tenacity, density, extension to break, modulus, and tenacity are strongly dependent on the properties of reinforcing fibers. Consequently, attempts have been made to enhance the properties of fibers by drawing operations and increasing crystallinity via post-crystallization.

In addition, the ballistic properties of composites are also strongly dependent on the texture of fibers. Therefore, a number of weavings have been studied, including plain, basket, twill, and satin weaves[9], along with unidirectional (UD) fibers. Among these, UD fibers are known to be the best for obtaining good ballistic properties, as long as fibers do not shift during composite processing[10] and products do not possess curvatures such as helmets. For application in curvature products, satin weaves have been reported to be suitable[11], while basket weaves have been used in US army helmets[12].

Another important factor in personal armor composites is the property of matrix resins, which need to efficiently absorb high impact energy of ballistic projectiles or their fragments and transfer this energy to adjacent fibers and/or provide integrity for the composites[13]. Currently, phenol and vinylester resins are two major resins utilized for personal armor composites. However, they are thermoset polymers exhibiting high modulus and high brittleness after curing. Therefore, these resins have been modified with polyvinylbutyral or rubbers for better toughness[14,15]. In addition, polyurethanes have also been utilized for personal armor composites in combination with vinylester[16,17] or epoxy resins[18]. In personal armor composites, the resin content should be as low as possible for good ballistic resistance, while being high enough to provide the consolidation of fibers. Thus, the resin of around 20% (by volume) is being utilized for helmets to afford good mechanical properties as well as ballistic resistance[19].

Considering the high speed of bullets, 3,110 ft/s (948 m/s) for a M16 rifle for example[20], the current personal armor composites are not good enough to provide complete protection, and further research on a new class of fibers, as well as matrix resins, is needed. In this study, therefore, we attempted to modify vinylester resins for personal armor composites by incorporating diacrylated polyurethane oligomers
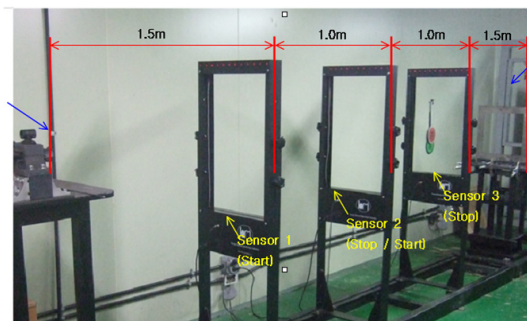


Fig. 1   **Anti-bullet testing facility at Samyang ComTech.**

(PUOs), which are very tough materials and can be cured with vinylester resin via acrylate end-groups. In addition to resin modification, spray coating of resins was also attempted to minimize resin impregnation and thus, to maximize the anti-bullet property, while prepregging by film lamination was also carried out for comparison purposes. The anti-bullet property was evaluated with 17 gr SFP by calculating $V_{50}$ from 9 shots. The flexural and Izod impact properties were also evaluated for selected composites in order to gain a better understanding of ballistic properties.

## 2. Experimental

### 2.1 Materials

Dyneema[®] fabric (19x19, plain, 1580 d) from DSM (Netherland) was cut into 200x240 mm size and used to prepare prepregs with vinylester (XSR10, 70% solid in MeOH and acetone mixture, Sewon Chemical Co.) or diacrylated polyurethane oligomers (PUO, SK Cytec) such as UA8297 (3k), UP127 (6k, 80% solid in ethylacetate) and EB8200 (8k, 50% solid in butylacetate). For the initiator, BPO was added at 0.5 wt%.

### 2.2 Prepregging

Prepregs were prepared by spray coating XSR10 or PUO on the Dyneema[®] fabric (240x200 mm) at the resin content of 21 % (volume) for maximum anti-bullet property[19]. For comparison, spray coating and film lamination of the resin mixture (XSR10/PUO) on UP127 PUO were also carried out. For spray coating, an air-spray gun was used to coat the fabric with the resin, which was diluted with acetone for easy spraying. The fabric was then dried at RT for 1~2 h to evaporate the solvent. For film lamination, a solution of resin

mixture was cast onto the glass plate, dried at RT for several hours, and overlaid on the Dyneema® fabric. The samples were then pressed with a roller and the fabric was removed. Next, the prepregs were dried at 100 °C for 10-30 min to further remove the solvent and to partially cure the resin in an effort to obtain good consolidation without squeezing out the resin during composite processing.

### 2.3 Composite fabrication and testing

Composites for anti-bullet tests were fabricated by stacking 24 layers of prepregs in various stacking sequences of XSR10 and PUO, followed by curing at 120 °C for 5 min under the contact pressure and for additional 25 min at 150 kg/cm$^2$. However, the stacking sequence was not considered when using prepregs from resin mixtures. The composite samples (240x200 mm) were subjected to anti-bullet property measurements with SFP (17 gr, 1.1g) at Samyang ComTech (Anseng, Korea). As seen in Fig. 1, the distance between the test barrel and the target is 5 m, and there are 3 sensors to measure the bullet speed. A maximum of 9 shots were fired to calculate $V_{50}$ and the shots ranged from complete to partial penetration, which was achieved by varying the speed of the bullet[21], as shown in Fig. 2.
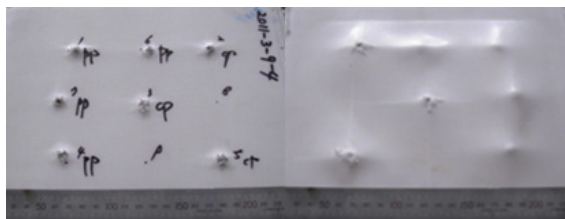


**Fig. 2  Tested composite panel; left- front, right-back.**

In addition, the samples for Izod impact and flexural tests were also prepared with 20 and 10 layers of prepregs (with mixed resin), respectively. The flexural property of samples (127 x 12.7 x3.2 mm) was evaluated by Instron 5567 at a crosshead speed of 5 mm/min under ASTM 790, while the Izod impact strength of samples (63.5 x 12.7 x 6 mm) with WL2200 (Withlab, Korea) was also measured under ASTM D256. However, due to the very high toughness of the samples, a deep notch (5 mm) was made, instead of a standard notch (2.5 mm), for the impact testing. At least 5 samples were tested and the results were averaged.

### 3. Results and discussion

### 3.1 Prepregging and composite fabrication

It is well known that the resin content in anti-bullet composites should be around 21% (by volume) to obtain the maximum property[19], which is much lower than ~30% benchmarked for conventional composites. Thus, the resin has to be coated on the fabric surface, instead of being impregnated into the fabric, which requires high resin viscosity. However, the high viscosity of as-received XSR10 and PUO resins necessitated a minimum amount of acetone to dilute the resins for easy spray coating; 20 phr for XSR10 and 40 phr for PUOs.

Next, the prepregs prepared on the Dyneema® fabric were dried at RT for 1~2 h, followed by additional dying at 100 °C for 10, 20, and 30 min. They were then subjected to a consolidation study using small composite samples (4-layer, 50x40 mm), which were prepared by curing at 120 °C for 5 min under the contact pressure and for an additional 25 min at 150 kg/cm$^2$. The prepregs of XSR10 dried at RT for 2 h provided good consolidation, while the POU-based prepregs needed additional drying at 100 °C for 30 min. After consolidation, the solubility of cured samples was evaluated in acetone, DMF, DMSO, and NMP. The samples exhibited insolubility, demonstrating that they have been completely cured.

Since a preliminary study showed good consolidation of prepregs with good solvent resistance (complete cure), large size composites were prepared for anti-bullet testing by varying the stacking sequence of XSR10 and PUO (XSR10/PUO/XSR10: 12/0/12. 6/12/6, 3/18/3, and 0/24/0). This was unnecessary for spray coating or film lamination of mixed resins, since the ratio of resin mixture has already been varied (XSR10/PUO: 100/0, 50/50, 25/75 and 0/100). The samples were cured at 120 °C for 5 min under the contact pressure and then for 25 min at 150 kg/cm$^2$.

The spray-coated prepregs from mixed resins were prepared similarly, while prepregs from film lamination of XSR10 and UP127 mixed resins were prepared by controlling the drying time at RT for the right viscosity (or tackiness) for each resin mixture. However, it was difficult to achieve resin content control to obtain 21% by volume. The prepregs were then dried at 100 °C for 30 min and used to fabricate the composites under the following cure cycle: 120 °C for 5 min under the contact pressure and for additional 25 min at 150 kg/cm$^2$.

## 3.2 Property evaluation

The anti-bullet properties of composites were evaluated using 17 gr SFP bullets (Fig. 1). As shown in Table 1, the control sample of XSR10 composites (12/0/12) exhibited $V_{50}$ of 480 m/sec, which decreased with the incorporation of UA8297(3k) prepregs to 478, 466, and 458 m/sec for 6/12/6, 3/18/3 and 0/24/0 samples corresponding to 50, 75, and 100 % PUO, respectively. Such unexpected behavior can be attributed to the low molecular weight of UA8297, which results in a tightly cross-linked molecular structure, thereby lowering the impact properties.

**Table 1  Effects of PUO type and stacking sequences on the anti-bullet properties of Dyneema/XSR10 composites**

| $V_{50}$ | 12/0/12 (PUO 0%) | 6/12/6 (PUO 50%) | 3/18/3 (PUO 75%) | 0/24/0 (PUO 100%) |
|---|---|---|---|---|
| UA8297 (3k) | 480 | 478 | 466 | 458 |
| UP127 (6k) | 480 | 487 | 493 | 511 |
| EB8200 (8k) | 480 | 482 | 490 | 523 |

However, $V_{50}$ increased with UP127 prepregs to 487, 493, and 511 for 6/12/6, 3/18/3, and 0/24/0 (XSR10/UP127/ XSR10), respectively. Similarly, it also increased with EB8200 (8k), from 480 to 482, 490, and 523 m/sec for 6/12/6, 3/18/3, and 0/24/0, respectively.  Compared to XSR10 composites, the addition of UP127 and EB8200 prepregs increased $V_{50}$ by as much as 6.5 and 9.0%, respectively, which can be attributed to the very high toughness of PUOs[22].

**Table 2  Effects of prepregging method on the anti-bullet properties of Dyneema/XSR10-UP127 composites**

| $V_{50}$ | 12/0/12 (UP127 0%) | 6/12/6 (UP127 50%) | 3/18/3 (UP127 75%) | 0/24/0 (UP127 100%) |
|---|---|---|---|---|
| Spray, sequential stacking | 480 | 487 | 493 | 511 |
| Spray, mixed resin | - | 486 | 490 | - |
| Film lamination, mixed resin | 480 | 508 | 515 | 528 |

The composite samples prepared by spray coating of the resin mixture (XSR10/UP127) also exhibited increased $V_{50}$ with UP127 content; 486 and 490 m/sec with 50 and 75% UP127 (Table 2). As noted, these values are very similar to those from sequential stacking, indicating that the sequential stacking of XSR10 and UP127 has the same effect as using a mixture of resins on the anti-bullet properties. On the other hand, the composites prepared from prepregs by film lamination of mixed resins exhibited slightly higher $V_{50}$ values, compared to samples from spray coating; 494, 508, 515, and 528 with 0, 50, 75 and 100% UP127, respectively (Table 2). This behavior can be attributed to lower resin impregnation in the fabric from film lamination, compared to spray coating, but it is at the expense of long processing time and difficulty in controlling the resin content.
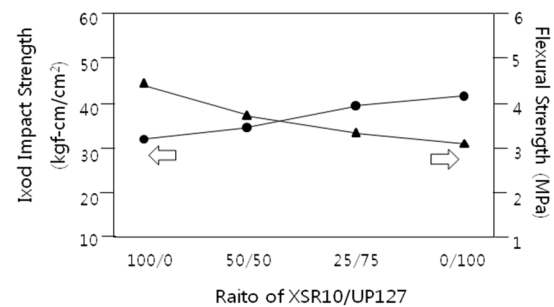


**Fig. 3  Izod impact and flexural strengths of Dyneema/ XSR10-UP127 POU.**

To gain a better understanding of the enhanced anti-bullet property, the impact property and flexural strength of the composites prepared with UP 127 were evaluated. As seen in Fig. 3, the impact strength of XSR10/UP127 (mixed resin) composites increased with increasing PUO content; 32.9, 33.9, 34.5 and 35.3 Kgf・cm/cm2 with 0, 50, 75, and 100% UP127, respectively, which is similar to what was reported earlier[17]. Therefore, the enhanced anti-bullet property ($V_{50}$) of PUO incorporated XSR10/Dyneema composites can be attributed to the high toughness of PUOs[22]. Their flexural strength, however, decreased with PUO incorporation; 4.5, 3.9, 3.6 and 3.4 MPa with 0, 50, 75, and 100 % UP127, respectively. This was expected given the low strength of UP127, based on the study reported by Lin and co-workers[22].

## 4. Conclusions

The anti-bullet property of XSR10/Dyneema composites, prepared by spray coating of the resins (XSR10 or PUO) followed by their sequential stacking, was highly enhanced by the incorporation of PUO resins such as UP127 and EB8200, showing an improvement as high as 6.5 and 9.0%, respectively. The composites prepared by spray coating of mixed resins (XSR10/UP127) also exhibited similar $V_{50}$ values as composites prepared by sequential stacking.

However, slightly higher values were obtained from the composites prepared by film lamination. Increased Izod impact properties and decreased flexural strengths with UP127 incorporation support the enhanced anti-bullet properties of XSR10/PUO/Dyneema composites.

## Acknowledgment

## References

1) http://en.wikipedia.org/wiki/Bullet-proof_vest

2) 김희재, 방탄공학, 청문각, 2004.

3) García, J.M., García, F.C., Serna, F., and de la Peña, J.L., "High-performance aromatic polyamides," *Progress in Polymer Science*, Vol. 35, No. 5, 2010, pp. 623-686.

4) Chodák, I., "High modulus polyethylene fibres: preparation, properties and modification by crosslinking," *Progress in Polymer Science*, Vol. 23, No. 8, 1998, pp. 1409-1442.

5) Dong, Z., and Sun, C.T., "Testing and modeling of yarn pull-out in plain woven Kevlar fabrics," *Composites Part A: Applied Science and Manufacturing*, Vol. 40, No. 12, 2009, pp. 1863-1869.

6) Samara, A.Z., Harel, H., Marom, G., and Yavin, B., "Polyethylene/polyethylene composite materials of ballistic protection," *SAMPE J.*, Vol. 33, No.4, 1997, pp 72–75.

7) Briscoe, B.J., and Motamedi, F., "The ballistic impact characteristics of aramid fabrics: The influence of interface friction," *Wear*, Vol. 158, No. 1-2, 1992, pp 229-247.

8) 최신 섬유기술동향, 한국섬유산업연합회, 2007.

9) Rao, M.P., Duan, Y., Keefe, M., Powers, B.M., and Bogetti, T.A., "Modeling the effects of yarn material properties and friction on the ballistic impact of a plain-weave fabric," *Composite Structures*, Vol. 89, No. 4, 2009, pp. 556-566.

10) http://www.dyneemamatters.com/about_dyneema_ud?category_id=28

11) 하헌승, 이태상, 육종일, "다공성/고강도 특수기능 경량소재개발," 국방과학연구소, 2005.

12) MIL-DTL-44050B; Cloth, Ballistic, Aramid.

13) Karahan, H., Kuş, A., and Eren, R., "An investigation into ballistic performance and energy absorption capabilities of woven aramid fabrics," *International Journal of Impact Engineering*, Vol. 35, No. 6, 2008, pp. 499-510.

14) 이승구, 박종규, 윤영주, 육종일, "케블라/PVB 변성 페놀 복합재료 경화거동," 한국복합재료학회지, 제5권 제1호, 1992, pp. 476-485.

15) Ahmad, M.R., Yunus, W., Ahmad, W., Jamil Salleh, J., and Samsuri, A., "Effect of fabric stitching on ballistic impact resistance of natural rubber coated fabric systems," *Materials & Design*, Vol. 29, No. 7, 2008, pp. 1353-1358.

16) Gryshchuk, O., Jost, N., and Karger-Kocsis, J., "Toughening of vinylester–urethane hybrid resins by functional liquid nitrile rubbers and hyperbranched polymers," *Polymer*, Vol. 43, No. 17, 2002, pp. 4763-4768.

17) Lin, S.P., Shen, J.H., Han, J.L., Lee, Y.J., Liao, K.H., Yeh, J.T., Chang, F.C., and Hsieh, K.H., "Volume shrinkages and mechanical properties of various fiber-reinforced hydroxyethyl methacrylate-polyurethane/unsaturated polyester composites," *Composites Science and Technology*, Vol. 68, No. 3-4, 2008, pp. 709-717.

18) Lin, S.P., Han, J.L., Yeh, J.T., Chang, F.C., and Hsieh, K.H., "Composites of UHMWPE fiber reinforced PU/epoxy grafted interpenetrating polymer networks," *European Polymer Journal*, Vol. 43, No. 3, 2007, pp. 996-1008.

19) Cheeseman, B.A., and Bogetti, T.A., "Ballistic impact into fabric and compliant composite laminates," *Composite Structures*, Vol. 61, No. 1-2, 2003, pp. 161-173.

20) http://www.colt.com/mil/M16_2.asp

21) Iremonger, M.J., and Went, A.C., "Ballistic impact of fibre composite armours by fragment-simulating projectiles," *Composites Part A: Applied Science and Manufacturing*, Vol. 27, No. 7, 1996, pp. 575-581.

22) Petrovic, Z.S., and Ferguson, J., "Polyurethane elastomers," *Progress in Polymer Science*, Vol. 16, No. 5, 1991, pp. 695-836.