AJChE 2013, Vol. 13, No. 1, 11 – 17

Thermomechanical Properties of Kevlar™ Reinforced Benzoxazine-Urethane Alloys

Rimdusit S. [*,1]
Okhawilai M.[1]
Kasemsiri P. [2]
[1] *Department of Chemical Engineering, Chulalongkorn University, Bangkok 10330 Thailand.*
[2] *Department of Chemical Engineering, Khon-Kaen University, Khon-Kaen 40000 Thailand.*
[*] *e-mail :* sarawut.r@chula.ac.th

Ballistic armor is one of an important application which required high performance of fiber-reinforced polymer due to its outstanding specific mechanical properties. Therefore, Kevlar™ reinforced benzoxazine-urethane alloys as ballistic impact resistance composites were developed in this research. The polybenzoxazine alloy composites were fabricated by compression molding at 200°C and 5 MPa by a compression molder. The amount of urethane fraction in the alloy matrix was ranging from 0-40wt% while the fiber content was kept constant at 80wt%. The mechanical properties of the matrix alloys and their Kevlar™ fiber composites were characterized by dynamic mechanical analysis and universal testing machine. The results revealed that storage modulus at room temperature of the composites was reduced from 16.82 GPa when using the neat polybenzoxazine as a matrix to the value of 11.89 GPa at 40wt% of urethane content in the alloy matrix. Moreover, the more urethane in the alloy matrix resulted in lower flexural modulus of the Kevlar™ composites i.e. 22 GPa when using the neat polybenzoxazine as a matrix to the value of 12 GPa when using 40wt% of urethane in the alloy matrix. Interestingly, glass transition temperature (T_g) obtained from the maximum peak of the loss modulus was observed to be in the range of 187-247°C, which was significantly higher than those of the two parent polymers. Furthermore, the activation energy of the alloys was found to increase with increasing urethane content, which corresponded to the observed T_g value enhancement. The observed synergism in T_g of Kevlar™ reinforced benzoxazine-urethane was an outstanding characteristic for a wide range of applications, which requires high thermal stability.

Keywords: Benzoxazine, Urethane, Fiber-reinforcement, Mechanical Properties, Ballistic armor

INTRODUCTION

A composite structure for high ballistic performance are characterized by high impact resistance, high strength, low specific weight and also low cost of production. The ballistic armor structure is effectively designed into two parts i.e. strike face and backing portion. Commonly used composites for backing portion are based on fiber reinforced polymer composites. The well-known ballistic fiber like polymer aramid fiber, glass fiber, high performance polyethylene fiber.

Various thermoset resins for example epoxy, phenolic, polyester have a wide range of interests. The encounter with by-product released upon curing, additional curing agent and also the low performance of these resins as ballistic materials are disadvantageous. Benzoxazine resin, a new phenolic resin, was stated to possess no by-product released, low thermal shrinkage, high mechanical and thermal properties and a distinctive ability to alloy with different materials (Rimdusit *et al.*, 2011, Takeichi *et al.*, 2005) to be a high useful performance resin for a wide range of applications. An important one was aimed to develop as a protective ballistic armor.

Benzoxazine-urethane copolymer was explored to obtain a high performance system. Therefore, the present research is aimed to characterize mechanical and thermal behavior of Kevlar^{TM} reinforced benzoxazine-urethane composite to be develop and used as ballistic armor. The effect of urethane content on those properties is mainly observed.

EXPERIMENTAL

Materials

Benzoxazine resin is based on bisphenol-A, aniline and paraformaldehyde. The bisphenol A (polycarbonate grade) was supplied by Thaipolycarbonate Co., Ltd (TPCC). Para-formaldehyde and aniline were purchased from Merck Company and Panreac Quimica SA Company, respectively. Urethane prepolymer was prepared using toluene diisocyanate and polyether polyol (molecular weight of 2000) which were obtained from South City Group and TPI Polyol CO., LTD. The fiber was purchased from Thai Polyadd Limited Partnership.

Resins Preparation

Benzoxazine monomer was synthesized using bisphenol A, aniline, and paraformaldehyde at a 1:2:4 molar ratio by solventless technology (Ishida 1996). Briefly, the three reactants were continuously mixed at about 110ºC for approximately 40 minutes. The obtained monomer was clear-yellowish solid at room temperature.

Urethane prepolymer was prepared from toluene diisocyanate and polypropylene glycolat (molecular weight of 2000). The two reactants were directly mixed in a four-necked round bottomed flask under a nitrogen stream at about 60ºC for 2 hours to yield a light yellow prepolymer.

Matrix and Composites Preparation

The benzoxazine monomer was mixed with the urethane prepolymer to provide benzoxazine (BA-a)/urethane prepolymer (PU) mixture at the desirable mass fraction. The mixture was thoroughly stirred at about 80°C in an aluminum container until a homogeneous mixture was obtained. The Kevlar^{TM} fabrics were pre-impregnated with the binary mixture using hand-lay up procedure at 80°C. The weight fraction of the fiber was kept constant at approximately 80%. The pre-prages were then molded using a compression molder at 200°C, 50MPa.

Characterization

Dynamic mechanical properties of the composits were investigated by Dynamic Mechanical Analyzer (DMA) (model DMA242, NETZSCH). 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.

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

RESULTS AND DISCUSSION

Dynamics Mechanical Properties of Kevlar^{TM} Reinforced BA-a/PU Composites

The dynamic mechanical properties of Kevlar^{TM} BA-a/PU composites were examined. The storage modulus (E′) of Kevlar^{TM} BA-a/PU composites with PU content in the range of 0 to 40 wt% are illustrated in Figure 1. The storage moduli of the obtained composites were systematically decreased from 16.82 GPa to 11.92 GPa with an addition of PU content from 0 to 40 wt%. Generally, the storage modulus of a solid sample at room temperature provides a stiffness of material. A decreasing in storage modulus with an increasing in PU content was due to

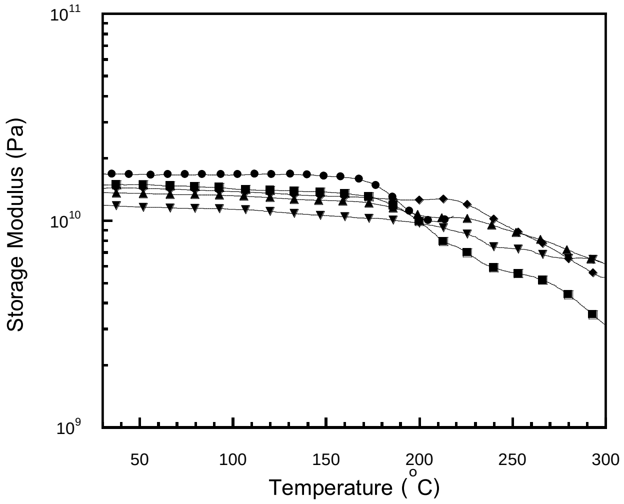

Fig. 1: Storage modulus ofKevlar^{TM} fiber reinforced BA-a/PU composite: BA-a/PU 100/0 (●),BA-a/PU 90/10 (■),BA-a/PU 80/20 (◆), BA-a/PU 70/30 (▲), and BA-a/PU 60/40 (▼).

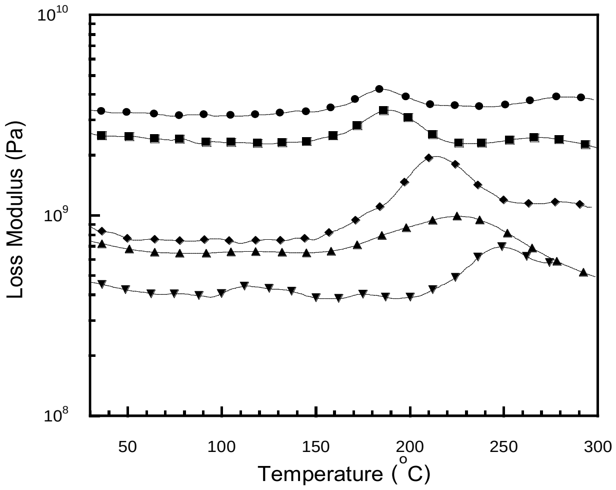

Fig. 2: Loss modulus of Kevlar™ fiber reinforced BA-a/PU composite: BA-a/PU 100/0 (●),BA-a/PU 90/10 (■),BA-a/PU 80/20 (◆), BA-a/PU 70/30 (▲), and BA-a/PU 60/40 (▼).

the incorporation of the more flexible PU molecule in the composite. This observation is in good agreement with previous studied of benzoxazine-urethane copolymer reported by Rimdusit *et al.* (2011).

The loss modulus (E") of Kevlar™ fabric composites were demonstrated in Figure 2. The Glass transition temperature (T_g) of the crosslinked materials were determined from the maximum peak of E"of the plots. The T_gs of Kevlar™ composites at 0, 10, 20, 30 and 40 wt% of PU content were 184, 187, 213, 225 and 247°C, respectively. It was observed that the addition of the PU into the composites was found to increase the T_g value of Kevlar™ fiber composites. These values were higher than those of BA-a/PU matrices which were reported to be in range of 165-245°C (Rimdusit *et al.*, 2011). The implication of these phenomena is probably due to the contribution of the substantial interfacial adhesion between the fibers and the polybenzoxazine alloys.

The α-relaxation peaks of the loss factor or tan δ of composites are shown in Figure 3. The magnitude of tan δ was observed to decrease with the increasing mass fraction of the PU resin in the alloy matrices and the peak maxima also shifted to higher temperature. The peak height of the tan δ in the vicinity of T_g was observed to be smaller with increasing PU content. Since tan δ is a ratio of a viscous to an elastic component of dynamic moduli of a specimen. Therefore, it can be implied that its decreasing height with the PU around T_g is associated with a lower segmental mobility, and thus is indicative of a higher degree of crosslinking for the urethane-rich samples as observed in our BA/PU alloy systems (Ishida *et al.*, 2001). In other words, polymer alloys are soft at room temperature due to PU fraction but possess higher degree of crosslinking that can inhibit large scale mobility at elevated temperature.

An Activation Energy of Kevlar™ Reinforced BA-a/PU Composites

The apparent activation energy for glass transition (ΔE) can be used to characterize

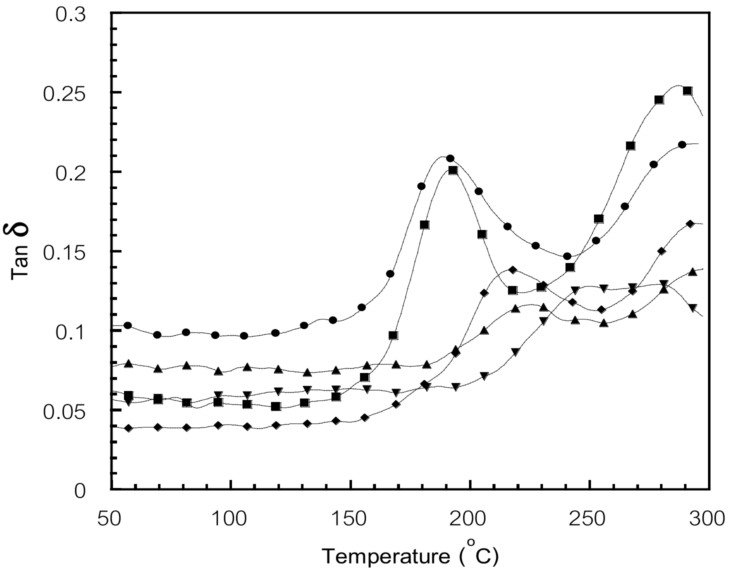

Fig. 3: Tan δ of Kevlar™ fiber reinforced BA-a/PU composites: BA-a/PU 100/0 (●),BA-a/PU 90/10 (■),BA-a/PU 80/20 (◆), BA-a/PU 70/30 (▲), and BA-a/PU 60/40 (▼).

the relationship between the shift of glass transition temperature and frequency. It is mentioned that T_g represents the relationship between the mobility of polymer chains and temperature whereas ΔE represents a relationship between mobility and time scale the energy barrier of transition temperature relaxation. The ΔE values for glass transition of the obtained composites can be calculated from the Arrhenius equation.

A good linear correlation was observed, and the activation energy was also calculated from the slope of the relationship between the frequency and glass transition temperature as depicted in Figure 4. The activation energy of matrices tended to be increase with increasing

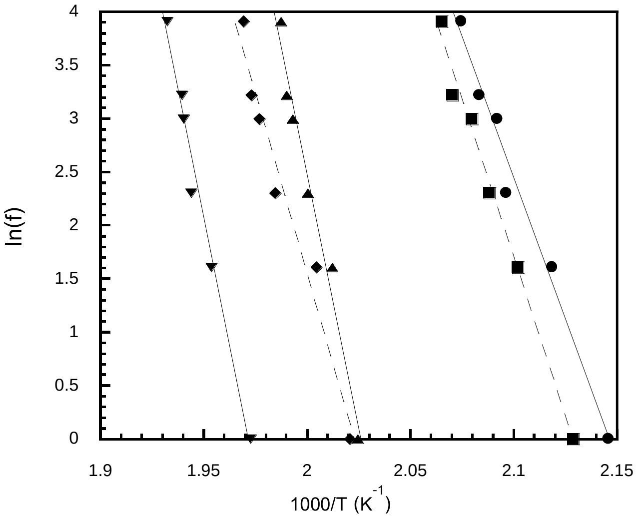

Fig. 4: The relationship between measurement frequency (f) and temperature of Tan δ :BA-a/PU 100/0 (●),BA-a/PU 90/10 (■),BA-a/PU 80/20 (◆), BA-a/PU 70/30 (▲), and BA-a/PU 60/40 (▼).

amount of PU content i.e. 434 kJ/mole (BA-a/PU 100/0), 491 kJ/mole (BA-a/PU 90/10), 544 kJ/mole (BA-a/PU 80/20), 789 kJ/mole (BA-a/PU 70/30) and 809 kJ/mole (BA-a/PU 60/40). This can be explained that in the glass transition region, the motion of molecules is governed by the crosslink density. The enhancement of crosslink density affects to the decreasing of the free volume and oscillations of molecules about mean position. This observation indicated the effective stress transfer between fibers and matrix at higher PU content, which decreased the polymer chain mobility (Saw *et al.*, 2011).

Mechanical Properties of Kevlar^{TM} Reinforced BA-a/PU Composites

The flexural strength and flexural modulus was observed at 0wt% of urethane content and was found to decrease with increasing in PU content. Moreover, the stress deflection curve of the Kevlar^{TM} composites were 2.04 mm for BA-a/PU (100/0), 3.37 mm for BA-a/PU (90/10), 4.27 mm for BA-a/PU (80/20), 3.37 mm for BA-a/PU (70/30) and 2.71 mm for BA-a/PU (60/40). The increased strain behavior may be caused by the addition of the more flexible PU fraction to the benzoxazine matrix. This indicates the improved flexibility with an addition of flexible urethane to the obtained composites that can provide more deflection during ballistic impact (Nayak et.al. (2012)). The flexibility of Kevlar^{TM} composites slightly decreased when PU content was greater than 30wt% which was likely from the discontinuous or imperfect network. This observation is in good agreement with our recent work. Rimdusit *et al.* (2008) reported the ability of network formation of BA-a/PU alloys at different composition.

CONCLUSIONS

Thermal and mechanical behaviors of Kevlar^{TM} reinforced BA-a/PU composite at various PU content (0-40 wt%) have been studied. The storage and loss modulus of the composites was found to decrease with an addition of flexible PU content into rigid benzoxazine. Correspond to the dynamic mechanical behavior, flexural strength and modulus were also decreased with increasing PU content. In contrast to T_g of Kevlar^{TM} reinforced BA-a/PU composite, the greater PU content resulted in the higher T_g which agreed with the higher in activation energy at higher PU content. The observed synergism in T_g of Kevlar^{TM} reinforced benzoxazine-urethane was an outstanding characteristic for a wide range of applications, which requires high thermal stability. The maximum stress deflection of 80/20 BA-a/PU composite was expected to provide the highest ballistic performance compared to the others.

ACKNOWLEDGEMENTS

This research is supported by the Royal Golden Jubilee Scholarship of Thailand Research Fund and the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission (AM1076A).

REFERENCES

1. Ishida, H.(1996). U. S.Pat. 543,516.
2. Ishida, H.; and Lee, Y. H.(2001). Study of hydrogen bonding and thermal properties of polybenzoxazine and poly-(epsilon-caprolactone) blends. *J. Polym. Sci. Pol. Phys.*,39, 736-749.
3. Nayak, N.; Sivaraman, P.; Banerjee, A.; Madhu, V.; Dutta, A.L.; and Misha, B.C.(2012). Effect of Matrix on the Ballistic Impact of Aramid Fabric Composite Laminates by Armor Piercing Projectiles. *Polym. Composite.,*33, 443-450.
4. Rimdusit, S.; Bangsen, W.; and Kasemsiri, P.(2011). Chemorheology and Thermomechanical Characteristics of Benzoxazine-Urethane Copolymers. *J. Appl. Polym. Sci.*,121, 3669-3678.
5. Rimdusit, S.; Kunopast, P.; and Dueramae, I.(2011). Thermomechanical Properties of Arylamine-Based Benzoxazine Resins Alloyed with Epoxy Resin, *Polym. Eng. Sci.*, 51, 1797
6. Saw, S. K.; Sarkhel, G.; and Choudhury, A.(2011). Dynamic Mechanical Analysis of Randomly Oriented Short Bagasse/Coir Ghosh, R., and Wong, T. (2006). Effect of module design on the efficiency of membrane chromatographic separation processes, *J. Membr. Sci.*, *281*, 532-540.
7. Takeichi, T.; Guo, Y.; Rimdusit, S.(2005). Performance Improvement of Polybenzoxazine by Alloying with Polyimide: Effect of Preparation Method on the Properties, *Polym.,* 46, 4909-4916.