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Volume shrinkages and mechanical properties of various fiber-reinforced hydroxyethyl methacrylate–polyurethane/unsaturated polyester composites

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Abstract

In this study, two kinds of hydroxyethyl methacrylate–polyurethane (HEMA–PU) were used as volume shrinkage modifiers, and several hydroxyethyl methacrylate–polyurethane modified unsaturated polyester (HEMA–PU/St./UP) resins crosslinked with styrene were synthesized and characterized using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and in terms of their mechanical properties, including their tensile strengths and Izod impact energies. The properties of the HEMA–PU–modified St./UP and St./UP were compared for potential applications as matrices for glass fiber-, aramid fiber-, and UHMWPE fiber-reinforced composites. The effects of the HEMA–PU content and the type of polyol in the HEMA–PU resin matrices of the composites were investigated through testing of their mechanical properties, bulletproof testing, and observations of their morphologies.

Keywords: A. Fibres; A. Polymer-matrix composites (PMCs); B. Mechanical properties; B. Infrared (IR) spectroscopy

1. Introduction

Although unsaturated polyester resins are used in many industrial applications because of their good mechanical properties, high processability, and high chemical resistance, they often undergo undesirably high volume shrinkage. To reduce the volume shrinkage of the matrix system, many researchers [1–3] have attempted to prepare modified polymer reins, for use as matrices in composites, from unsaturated polyester resins. Cao et al. [4,5] found that the addition of low-profile additives (LPA) reduced the UP resin's shrinkage, but increased the residual styrene (St.) content; they also found that the use of an unsaturated polyester at a low MMA/styrene ratio led to a lower amount of styrene residue with almost unchanged shrinkage, whereas a high MMA/styrene ratio reduced the residual styrene adequately but with poor volume shrinkage control. Li et al. [6–9] studied the low-temperature curing shrinkage control mechanism of LPA; they demonstrated that the shrinkage behavior of the resin mixture is dependent upon the competition between the shrinkage arising from polymerization and the expansion arising from microvoid formation. Huang et al. [10–12] found that the addition of LPA enhanced the degree of phase separation between LPA and a styrene-crosslinked polyester resin, such that microgel particles could be identified throughout

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the reaction; they also observed the morphologies of styrene-crosslinked polyester containing various LPA content. Zhang et al. [13] described how compatible LPAs yielded more-homogeneous matrices than did immiscible ones.

Fiber-reinforced polymer composites are used widely in material applications. Several kinds of fibers have been applied as reinforcing materials, including carbon fibers [14,15], glass fibers [16–19], aramid fibers, and ultrahigh-molecular-weight polyethylene (UHMWPE) fibers [20,21].

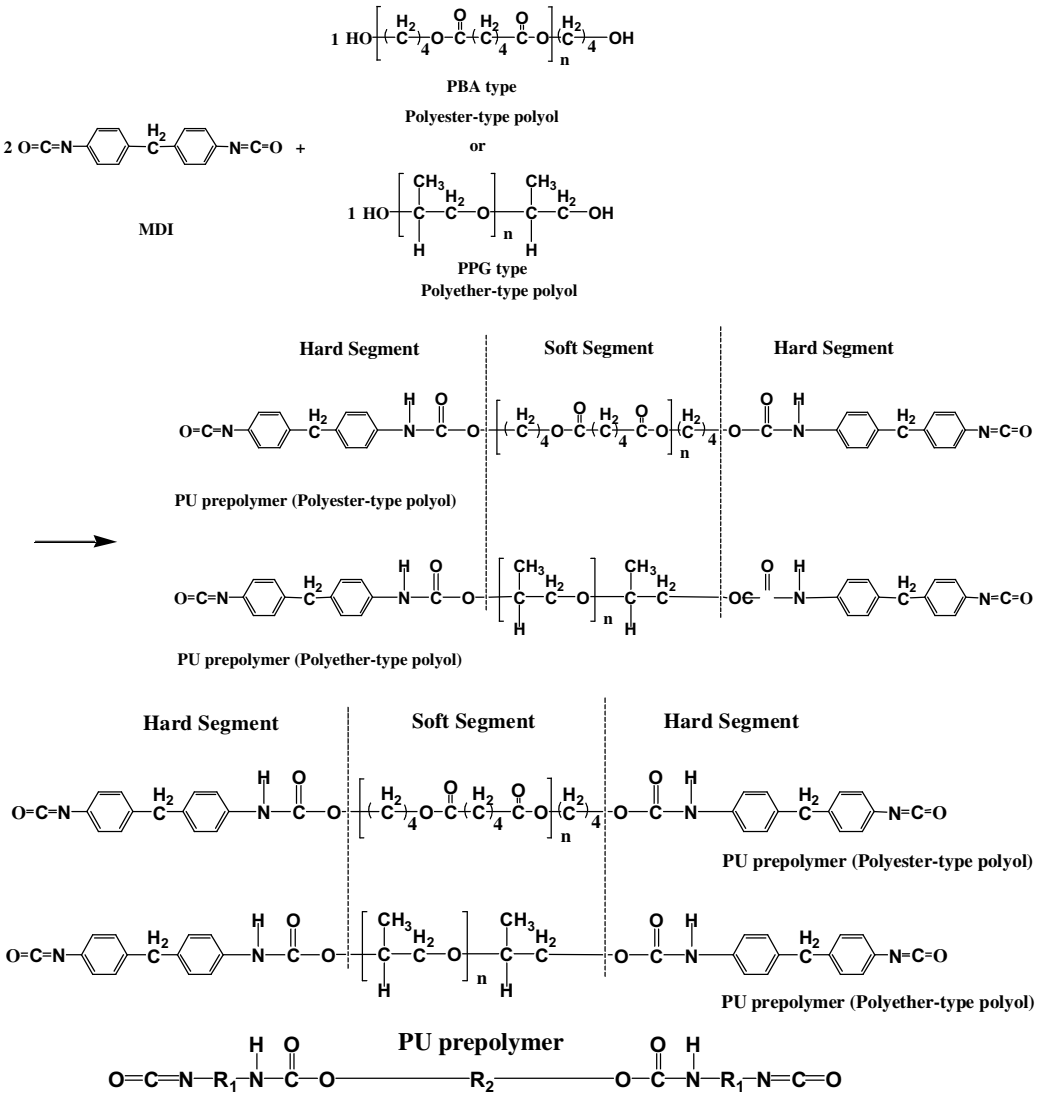
In this study, we synthesized eight sets of HEMA–PU/St./UP resin systems possessing various HEMA–PU contents and polyol types to investigate their volume shrinkages and mechanical properties, including their tensile strengths and Izod impact energies, and compared them with those of traditional UP resins. For the manufacture of the fiber-reinforced composites, we incorporated four types of fiber reinforcement material (i.e., E- and P-type glass fibers, aramid fiber, and UHMWPE fiber) into two different HEMA–PU/St./UP matrices and then determined the bulletproof nature and mechanical properties of the systems, including their tensile strengths and elongations. We obtained SEM images to observe the fracture behavior and wet-out properties of these composites. The bulletproof properties of the UHMWPE fiber reinforced HEMA–PU/St./UP and aramid fiber reinforced HEMA–PU/St./UP composites of different thickness were also investigated in this study [22,23].

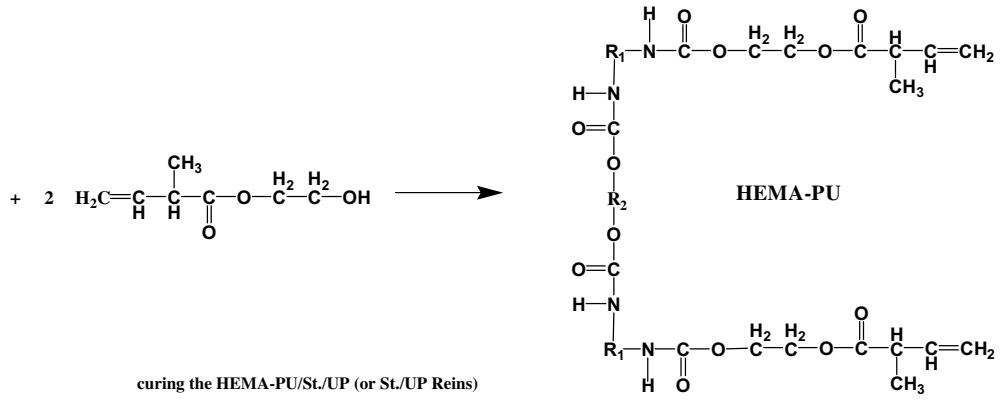
2. Experimental

The materials used are listed in Table 1. Two polyols, PBA 700 and PPG 400, were heated and degassed under vacuum overnight prior to use.

2.1. Preparation of Polyurethane prepolymer and HEMA–PU

The preparation of PU prepolymer was mentioned elsewhere before [23,24]. The HEMA–PU polymer was prepared by reacting HEMA (2 equiv.) with PU prepolymer (1 equiv. based on PPG 400 or PBA 700). The molecular structures of the HEMA–PU polymers (based on PPG 400 or PBA 700) are presented below.





2.2. Curing the HEMA–PU/St./UP (or St./UP reins)

Methyl ethyl ketone peroxide (MEKPO, 5 phr, initiator) and the HEMA–PU/St./UP system which containing a particular HEMA–PU content (or the UP resin with various styrene contents) were mixed individually, and then poured into an aluminum mold coated with polytetrafluoroethylene (PTFE) and pressed at 100 kg/cm^2 and 60 °C for 1.5 h before post-cured at 150 kg/cm^2 and 80 °C for 1.5 h.

2.3. Preparation of glass fiber-reinforced HEMA–PU/St./UP and St./UP composites

Each 0.125-mm-thick glass fiber mat was impregnated with HEMA–PU/St./UP and St./UP resins containing various St. contents. The impregnated mats were fabricated using eight plies; the dimensions of the compression mold were $200 \times 200 \times 1$ mm (length × width × thickness). The pre-pregs were stacked and compression-molded at 100 kg/cm^2 and 60 °C for 1.5 h prior to post-curing at 150 kg/cm^2 and 80 °C for 1.5 h.

2.4. Preparation of UHMWPE and aramid fiber-reinforced HEMA–PU/St./UP composites

The preparation of UHMWPE and aramid fiber-reinforced HEMA–PU/St./UP composites was described elsewhere [22,23]. The MEKPO initiator (5 phr) and HEMA–PU/St./UP systems with various HEMA–PU contents were chosen as the matrices in this study. Unidirectional fiber reinforced composites ($[0°]_8$) and cross-ply ones ($[0°, 90°]_{2S}$) were fabricated using eight plies of manufactured pre-pregs. For mechanical testing, the various composite specimens were cut into smaller sizes using a hydraulic power cutting machine (UHO Enterprise Corporation, Taiwan).

2.5. Testing methods

Infrared spectra were recorded using a BIO-RAD FTS-40 FT-IR spectrophotometer operated at 4 cm^{-1} resolution. Morphological studies were performed using a Tescan 5136 MM scanning electron microscope (SEM). The tensile strengths and Izod impact energies of the various HEMA–PU/St./UP and St./UP samples were measured according to the ASTM-638 and ASTM-256 protocols. The stress–strain properties of the various UHMWPE fiber-reinforced composites were measured according to the ASTM-D3039 protocol. The method of bulletproof testing was performed under National Institute of Justice ballistic standards (NIJ 0108.01 IIA and NIJ 0108.01 IIIA). The UHMWPE and aramid fibers were knitted using the Plain Weaves method of the Super Textile Corporation, Taiwan. Every 0.5-mm-thick UHMWPE and aramid fiber knit was impregnated with HEMA–PU/St./UP (20/20/60, weight ratio) resin. The impregnated knits were fabricated using 6, 10, and 20 plies; and the compression method was the same as mentioned before.

3. Results and discussion

3.1. FTIR spectroscopic analysis

Fig. 1 displays the FTIR spectra of HEMA–PU(PBA 700) resin. A broad peak for the –OH groups

Table 1
Experimental materials

Designation	Description
UHMWPE fiber	Spectra@900 Denier 1200
Aramid fiber	Technora@ T-200
Glass fiber	450 g/m^2 (E-type), 300 g/m^2 (P-type) (Taiwan Glass Industry Co., Taiwan)
PBA 700 (polyol)	Poly(tetramethylene adipate)glycol; MW = 700 (Tai Gin Co., Taiwan)
PPG 400 (polyol)	Poly(oxypropylene)glycol; MW = 400 (Tai Gin Co., Taiwan)
MDI	4,4′-Diphenyl methane diisocyanate (TCI Chem.)
St.	Styrene (Acros Organics)
HEMA	Hydroxyethyl methacrylate (Acros Organics)
UP	Unsaturated polyester (Eternal Co., Taiwan)
MEKPO	Methyl ethyl ketone peroxide (Eternal Co., Taiwan)
Acetone	2-Propanone (Acros Organics)

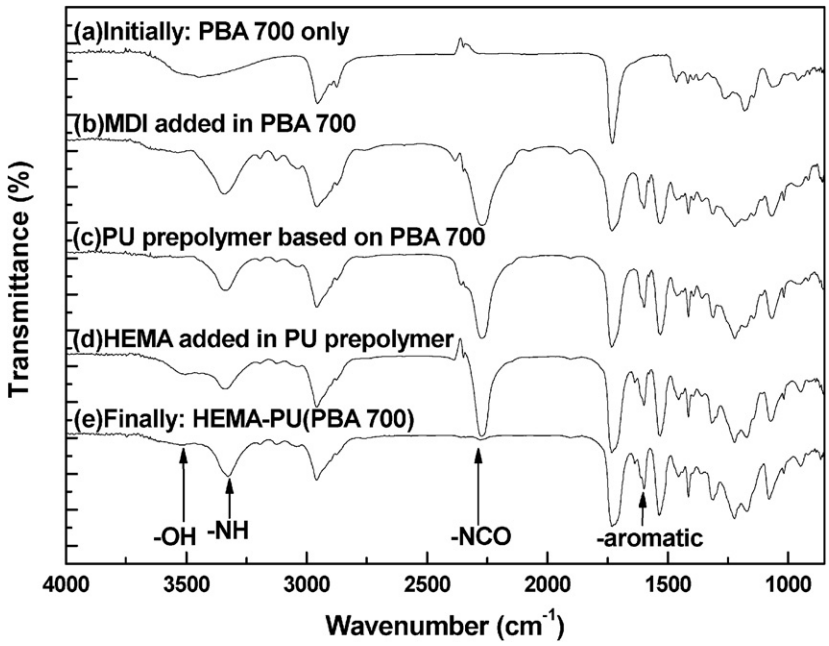


Fig. 1. FTIR spectra recorded at five different reaction stages during the synthesis of PU prepolymer based on PBA 700: (a) Initially: PBA 700 only; (b) MDI added in PBA 700; (c) PU prepolymer based on PBA 700; (d) HEMA added in PU prepolymer; (e) Finally: HEMA–PU(PBA 700).

(3500 cm^{-1}) of the polyol is evident in Fig. 1a. The spectrum of the sample obtained after mixing MDI (2 equiv.) and PBA 700 (1 equiv.) in a purged reaction kettle is presented in Fig. 1b. During the middle stages of the reaction, the intensity of the signal of the –OH groups (3500 cm^{-1}) gradually disappeared, while that of the signal for the –NCO groups (2270 cm^{-1}) reduced to half of its original value (based on the signal for the *p*-phenylene moieties at 840 cm^{-1}), as presented in Fig. 1c. Finally, HEMA (2 equiv.) was added to the reaction systems, as indicated in Fig. 1d. During the final stages, the peak intensity of the residual –NCO groups (2270 cm^{-1}) continued to reduce until finally it remained constant, as indicated in Fig. 1e.

3.2. Volume shrinkages and mechanical properties of various St./UP systems

The compatibility between the styrene and the unsaturated polyester was high because they both contain benzene rings. Thus, the addition of styrene acted as a diluting modifier in the St./UP system; it diluted the viscosity of the neat unsaturated polyester resin, and enhances the mechanical properties by increasing the cross-linking density in the final St./UP networks. Table 2 lists the volume shrinkages and tensile properties of St./UP systems containing various styrene contents.

As presented in Fig. 2, the values of volume shrinkage increased linearly upon increasing the styrene contents in

Table 2
Physical properties of UP resins with different St. contents and HEMA–PU/St./UP resin systems with various HEMA–PU contents

Modified UP resin systems	PU content (wt%)	Styrene content (%)	Tensile strength (MPa)	Izod impact energy (J/m)	Volume shrinkage (%)
Styrene/unsaturated polyester	0	12.6	13.7	52.0	4.1
	0	19.6	15.1	53.5	5.9
	0	26.4	17.3	54.5	6.7
	0	30.5	23.3	57.7	8.2
	0	40.0	25.3	58.2	11.3
	0	44.8	25.2	58.3	12.1
	0	54.9	21.3	56.6	13.6
HEMA–PU(PPG)/Styrene/unsaturated polyester	8.0	32.0	18.6	57.6	7.3
	10.0	30.0	17.0	57.9	7.0
	13.3	26.6	15.1	60.1	5.5
	20.0	20.0	12.9	60.8	3.5
HEMA–PU(PBA)/Styrene/unsaturated polyester	8.0	32.0	24.0	58.2	7.1
	10.0	30.0	14.1	58.8	6.9
	13.3	26.6	12.6	63.0	5.6
	20.0	20.0	5.0	82.3	2.9

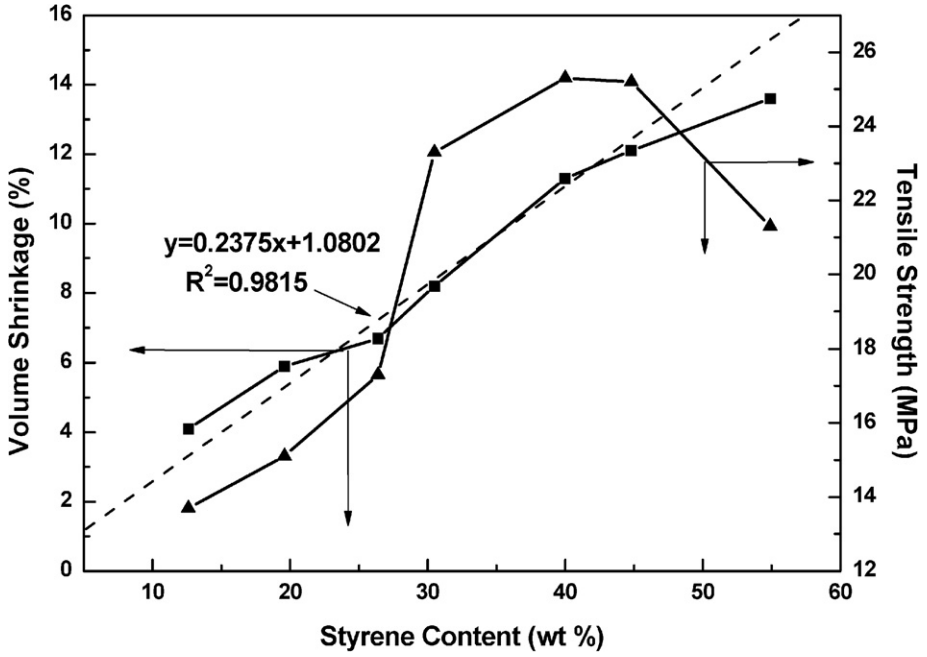


Fig. 2. Effect of the styrene content on the tensile strengths and volume shrinkages of St./UP resin systems.

the St./UP system, and the regression equation, $y = ax + b$, had values of a and b of 0.2375 and 1.0802, respectively (R^2=0.9815). Extending the regression equation to the Y axis (the styrene content = 0%), the value of b (1.0802%) represents the volume shrinkage of the neat unsaturated polyester. The positive slope value of a, increased upon increasing the styrene content. The tensile strength increased upon increasing the styrene content in the St./UP system up to 40 wt%, but then it decreased to 21.3 MPa at a styrene content of 54.9 wt%. Thus, the optimal styrene addition for the St./UP system to provide the strongest material was 40 wt% (25.3 MPa). Thus, for subsequent experiments, the HEMA–PU/St./UP resin materials were prepared with the modifier (HEMA–PU/St.) content of 40 wt% in the unsaturated polyester resin.

3.3. Volume shrinkages and mechanical properties of various HEMA–PU/St./UP systems

Table 2 lists the volume shrinkages and mechanical properties, including tensile strengths and Izod impact energies, of HEMA–PU/St./UP systems containing various HEMA–PU contents and two types of polyol (PPG 400 and PBA 700). The values of tensile strength decreased upon increasing the HEMA–PU content in the HEMA–PU(PPG 400)/St./UP and the HEMA–PU(PBA 700)/St./UP systems. The HEMA–PU(PPG 400)/St./UP system exhibited higher values of tensile strength than did the HEMA–PU(PBA 700)/St./UP system when the HEMA–PU content was greater than 8 wt%. This situation arose presumably because the HEMA–PU(PBA 700)/St./UP system contained a greater number of soft segmental structures, causing the cross-linking density in the HEMA–PU, styrene, and the unsaturated polyester network to be lower than that in the HEMA–PU(PPG 400)/St./UP system at the same HEMA–PU content.

The values of the volume shrinkage decreased upon increasing the HEMA–PU content in the HEMA–PU(PBA 700)/St./UP and the HEMA–PU(PPG 400)/St./UP systems; these two types of HEMA–PU-modified St./UP resin systems exhibited seemingly identical volume shrinkages. The lowest volume shrinkages were 3.5% for the 20 wt% HEMA–PU(PPG 400)- and 2.9% for the 20 wt% HEMA–PU(PBA 700)-modified St./UP resin system. As mentioned above in the discussion of the St./UP system, the volume shrinkage of the neat unsaturated polyester resin was 1.0802%; therefore, these two polyol-containing 20 wt% HEMA–PU-modified St./UP resin systems possessed highly improved volume shrinkage properties. It seems that the soft segmental structures of the two polyol-modified HEMA–PU systems had been dispersed uniformly in the microvoids during the course of UP cross-linking, such that the HEMA–PU units reacted with the styrene and the unsaturated polyester resins to result in the formation of network structures during the cross-linking reaction.

In the HEMA–PU(PPG 400)/St./UP system, the Izod impact energy decreased to 57.6 J/m at an HEMA–PU content of 8 wt%, but increased to 60.8 J/m at an HEMA–PU content of 20 wt%, relative to that of the St./UP (40/60 in weight ratio) (see Table 2). This result is consistent with the SEM images of the fracture surfaces of the HEMA–PU(PPG 400)/St./UP systems. For the 10 wt% HEMA–PU-containing HEMA–PU/St./UP system as shown in Fig. 3a, the fracture surface revealed many con-

tinuous narrow shear band structures, indicating rapid crack propagation [22]. In the HEMA–PU/St./UP system containing 20 wt% HEMA–PU (Fig. 3b), the crack propagated from the surface across the cross-sectional area, and fracture surfaces revealed non-continuous, broader cracks. This finding suggests that the HEMA–PU(PPG 400)-modified St./UP systems exhibit better load bearing characteristics. For the HEMA–PU(PBA 700)/St./UP system, the value of Izod impact energy increased from 58.2 J/m at an HEMA–PU content of 8 wt% to 82.3 J/m at an HEMA–PU content of 20 wt%, relative to that of the St./UP (40/60 in weight ratio) resin. This result is consistent with the SEM images in Fig. 3c and d. At higher HEMA–PU content in the HEMA–PU(PBA 700)/St./UP systems, the

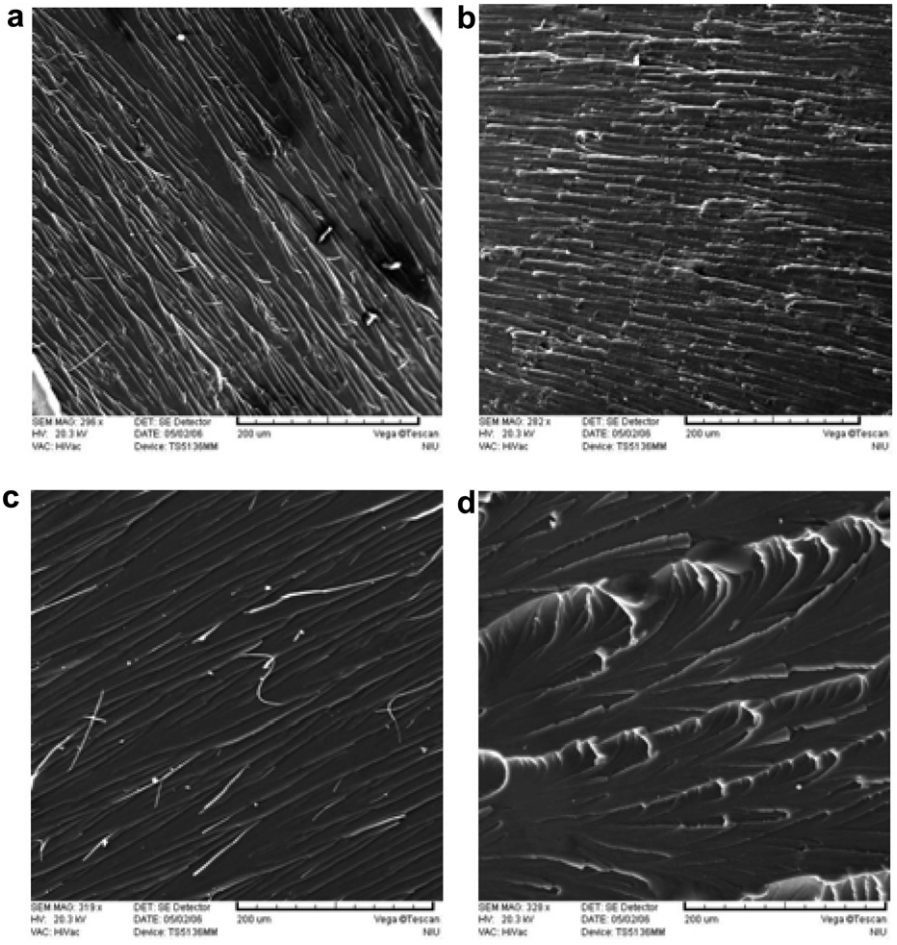


Fig. 3. SEM images of side-view fracture surfaces with various PU content in HEMA–PU/St./UP reins: (a) HEMA–PU(PPG 400) content = 10 wt%; (b) HEMA–PU(PPG 400) content = 20 wt%; (c) HEMA–PU(PBA 700) content = 10 wt%; (d) HEMA–PU(PBA 700) content = 20 wt%.

Table 3
Mechanical properties of various UHMWPE fiber-, Aramid fiber-, and glass fiber-reinforced HEMA–PU(PBA 700)/St./UP composites

Matrix	Reinforcement	Packing way	Tensile strength (MPa)	Elongation (%)
HEMA–PU(PBA 700)/St./UP = 20:20:60	UHMWPE fiber	$[0°, 90°]_{2S}$	330.8	31.9
		$[0°]_8$	586.8	39.7
	Aramid fiber	$[0°, 90°]_{2S}$	270.8	26.2
		$[0°]_8$	526.5	28.5
	Glass fiber A	Mat type	102.4	21.3
	Glass fiber B	Mat type	74.8	20.6
HEMA–PU(PBA 700)/St./UP = 8:32:60	UHMWPE fiber	$[0°, 90°]_{2S}$	399.9	30.3
		$[0°]_8$	739.6	33.1
	Aramid fiber	$[0°, 90°]_{2S}$	314.8	15.3
		$[0°]_8$	647.0	23.8
	Glass fiber A	Mat type	114.9	18.6
	Glass fiber B	Mat type	79.7	14.7

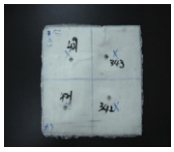
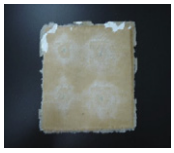
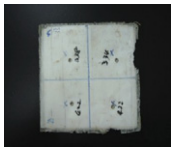
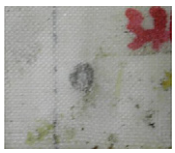
fracture paths exhibited discontinuous, convoluted, and large feather-like features; the fracture surfaces that spread from the bottom upward are presumably responsible for the higher toughness and load bearing characteristics.

Thus, a lower HEMA–PU content (8 wt%) in the HEMA–PU/St./UP resin system led to a higher tensile strength, whereas a high HEMA–PU content (20 wt%) improved the Izod impact energy and led to a smaller volume shrinkage for both types of polyol-containing HEMA–PU/St./UP systems. The HEMA–PU(PBA 700)/St./UP systems exhibited superior values for their tensile and Izod impact energies relative to those of the HEMA–PU(PPG 400)/St./UP systems at both 8 and 20 wt% HEMA–PU content. Thus, for manufacturing subsequent fiber-reinforced composite materials, we incorporated 8 and 20 wt% of HEMA–PU into the HEMA–PU(PBA 700)/St./UP systems.

3.4. Mechanical properties of various fiber-reinforced composites

Table 3 lists the mechanical properties, including tensile strength, elongation, and Izod impact energy, of various glass fiber-, aramid fiber-, and UHMWPE fiber-reinforced HEMA–PU(PBA 700)/St./UP composites containing two different contents of HEMA–PU(PBA 700). The values

Table 4
Bulletproof tests of UHMWPE fiber/HEMA–PU/St./UP composites and Aramid fiber/HEMA–PU/St./UP composites

System (fiber content; vol.%)	Standard testing method	Results	Fiber weight/unit composite area (g/cm^2)	Result photographs	
				Front face	Rear face
3 mm UHMWPE fiber composite (30.93 vol.%)	NIJ 0108.01 II A (380 m/s)	Penetrated	0.09		
3 mm Aramid fiber composite (31.18 vol.%)	NIJ 0108.01 II A (380 m/s)	Penetrated	0.13		
5 mm UHMWPE fiber composite (26.80 vol.%)	NIJ 0108.01 II A (380 m/s)	Penetrated	0.13		
5 mm Aramid fiber composite (27.34 vol.%)	NIJ 0108.01 II A (380 m/s)	Penetrated	0.19		
10 mm UHMWPE fiber composite (28.87 vol.%)	NIJ 0108.01 III A (433 m/s)	Not penetrated	0.28		
10 mm Aramid fiber composite (28.78 vol.%)	NIJ 0108.01 III A (433 m/s)	Not penetrated	0.40		

of tensile strength and elongation of the UHMWPE fiber- and aramid fiber-reinforced HEMA–PU(PBA 700)/St./UP composites incorporating HEMA–PU content of 8 and 20 wt% were clearly higher than those of the two corresponding glass fiber-reinforced composites. These findings suggest that the UHMWPE and aramid fibers have potential for application as next-generation fiber-reinforcement materials.

3.5. Bulletproof properties

Because the HEMA–PU(PBA 700)/St./UP (20/20/60 in weight ratio) system exhibited the lowest volume shrinkage and highest Izod impact energy, we manufactured UHMWPE fiber knit- and aramid fiber knit-reinforced HEMA–PU(PBA 700)/St./UP (20/20/60, weight ratio) composites and subjected them to tests of their bulletproof nature. Table 4 lists the results of bulletproof testing of these two kinds of fiber knit-reinforced HEMA–PU(PBA 700)/St./UP (20/20/60, weight ratio) composites. From standard testing using the NIJ 0108.01 IIA method at thickness of 3 and 5 mm, neither the UHMWPE fiber knit/HEMA–PU/St./UP composite nor the aramid fiber knit/HEMA–PU/St./UP composite was bulletproof (i.e., they were penetrated). In contrast, from standard tests using the NIJ 0108.01 IIIA method at a thickness of 10 mm, both the UHMWPE fiber knit/HEMA–PU/St./UP and aramid fiber knit/HEMA–PU/St./UP composites were bulletproof (i.e., they were not penetrated). The fiber weight per unit composite area played an important role in affecting the bulletproof nature. For example; using the NIJ 0108.01 IIIA method at a thickness of 10 mm, the fiber weight per unit composite area of 10 mm thickness composites were greater than other two smaller thickness (3 and 5 mm), and they could passed the bullet-proof testing via produced the deformation and delimination of composites to adsorb the high-speed impact energy.

4. Conclusion

The optimal addition of styrene to the St./UP system to provide the strongest material was 40 wt%, albeit with a high volume shrinkage. After the addition of two kinds of HEMA–PU as volume shrinkage modifiers for the St./UP system, we found that a lower HEMA–PU content (8 wt%) led to a higher tensile strength, whereas a higher HEMA–PU content (20 wt%) increased the Izod impact energy and decreased the degree of volume shrinkage in both types of polyol-modified HEMA–PU/St./UP systems. The HEMA–PU(PBA 700)/St./UP system exhibited higher values of tensile and Izod impact energies relative to those of the HEMA–PU(PPG 400)/St./UP system at both 8 and 20 wt% HEMA–PU addition.

The UHMWPE fiber- and aramid fiber-reinforced HEMA–PU(PBA 700)/St./UP composites displayed clearly higher values of tensile strength and elongation than did the two corresponding types of glass fiber-reinforced composites. Thus, it seems that the UHMWPE and aramid fibers have the potential for application as next-generation fibers reinforcement materials. The mechanical properties of the UHMWPE fiber- and aramid fiber-reinforced composites were different, suggesting that these two kinds of fibers were suited to applications in different fields.

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