

Synthesis, Characterization, and Mechanical Property of Poly(urethane-glycidyl methacrylate-methyl methacrylate) Hybrid Polymers

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Received 22 June 2010; accepted 12 December 2010

DOI 10.1002/app.34003

Published online 31 March 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Hybrid particles of polyurethane (PU) containing a number of small poly(methyl methacrylate) (PMMA) nanoparticles inside were prepared using glycidyl methacrylate (GMA) monomer as a linker between PU and PMMA; the resulting polymers were poly(urethane-glycidyl methacrylate-methyl methacrylate) (PUGM). It was found that the average particle size (D_p) of the PU particles decreased by the inclusion of PMMA particles possibly owing to the low-solution viscosity of PU. However, D_p of the PUGM hybrid particles increased with increasing the number of covalent bonds between PMMA and PU, which might be due to decreasing the amount of ionic groups per PU chain. Subsequently, the tensile properties of the films made of the PUGM hybrid particles were investigated. It was observed that the modulus of the PU films increased upon the addition of PMMA particle

because of a filler effect. In addition, it was seen that the modulus of PUGM hybrid films increased further with increasing the number of covalent bonds. This was attributed to "restricted mobility" of PU chains anchored to the PMMA particles. It was also observed that the tensile strength changed only slightly for PUGM particles, suggesting that the PU matrix was probably responsible for the necking behavior of the films. The elongation of the samples was found to depend on both the presence of covalent bonds between the PMMA particles and PU matrix and the reduced mobility of the PU chains anchored to PMMA particles. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3111–3121, 2011

Key words: hybrid polymers; crosslinking; mechanical property; polyurethane; methyl methacrylate

INTRODUCTION

As ecofriendly materials, water-borne acrylic and urethane polymers have been used in the forms of fibers, synthetic leathers, rubbers, adhesives, coatings, and so on. Even though their wide use in the fields of paints, printer inks, and special coatings, however, the water-borne polymers have some drawbacks, compared with the solvent-borne polymers. The drawbacks are weak water-resistance and poor film performance arising from the presence of hydrophilic moieties in polymer backbone chains. Thus, over the years, several methods have been

developed to prepare water-borne polymers that are similar to organic solvent-borne polymers in their properties. The methods include the structural control of emulsion particles, the seeded polymerization, and the preparation of emulsion particles having multiphase morphology.^{1–5}

In general, acrylic polymers are widely used in a coating industry because of their excellent toughness, weatherability, reactivity, compatibility and miscibility, and gloss and low price. However, some of physical and mechanical properties of acrylic polymers (for example, flexibility, elongation, adhesive strength, hardness) are not as good as those of polyurethane (PU). Thus, recently it was attempted to synthesize water-borne PU-acrylic hybrid polymers that have both the excellent adhesive strength and flexibility of PU and the weatherability, chemical resistance, and gloss of acrylic polymers.^{1,3,6–25} At this point, it should be mentioned that to prepare PU-acrylic hybrid nanoparticles, a mini-emulsion polymerization process can be applied,^{13,21,23,24} while a UV-induced hardening method can be used for

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Contract grant sponsor: Korean Government (National Research Foundation of Korea Grant); contract grant number: NRF-2009-352-D00076.

PU-acrylate coating.^{19,22} Interestingly, most of the studies on the PU-acrylate hybridization process have been focused on the swelling of acrylic monomers in the PU domains.^{9,18} Cheong et al.²⁰ prepared spherical poly(urethane-ethyl acrylate) hybrid particles of high molecular weight (MW) and 100 nm in their average diameter. They found that as the amount of ethyl acrylate in the PU increased, the cast films made of hybrid particles showed decreasing tensile strength and modulus. They also observed that the tensile strength values of the hybrid particle films were higher than that of the films prepared by simple blending of PU and poly(ethyl acrylate). Yeom et al.²⁵ prepared poly(urethane-methyl methacrylate) (PUM) hybrid particles using prepolymer synthesis and soap free emulsion polymerization methods. They reported that the average size of the poly(methyl methacrylate) (PMMA) particles became larger with increasing amount of MMA monomers and that the tensile strength of the PUM increased with increasing PMMA contents. However, it should be noted that in their PUM hybrid system there were no covalent bonds between PU chains and PMMA particles.

In this study, we fabricated PUM hybrid particles by adding glycidyl methacrylate (GMA) monomers as linkers between PMMA particles and PU matrix; the resulting polymers were poly(urethane-glycidyl methacrylate-methyl methacrylate) PUGM polymers. Then, we investigated the mechanical properties of the films made of PUGM hybrid particles as a function of the number of covalent bonds (i.e., the degree of crosslinking) between PU and PMMA. This study reveals the importance of the covalent bond between nano-sized particles and polymer matrix in a hybrid polymer system in the improvement of the mechanical properties of the hybrid polymers.

EXPERIMENTAL

Materials

Polyoxytetramethylene glycol (PTMG, MW = 2000 g/mol, OH functionality = 2.0, Dongsung Chemical, Korea) was dried at 120°C under a vacuum for 6 h prior to use. Isophorone diisocyanate (IPDI, Aldrich, USA), triethylamine (TEA, Duksan Chemical, Korea), dibutyltin dilaurate (DBDTL, Aldrich, USA), and ethylene diamine (EDA, Junsei Chemical, Japan) were used as received. Dimethylol propionic acid (DMPA, Aldrich, USA) was dried at 60°C for 24 h under a vacuum. *N*-methyl-2-pyrrolidone (NMP, Lancaster, UK) stored with well-dried molecular sieves was used without further purification. Methyl methacrylate (MMA, Kanto Chemical, Japan) monomer was purified using an inhibitor remover column

(Aldrich, USA). The purified monomer was degassed and stored at -5°C before use. Ethylene glycol dimethacrylate (EGDMA, Aldrich, USA), acting as a PMMA crosslinking agent, and glycidyl methacrylate (GMA, Aldrich, USA), used as linker molecules between PMMA particles and PU polymer chains, were used as received. Distilled and deionized (DDI) water was used throughout the experiments. Potassium persulfate (KPS, Aldrich, USA) was extra pure grade and used without further purification.

Synthesis of PUGM hybrid particles

The reaction scheme for PUGM hybrid particles is given in Figure 1. NCO-terminated PU prepolymers are synthesized and dispersed in an aqueous phase as PU nanoparticles. Then, MMA and a small amount of GMA monomers are added to the PU nanoparticle dispersion for PUGM hybrid particles.

A 1000-mL, four-necked double-jacketed glass reactor, equipped with a mechanical stirrer, a nitrogen inlet, a thermometer, and a condenser, was charged with PTMG, an excess of IPDI, and three drops of DBTL catalyst. The reaction mixture was agitated at 80°C for 2.5 h to obtain NCO-terminated PU prepolymers. DMPA was dissolved in NMP and added to the reaction solution, and the reaction mixture was further stirred for 1.5 h under a N₂ atmosphere until the residual isocyanate content of the NCO-terminated urethane prepolymers, determined separately with a standard di-*n*-butylamine back-titration method, coincided with a theoretical value. Then, the reaction temperature was decreased to 60°C, and TEA was added to neutralize the carboxylic acid groups of the DMPA units. Subsequently, methacrylate monomers (i.e., MMA, EGDMA, and GMA) were added to the viscous PU prepolymer solution, and the solution was stirred for 20 min. After that, the solution was transferred by a dripping method to a 2-L glass reactor that contained DDI water and was purged with an N₂. Afterward, the chain extender EDA in a small amount of DDI water was slowly added to the reactor, kept at 60°C, in a period time of 1 h to make PU particles swollen with the MMA monomers. To prepare the PUGM hybrid particles, KPS aqueous solution was injected to the reactor and the reactant was kept stirring at 200 rpm for 4 h. The reaction temperature was 70°C. The amount of the resulting product was targeted on 40 wt %. The recipe was given in Table I. In this study, the sample notations used are PUGM_x, where *x* indicates the percentage of un-neutralized acid groups of DMPA units, which can form covalent bonds between crosslinked PMMA particles and PU polymer chains.

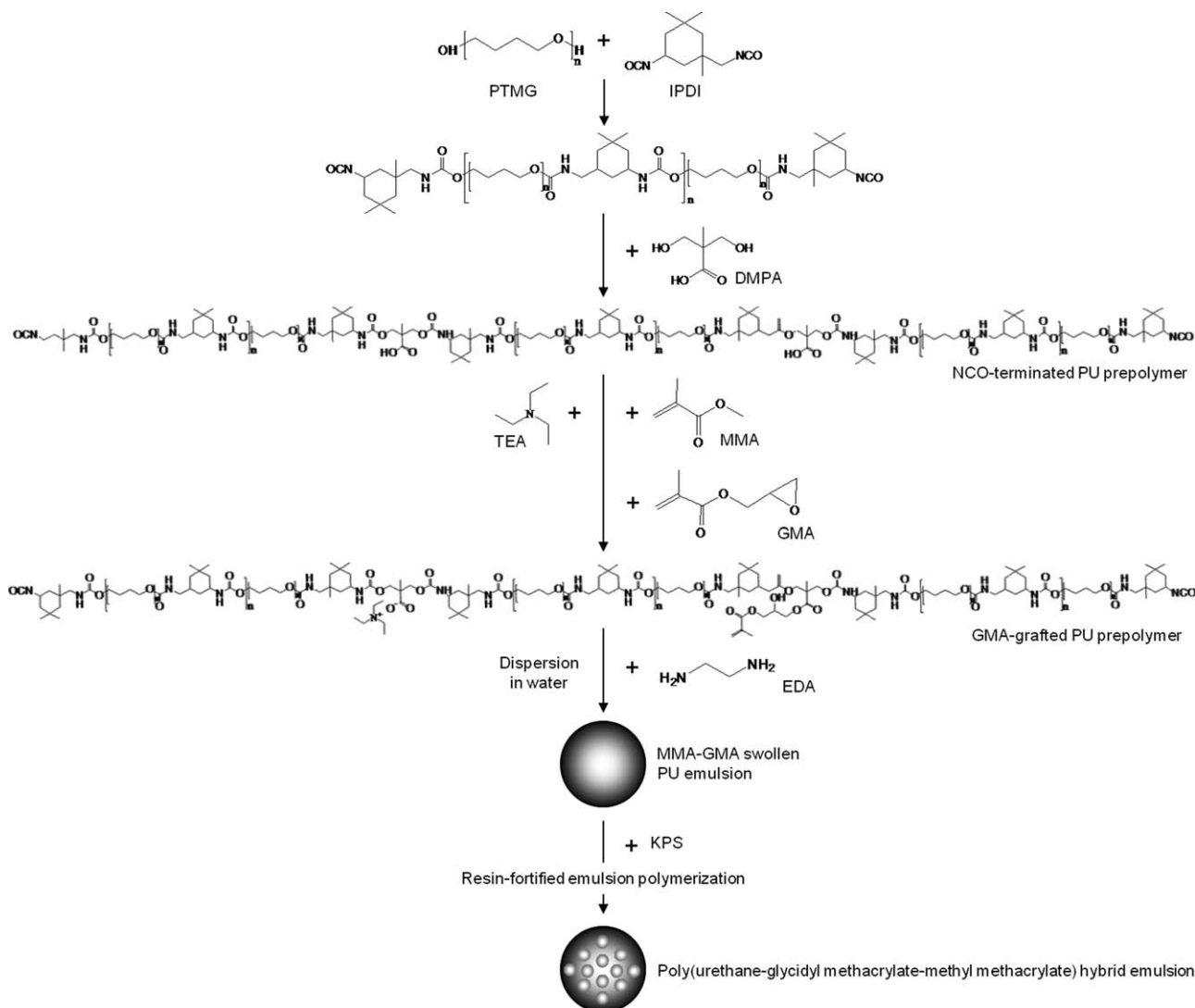


Figure 1 The reaction scheme for the preparation of PUGM hybrid particles via emulsifier-free emulsion polymerization methods.

TABLE I
The Recipe for the Preparation of PUGM Hybrid Particles (Weight in Grams)

Chemicals	PU	PUM	PUGM0	PUGM10	PUGM20	PUGM30	PUGM40
PTMG	100.00	100.00	100.00	100.00	100.00	100.00	100.00
IPDI	40.00	40.00	40.00	40.00	40.00	40.00	40.00
DBTL	0.4	0.4	0.4	0.4	0.4	0.4	0.4
DMPA	6.50	6.50	6.50	6.50	6.50	6.50	6.50
NMP	16.25	16.25	16.25	16.25	16.25	16.25	16.25
TEA	4.90	4.90	4.90	4.41	3.92	3.43	2.94
EDA	3.43	3.43	3.43	3.43	3.43	3.43	3.43
MMA	–	43.95	43.95	43.95	43.95	43.95	43.95
EGDMA	–	1.32	1.32	1.32	1.32	1.32	1.32
GMA	–	–	1.32	1.32	1.32	1.32	1.32
KPS	–	0.18	0.18	0.18	0.18	0.18	0.18
DDI water ^a	225	225	225	225	225	225	225
Solid content (%)	38.2	41.1	38.7	42.3	43.2	45.1	39.1

^a Appropriate amount of water was added for adjustment of solid contents at 40 wt %.

Characterization and mechanical property measurements

Characterization of PUGM hybrid particle

The chemical structures of the PUGM hybrid particles were identified using a proton NMR (AMX-500, Bruker, Germany); DMSO- d_6 was used as the solvent. The average particle size (D_p) and size distribution of the PUGM hybrid particles were measured using capillary hydrodynamic fractionation (CHDF) (CHDF-2000, Matec Applied Sciences, USA) at 20°C. To prepare sample solution for the size analysis, all particles were diluted with DDI water and redispersed using an ultrasonic processor (VCX-500, Watt, Sonics and Materials, USA) equipped with a microtip at 20% power for 10 s.

Morphology of the PUGM hybrid particles was investigated using a transmission electron microscope (TEM) (H-7600, Hitachi, Japan). To prepare samples for the TEM study, the solution containing 0.1 wt % of polymer was deposited onto copper grids (200-mesh) that were then stained with RuO₄ at 40°C and kept for 1 h in a fume cupboard. Afterwards, the grids were dipped into 0.4 wt % aqueous phosphotungstic acid solution and dried.

Mechanical properties of PUGM films

The PUGM hybrid particle dispersions were cast on the clean glass plates to make ~ 200 μm thick films, and the films were then dried in a vacuum oven at 80°C for 24 h. For mechanical tests, the film samples of 10 mm \times 50 mm were loaded into the sample grips of materials testing machine (LR10KPlus series, Lloyd Instruments, UK) with a grip distance of 20 mm; a crosshead speed was 10 mm/min. From each film, 10 specimens were prepared and tested mechanically, and the average values of 10 individual mechanical data were reported here.

RESULTS AND DISCUSSION

Characterization of the PUGM hybrid particles

Figure 2 shows the ¹H-NMR spectra of PUM, PUGM0, and PUGM30 polymers. The chemical structures and chemical shifts of the constituent units of PUGM are listed in Table II. It is seen in Table II that the ¹H-NMR spectra of IPDI are very complicated, and only some peaks, such as 7–9H in $\delta = 1.4$ – 1.9 ppm, can be assigned. The NMR peaks of IPDI in the range of $\delta = 6.8$ – 7.2 ppm are related with primary (1H) hydrogen in *cis* positions of the urethanes and secondary (2H) hydrogen.²⁶

As seen in Figure 2, the NMR peaks for methacrylate group (15H, 16H) are detected; this confirms the chemical structures of the GMA-containing PMMA. The peaks for PTMG polyol are distinct, and the

others are very weak because a large amount of PTMG has been used, compared to other materials of small molar masses. Some peaks for DMPA, TEA, and EDA are hardly identified. The NMR peaks for the epoxy group of GMA unit are detected at $\delta = 3.8$ ppm for PUGM0 sample, as seen in Figure 2(b), but are not observed for PUGM30 sample [Fig. 2(c)]. This illustrates that the epoxy groups have been reacted with carboxylic acid (–COOH) groups. Thus, we can suggest that the GMA that can be copolymerized with PMMA backbone acts as a linker between crosslinked PMMA particles and PU matrix in this reaction.

Particle size of the PUGM hybrid nanoparticles

The average particle sizes of PU, PUM, and PUGM x determined by a CHDF method are listed in Table III. One can find that the average size of the PU particles decreases upon the inclusion of PMMA particles in the PU. This may be due to the fact that the MMA monomers in the PU prepolymer colloids act as a solvent and/or plasticizer for the PU prepolymer. If this is the case, the viscosity of the PU prepolymer solution inside the colloidal particles will decrease, to some extent. This will lead to the formation of smaller size droplets of the PU prepolymer solution containing MMA monomers, compared to that of the PU prepolymer without MMA monomers.²⁷ On the other hand, in the case of PUGM x hybrid particles, the average particle size increases with decreasing degree of ionization of the acid groups of PUGM x (i.e., with increasing number of covalent bonds between PMMA and PU). This can be explained as follows: when partly neutralized PU prepolymers are dispersed in water, the prepolymer chains start rearranging themselves to minimize the enthalpy penalty by placing their ionic groups on the particle surface as much as possible; this rearrangement leads to the formation of relatively stable PU particles. This process naturally results in the formation of larger particles for a polymer having a smaller amount of ionic groups. Thus, the PUGM0 needs fewer polymer chains to stabilize the particle surface with ionic groups, compared with the PUGM40; the average size of the PUGM0 hybrid particles is smaller than that of the PUGM40 particles. However, it should be noted that the size increases drastically from about 50 nm for PUGM20 to 110 nm for PUGM30, which is also larger than that of the PU and PUM; at this point, we do not have a clear explanation for this finding.

Morphology of the PUGM hybrid particles

The representative TEM images of PUGM hybrid nanoparticles are shown in Figure 3. First, it is seen

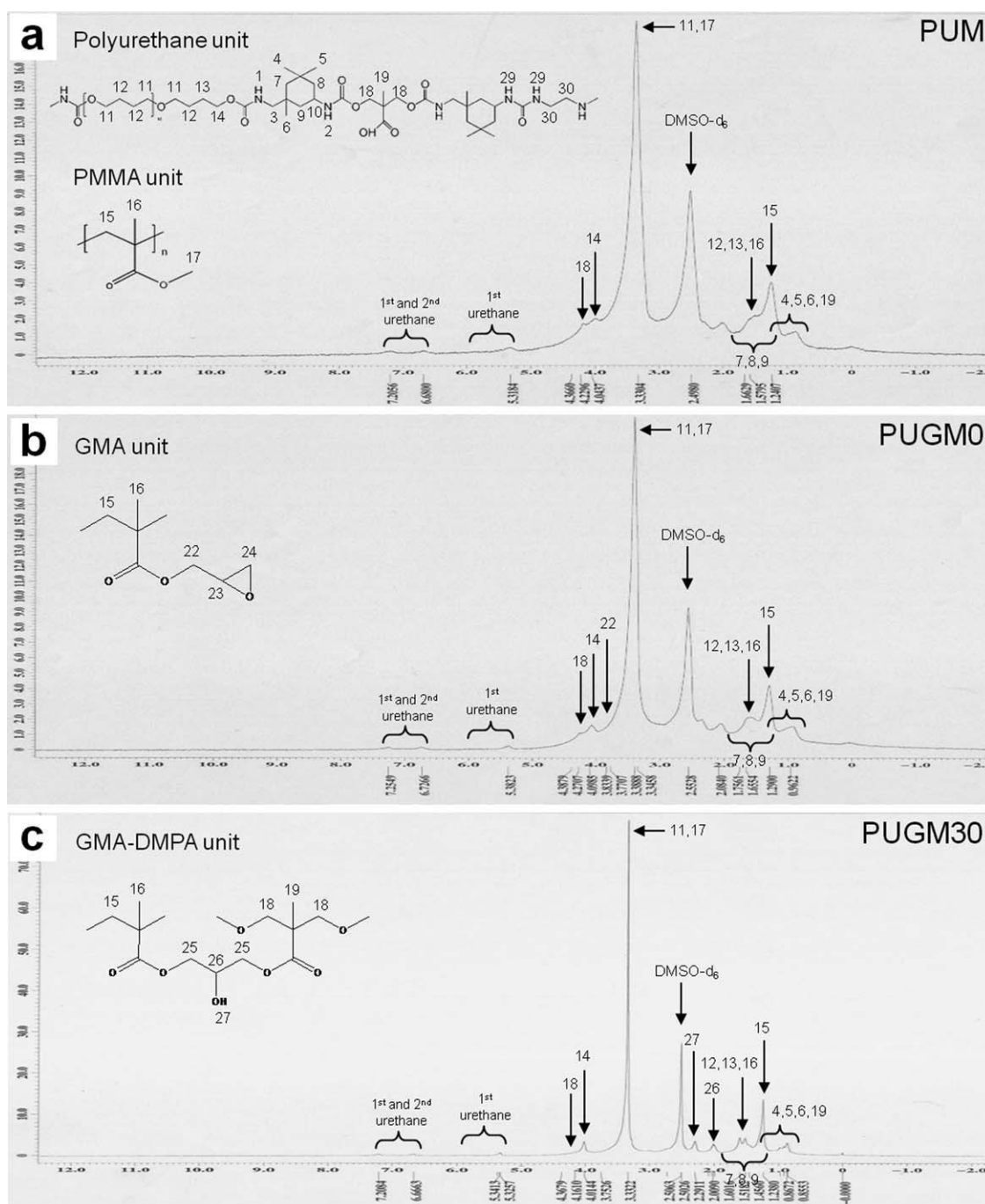
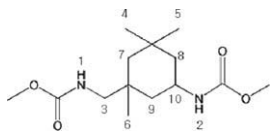
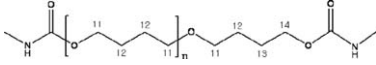
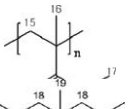
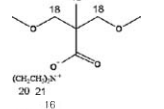
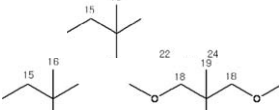
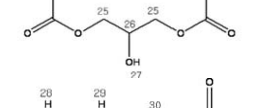
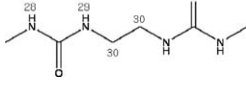


Figure 2 NMR spectra of PUM, PUGM0, and PUGM30.

that the sizes of relatively spherical particles are in the range between 40 and 100 nm, which are in good agreement with those measured using a CHDF method, listed in Table III. Second, the PU homopolymer particles, judging from its TEM image with a regular contrast [Fig. 3(a)], seem to show one phase, which is again in good accordance with previous results.²⁶ Third, unlike poly(urethane-ethyl acrylate) hybrid particles, in which poly(ethyl acrylate) polymer does not form separated particles inside the PU particles, rather grafted onto the PU chains, the TEM

images of the PUM and PUGM hybrid particles show that the PU particles contain a number of phase-separated small PMMA particles inside. This difference is mainly due to the addition of crosslinking agents in the formation of PMMA particles; again, it should be recalled that in the case of poly(urethane-ethyl acrylate) hybrid particles, crosslinking agents were not used. Fourth, the TEM image of PUM particle is similar to those of PUGM hybrid particles. This implies that the presence of GMA does not alter significantly the morphology of PU

TABLE II
Chemical Structures and Chemical Shifts of Constituent Units of PUM and PUGM_x

Constituent unit	Chemical structure	Assignment	
		H species	Chemical shift/ppm
IPDI		1 H ^a	5.4–6.0 (trans)
		2 H ^b	6.8–7.2 (cis)
		3 H	6.8–7.2
		4–6 H	2.72 N/A ^c
		7–9 H	0.9–1.2
		10 H	1.4–1.9
			3.2–3.8
			N/A ^c
			3.3
			1.52 N/A ^c
PTMG		11 H	1.61 N/A ^c
		12 H	4.04
		13 H	1.90
		14 H	1.24
PMMA		15 H	3.6 N/A ^c
		16 H	4.11
		17 H	1.09
DMPA (neutralized with TEA)		18 H	N/A ^d
		19 H	N/A ^d
		20 H	3.8
		21 H	3.25 N/A ^c
			2.63 N/A ^c
GMA		22 H	4.17 N/A ^c
		23 H	4.17 N/A ^c
GMA-DMPA		24 H	2.0
		25 H	2.29
EDA		26 H	N/A ^d
		27 H	N/A ^d
		28 H	2.99 N/A ^c
		29 H	2.99 N/A ^c
		30 H	2.99 N/A ^c

^a Primary urethane bond of IPDI.

^b Secondary urethane bond of IPDI.

^c Not available: indiscernible due to overlapping.

^d Not available: indiscernible due to weak intensity.

particles containing a number of small-sized PMMA particles. This is reasonable because the role of the GMA in the formation of PUGM hybrid particles is simply linkers between the PMMA particles and PU polymer chains.

Mechanical properties of PUGM films

In the case of the cast films of PUGM_x, a number of PMMA particles are distributed randomly in the PU film, a continuous phase. Figure 4 shows the stiffness and modulus values of the PUGM_x films as a function of the amount of acidic DMPA that can

react with GMA to form covalent bonds between PU chains and crosslinked PMMA particles (for clarity, only the standard deviations of one data set are indicated). The data obtained from PU and PUM films are also shown in Figure 4.

It is seen that the stiffness and modulus of PU increase upon the inclusion of crosslinked PMMA particles. At this point, it should be mentioned that even though similar results had already been reported in our previous paper,²⁰ the detailed discussion on the data was not given in the article. Thus, we try to interpret the data in more detail here. Now, it is worth noting that the stiffness of a

TABLE III
Particle Size of PU, PUM, and PUGM_x Measured by CHDF Methods

Particle size/nm	PU	PUM	PUGM0	PUGM10	PUGM20	PUGM30	PUGM40
D_n	69.9	43.3	38.7	41.8	44.2	106.5	110.2
D_v	76.9	49.7	43.9	49.4	51.1	107.1	113.3
D_w	88.0	63.8	55.6	67.3	67.5	108.5	119.5

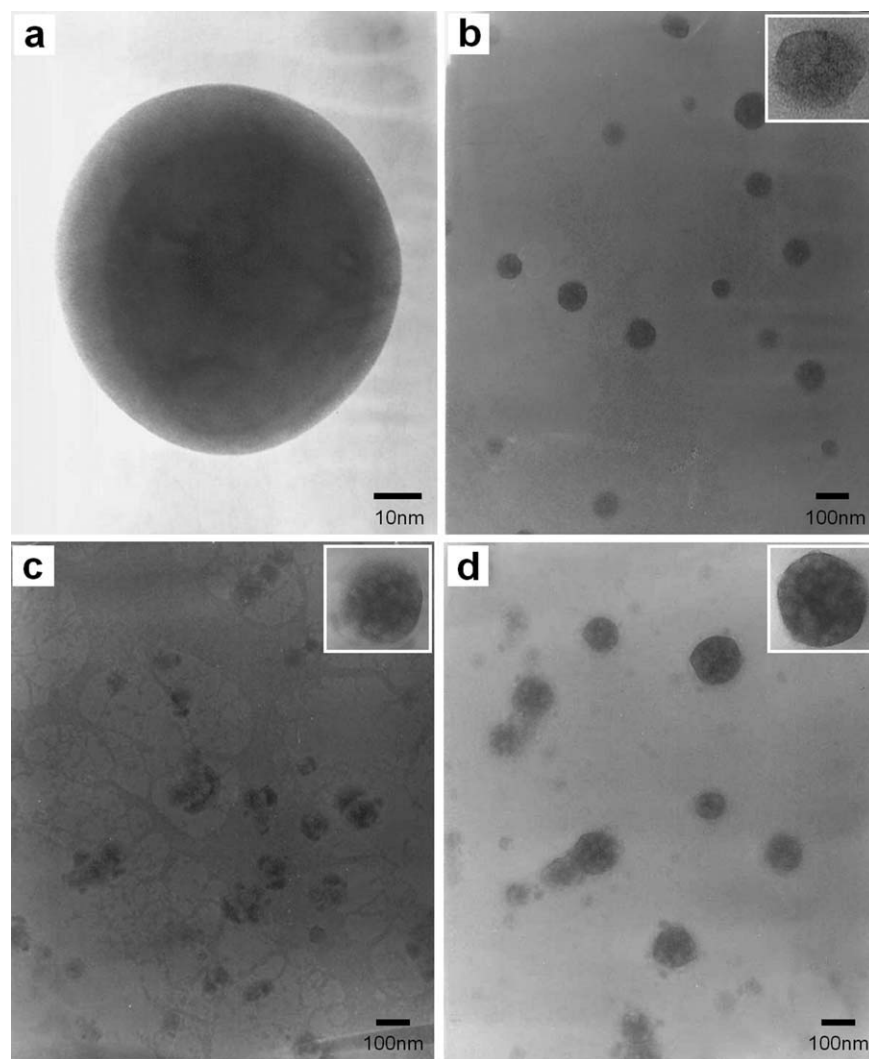


Figure 3 TEM micrographs of PUGM hybrid nanoparticles. (a) PU (bar = 10 nm at $\times 50,000$), (b) PUM (bar = 100 nm at $\times 50,000$), (c) PUGM0 (bar = 100 nm at $\times 50,000$), and (d) PUGM30 (bar = 100 nm at $\times 50,000$).

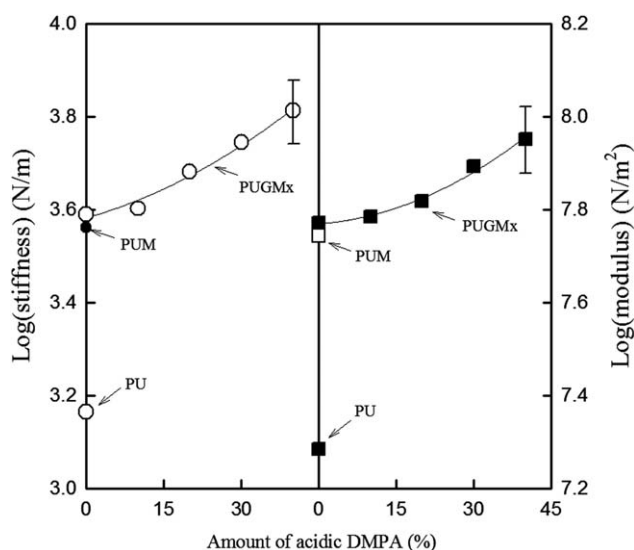


Figure 4 Stiffness and modulus of PUGM hybrid films as a function of the amount of acidic DMPA.

material is a measure of resistance to the deformation of an elastic material and depends on the nature and shape of the material, and that the elastic modulus is a property of constituent material. In this study, the nature and shape of the specimens of each sample are very similar, and, thus, the modulus can be assumed as a measure of the stiffness of the materials. Therefore, we discuss only the modulus in more detail. First of all, it is seen that the modulus increases from about $10^{7.28}$ to $10^{7.74}$ N/m² upon the inclusion of the PMMA particles in the PU matrix. At this point, it should be noted that at 25°C the PU matrix is a relatively soft material, but the PMMA particles are hard inclusions (i.e., filler) because the storage modulus of PMMA at 25°C is about 10^9 N/m².^{28,29} Thus, one can consider that the PUM and PUGMx polymers resemble polymeric composite materials and can predict the modulus of polymer composites using various models that can be applied

to explain the mechanical data.³⁰ According to the Kerner equation for the system that contains rigid inclusions in nonrigid matrix, one can calculate the modulus of composite material consisting of spherical particles in a matrix as follows³¹:

$$E_c/E_m = 1 + (V_p/V_m) \times [15(1 - \nu_m)/(8 - 10\nu_m)], \quad (1)$$

where E_c and E_m are the moduli of a composite and a pure matrix, respectively, V_p and V_m are the volume fraction of filler particles in the composite and that of the matrix, respectively, and ν_m is the Poisson ratio of the matrix. In this study, one can assume that crosslinked PMMA particles are filler particles and PU is the matrix. Thus, to calculate the V_p and V_m , one can use the density values (d) of PMMA and PU ($d_{\text{PMMA}} = 1.188 \text{ g/mL}$ and $d_{\text{PU}} = \text{ca. } 1.3 \text{ g/mL}$).³² In addition, as the Poisson ratio of PU, one may use that of elastomer ($\nu_m = 0.49$).³³ Then, assuming the modulus of PU (i.e., $10^{7.28} \text{ N/m}^2$) as E_m , one can obtain $10^{7.54} \text{ N/m}^2$ as a modulus value for PUM (i.e., E_c), which is smaller than the actual value, i.e., $10^{7.74} \text{ N/m}^2$. This difference leads us to the conclusion that the V_p might be higher than what we might think of. However, at least, this result tells us that the PMMA particles indeed act as filler, to some extent. At this point, it should be mentioned the moduli of PUGMx are even higher than that of PUM, which indicates that there must be a synergistic effect of the presence of PMMA particles and the formation of covalent bonds between the PMMA particles and the PU chains on the mechanical properties of PUGMx; this will be discussed more later (Fig. 6).

Another early relations between the modulus of filled system and the volume fraction of filler can be found in the Guth equation that is a generalized Einstein relation with a particle interaction term.³⁴

$$E_c/E_m = (1 + 2.5 \times V_p + 14.1 \times V_p^2) \quad (2)$$

This eq. (2) can be applicable up to ~ 30 vol % of filler. The application of the Guth equation to our mechanical data results in the E_c value of $\sim 10^{7.70} \text{ N/m}^2$ that is still slightly lower than the modulus of PUM. However, this result also indicates that the PMMA particles in the PU matrix act as hard filler. The slight difference in modulus values may be due to the same reason mentioned earlier and will be discussed later in more detail.

The Mooney's crowding concept, accounting for a filler packing effect, can be applied to the Einstein relation to interpret the viscosity data of a monodisperse suspension of spheres in the concentration range from 0 to 50% in volume.³⁵ In this model, particle-to-particle hydrodynamic interactions are responsible for the associated crowding action. We

also apply the Mooney equation to explain the modulus of PUM.

$$E_c/E_m = \exp[2.5 \times V_p/(1 - k \times V_m)] \quad (3)$$

Here, k is the crowding factor that is the ratio of the unit volume occupied by filler to the volume of the filler itself. For densely packed spheres, placed in either a face-centered cubic (fcc) lattice or a body-centered cubic (bcc) lattice or a simple cubic (sc) lattice, k is either about 1.35 (i.e., $1/0.74$) or about 1.47 (i.e., $1/0.68$) or about 1.91 (i.e., $1/0.52$), respectively. Using these crowding factors, one can obtain the moduli of PUM as either $10^{7.72} \text{ N/m}^2$ or $10^{7.74} \text{ N/m}^2$ or $10^{7.85} \text{ N/m}^2$, respectively. Interestingly enough, the calculated modulus value for the spheres in a bcc lattice is the same as the actual modulus of PUM. This result may suggest that the PMMA particles in the PU matrix are in the geometric crowding action for increasing modulus.

In the case of PUGMx films, the modulus of PUGM0 is slightly higher than that of PUM. This is not surprising because the only difference in the PUGM0 and PUM samples is that the PUGM0 sample contains a small amount of GMA units that the PUM does not have. Again, the PMMA particles containing GMA units in the PUGM0 and the PMMA particles in the PUM do not form any covalent bonds with the PU chains. Once the acid groups of DMPA units of PU chains are partly neutralized with TEA, the un-neutralized acid groups can form covalent bonds with GMAs that are also polymerized with MMA units; now, the PMMA particles are covalently bonded to the PU chains via GMA linkages. In this case, the PUGMx samples can be thought as polymeric composite materials containing "reactive" filler particles; the PMMA particles act as ~ 100 nm-sized multi-cross-linking sites. In Figure 4, it is seen that the modulus of PUGMx increases further and regularly with increasing amounts of the unneutralized acid groups of the DMPA units. The increasing modulus values can be fitted with a second-order polynomial. We can also express the modulus values as a function of the concentration of acidic DMPA (mol/L) with the densities of PU and PMMA and the amounts of various precursors, DMPA, and TEA:

$$\begin{aligned} \text{Log(modulus)} (\text{N/m}^2) &= 7.8 + 8.3x \\ &+ 9.6x^2 (r^2 = 0.9902) \text{ and } \text{log(modulus)} (\text{N/m}^2) \\ &= 7.8 + 1.2c + 227c^2 (r^2 = 0.9902). \end{aligned} \quad (4)$$

Here x is the percentage of unneutralized (i.e., acidic) DMPA units, c is the concentration of acidic DMPA (mol/L), and r^2 is the linear least-squares correlation coefficient.

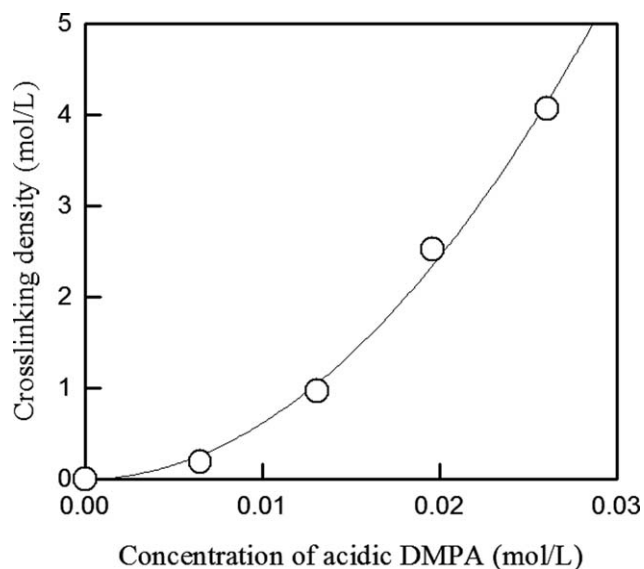


Figure 5 Calculated crosslinking density as a function of the concentration of acidic DMPA.

It is known that the crosslinking increases the rubbery modulus of the material as follows³⁶:

$$E = 3 \times v \times RT, \quad (5)$$

where v is the crosslinking density (mol/L).

In this study, since the formation of covalent bonds between the PMMA particles and the PU chains induces an increase in the modulus of the PUGM, it would be useful to calculate the v value of the PUGMx. However, it should be mentioned that the PUGMx at 25°C does not behave like “real” rubbery materials, and, thus, the moduli of the PUGMx at 25°C are not the “real” rubbery moduli. In addition, the aforementioned equation is usually applied to the system that has crosslinking points from which three or four polymer chains emanate, and the increasing amounts of crosslinking agents lead naturally to the increasing v of the material. For the present system, however, an increment of the acid group contents increases the number of polymer chains emanating from the PMMA particles, not the number of PMMA particles that might act as crosslinking points. Nevertheless, the calculation would give us a hint as to the possible crosslinking effect of the PUGMx system. Thus, we show the calculated v values as a function of the amount of acidic DMPA units in Figure 5.

As expected, the v value increases drastically with increasing acidic DMPA units. The data can be fitted with a second-order polynomial as follows:

$$v(\text{mol/L}) = 1.0c + 6048c^2 (r^2 = 0.9979) \quad (6)$$

Here, c is the concentration of acidic DMPA. The above result clearly indicates that the increase in the

number of covalent bonds between the PU matrix and PMMA particles indeed enhances the crosslinking density of the PUGMx significantly, which, in turn, may explain the increasing modulus of PUGMx at 25°C.

Since the Guth equation dealt with the relationship between the moduli of filled systems and the volume fractions of filler, we tried to calculate the volume fraction of filler particles in PUGMx, assuming that the modulus of the PUGMx increased as much as the Guth equation predicted. The results are shown in Figure 6. It is clear that the volume fraction of filler particles, i.e., PMMA particles, increases drastically as the acidic DMPA content increases.

At first glance, it seems unreasonable because the sizes and numbers of filler particles, PMMA, seem to be similar for all the PUGMx samples; only the difference is the number of covalent bonds between PMMA and PU. However, if one considers a “restricted mobility” concept,³⁷ one can understand the above results. According to the work by Tsagaropoulos and Eisenberg,^{38,39} several polymers filled with very fine silica particles showed two glass transition temperatures; one at relatively low temperature was related to the usual polymer glass transition and the other at relatively high temperature was assigned to the glass transition of polymer chains of reduced mobility, which were in the vicinity of filler particles. In the present system, the formation of covalent bonds between the PMMA particles and PU polymer chains may result in the reduction in the mobility of PU polymer chains in the vicinity of the PMMA particles, which are anchored to the PMMA particles. The mechanical property of these PU polymer chains of reduced mobility

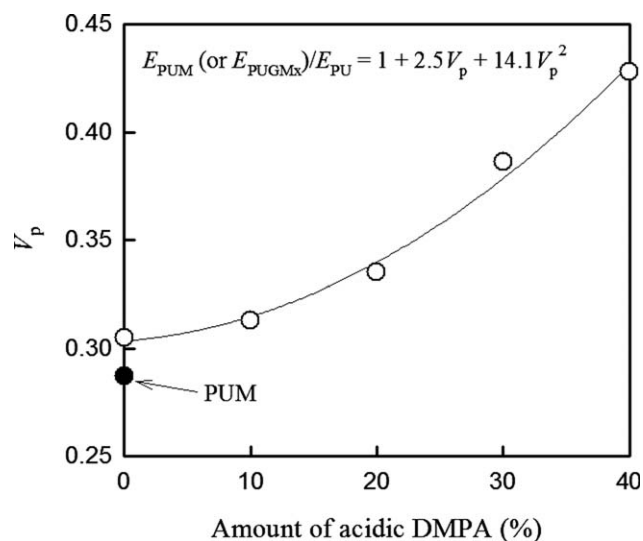


Figure 6 Calculated V_p using the Guth equation as a function of the amount of acidic DMPA.

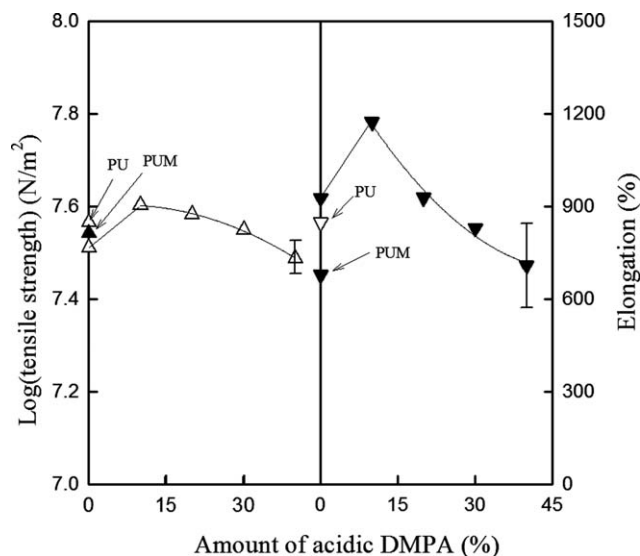


Figure 7 Tensile strength and elongation of PUGM hybrid films as a function of the amount of acidic DMPA.

should be different from that of the PU chains of unrestricted mobility; the latter would show a rubbery modulus at 25°C, but the former would exhibit a higher modulus that might be similar to the modulus of PMMA at that temperature. Thus, if the restricted mobility concept is applicable to our system, the hard particles in the PUGM x are no longer PMMA particles, but the PMMA particles with the layer of PU chains of restricted mobility. This means that the size of filler increases, which, in turn, increases the modulus. In addition, it should be noted that as the crosslinking density increases, the mobility of the chains in the vicinity of the PMMA particle will be reduced more significantly due to the increase in the crowding effect of the chains, which also leads to even higher modulus.

Tensile properties of the PUGM hybrid films

The tensile strength and elongation data of the PUGM samples as a function of the amount of acidic DMPA units (for clarity, only the standard deviations of one data set are indicated) are shown in Figure 7. In Figure 7, even though the tensile strength increases slightly for PUGM10 and then decreases very slowly with the amount of acid groups, the tensile values do not change significantly, with the average $\log(\text{tensile strength})$ being $7.55 (\pm 0.04) \text{ N/m}^2$. Since the tensile strength is the maximum stress where the strain of the material changes from elastic deformation to plastic deformation, the tensile experiments cause permanent deformation of polymers. In the present system, the matrix polymer, PU (wt % of PU in the film = ca. 73%), is mainly responsible for the deformation (i.e., necking behavior) of the films. Thus, a small change in tensile strength

values is understandable. The highest tensile strength of PUGM10 will be discussed below.

In the case of elongation, the PUGM10 shows higher value than the rest of the PUGM x samples. This may be due to the fact that the reactive PMMA particles in PU matrix can hold the PU polymer chains to some extent, under a controlled, gradually increasing force; this leads to high elongation of the polymer film. On the other hand, the increasing number of covalent bonds between the PMMA particles and PU chains in the PUGM x ($x > 10$) results in the reduction in the mobility of PU chains in the vicinity of the PMMA particles. These PU chains anchored to the PMMA particles do not participate in the relaxation of normal PU chains at 25°C. This naturally reduces the elongation of polymer films. These two opposite effects result in the highest elongation and tensile strength of PUGM10, compared to those of the rest.

CONCLUSIONS

This study revealed that GMA monomers could be used to form covalent bonds between PU matrix and PMMA nanoparticles. The average particle size of PUM was found to be smaller than that of PU, possibly due to low solution viscosity. On the other hand, the sizes of PUGM hybrid particles increased with increasing acidic DMPA amount. This might be due to the decreasing amount of ionic groups per PU chain, which were needed to stabilize the colloidal particle. In the cases of the samples cast into films, the modulus of the PU increased by the addition of PMMA nanosized particles, which was probably due to a filler effect of PMMA particles. For the films of PUGM hybrid samples, the modulus was found to increase further with increasing number of covalent bonds between the PMMA particles and PU matrix. This was due to the fact that a certain length of PU chain from the anchoring point to the PMMA particles would have reduced mobility and should behave differently at 25°C, compared to the PU chains far from the anchoring points; these PU chains of reduced mobility increased the modulus of the hybrid sample. It was also observed that the inclusion of PMMA particles in the PU matrix did not change the tensile strength of the materials strongly, with slightly higher value for PUGM10. It was suggested that since the major component of the films was the PU that might be a controlling factor of the deformation behavior of the films, and, thus, that the tensile strength values would not be changed significantly. Finally, the elongation of the films depended on both the holding and reduced mobility effects of the PU chains that anchored to the PMMA particles, which also affected the tensile properties of the films simultaneously.

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