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Characterization and Use of Ultraviolet-Reactive Low-Molecular-Weight Polyhydroxybutyrate to Prepare Biodegradable Acrylates

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ABSTRACT: The characterizations of prepared low-molecular-weight polyhydroxybutyrate (LMWPHB) and the properties of LMWPHB photopolymerized with hydrophilic and hydrophobic acrylic monomers were studied with ^{1}H-NMR spectroscopy, Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy, Instron tensile testing, and biodegradation tests. The results of ^{1}H-NMR and FTIR spectroscopy confirmed that the prepared LMWPHB had transformed unsaturated ends that were photoreactive under UV light. The tensile strengths of the LMWPHB/acrylates decreased with increasing content of the added biodegradable LMWPHB because of the relatively long chains and large equivalent molar weights of LMWPHB. However, the flexibility of LMWPHB/acrylates changed differently with the type of acrylic monomer used. The LMWPHB/hydrophilic acrylate had a much more rapid biodegradation rate than the LMWPHB/hydrophobic acrylate because of the fast penetration of microorganisms. We demonstrated that the prepared LMWPHB could be used to control the biodegradation properties of acrylates and then could potentially be applied in biomedical fields. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39501.

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INTRODUCTION

Polyhydroxybutyrate (PHB) has attracted a lot of attention because of its biosynthesized nature, biodegradation capabilities, and biocompatibility.[1–7] Despite these attractive properties, the one major inferior property of PHB other than the known relatively high cost and postcrystallization during storage results from the early degradation that occurs around its melting temperature; this limits its acceptance for industrial applications. It has been indicated that a severe random chain-scission reaction of PHB at a temperature near 180°C, which involves a cis elimination reaction of β-CH and a six-membered ring transition, is usually found and is accompanied by the formation of degraded olefinic and carboxylic acid products and various oligomers.[7–9] Although the fast degradation of PHB is a main disadvantage in processing, the produced low-molecular-weight products (LMWPs) could have great potentials in different applications.

It has been indicated that the LMWPs can be functionalized to prepare different copolymers or to graft onto other polymers with new physical or chemical properties, which can then be applied as separation membranes, drug controlled release coatings, polymeric compatibilizers, surfactants, special chemicals, biofuels, green composites, and so on.[10–17] Many processes, including enzymatic hydrolysis, solventless thermal degradation, thermal degradation under solvent, chemical decomposition, ring-opening polymerization of butyrolactone, and hydrolysis in solutions, have been shown to successfully produce different LMWPs of PHB for further applications.[11–22]

It has been reported that the hydrolysis of PHB in acidic or alkaline solutions can produce insoluble and soluble oligomers, including monomeric acids (2-butenoic acid and crotonic acid) and a large number of oligomers with unsaturated end groups through the random scission of ester bonds.[11,12,16] The formation of unsaturated end groups during hydrolysis occurs via the dehydration of the chain ends by β elimination after ester hydrolysis; this is different from the formation of unsaturated ends in the thermal decomposition of PHB mentioned previously.[12] These formed hydroxyl, acid, or unsaturated bonds can be used directly or can be further functionalized to become diols, diacids, diisocyanates, amino compounds, or crosslinkers with two vinyl groups for polymerization through step-growth or free-radical reactions.[23–28] For example, it has been demonstrated that PHB diols produced through a transesterification reaction in the presence of ethylene glycol [or poly(ethylene glycol) (PEG)] and dibutyltin dilaurate catalyst can be used as functional oligomers (or macromers) to prepare amphiphilic poly (hydroxy alkanoate) (PHA) copolymers and copolymers of esters with hard–soft segments and PHB–polyurethanes.[14,23–27,29–33]

Unsaturated PHAs can also be obtained from unsaturated edible oils and synthetic olefinic substrates by biosynthesis and can

then be oxidized to diols, pendant hydroxyl groups, carboxylic acids, and epoxy groups to synthesize different PHA-based derivatives.[14,29] Moreover, it has been shown that unsaturated PHAs with pendent alkyne end groups, which can be used to prepare novel block polymers, can be produced by either bacterial fermentation or direct alcoholysis from natural polyesters with propargyl alcohol.[34] With regard to the use of unsaturated bonds, biodegradable molecularly imprinted polymers and bone cements based on low-molecular-weight polyhydroxybutyrate (LMWPHB) diols have been prepared from bacterial PHB and used to synthesize acrylate end-capped PHB macromers, which can be polymerized with different acrylic monomers.[18,22,28] The use of unsaturated bonds formed directly from the hydrolysis or thermal degradation in grafting or polymerization reactions is also possible, although it has been indicated that polymerization via crotonate end groups with free-radical reactions has difficulties because the β-methyl substituent on the unsaturated bonds induces a steric hindrance with the α-substituent and an unwanted chain transfer.[10]

In previous studies, the inferior thermal stability of PHB has been shown to be improved by either the grafting of maleic anhydride, maleic acid, and exo-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride onto PHB molecules or by the addition of small amounts of polymeric additives, such as carboxyl-terminated butadiene acrylonitrile rubber and biocompatible poly(vinyl pyrrolidone) directly into PHB.[35–38] Instead of improving the thermal stability, researchers prepared a useful LMWPHB by taking advantage of the early degradation of PHB at a high temperature, and then the LMWPHB was used as a plasticizer in PHB.[39] It was indicated that the addition of the prepared LMWPHB decreased the crystallinity, crystallization rate, and melting temperature but increased the flexibility and biodegradation rate of PHB.[39]

In this study, the detailed chemical characterization of the prepared LMWPHB via the thermal treatment of PHB in a solvent and the use of LMWPHB to prepare different photopolymerized polyacrylates (hydrophobic and hydrophilic) were demonstrated. Polyacrylates are common materials that are popularly used in coatings, inks, commodity products, optical lenses [e. g., hydrophilic poly(hydroxyethyl methacrylate) (pHEMA) hydrogels for disposable contact lenses and treated hydrophobic pHEMA for traditional long-wearing contact lenses], biomedical products [e.g., pHEMA used for artificial skin manufacturing/dressings, marrow/spinal cord cell regeneration, drug delivery, scaffolds for cell adhesion and artificial cartilage production and poly(methyl methacrylate) (PMMA) for bone cements], and so on.[28,40–45] In general, polyacrylates may have biocompatibility, but they are not biodegradable. It is shown here that the mechanical and biodegradation properties of the prepared polyacrylates changed with the amount of LMWPHB added and the hydrophilic properties of the monomers used.

EXPERIMENTAL

Preparation and Characterization of LMWPHB and LMWPHB/Acrylate Films

The PHB used was biosynthesized from *Escherichia coli* with crude glucose as the medium [98% pure, Nan-Tien Co., weight-average molecular weight (M_w) $\approx$ 750,000 g/mol, polydispersity index $\approx$ 1.82, residual Ca^{2+} $\approx$ 700 ppm, and Mg^{2+} $\approx$ 90 ppm, hermetically stored in a refrigerator below 0°C and randomly selected from different packages]. To prepare LMWPHB, the PHB was mixed with PEG 400 (obtained from Fluka Chemical Co.) with a ratio of 1:2, purged with nitrogen gas, sealed, and heated at 165°C for 6 h. The reacted PHB was subsequently rinsed with deionized water three times to remove the PEG, filtered, and then dried *in vacuo* to obtain LMWPHB [M_w $\approx$ 1760, number-average molecular weight (M_n) $\approx$ 1200 g/mol, polydispersity index $\approx$ 1.47]. The molecular weight distributions of LMWPHB were measured by gel permeation chromatography. A PerkinElmer 1700 Fourier transform infrared (FTIR) spectrophotometer was used to obtain the IR transmission spectra of the LMWPHB and as-received PHB after annealing at 80°C for 24 h. The IR spectra were taken from 4000 to 450 cm^{-1} at a resolution of 4 cm^{-1} for 30 scans. A Bruker 500-MHz NMR analyzer was used to obtain the ^{1}H-NMR spectra of LMWPHB. The prepared LMWPHB was added to two acrylates, a hydroxyethylmethacrylate (HEMA) solution (HEMA with the addition of 1 wt % Irgacure 819 photoinitiator from Aldrich, with a 40 wt % glycerin diluent based on the total weight), and a methyl methacrylate (MMA)/butyl acrylate (BA) solution (MMA/BA = 1:1), with different weight ratios [LMWPHB/acrylate (HEMA or MMA/BA solution) = 1:3, 1:4, 1:5, 1:6, and 1:7, and with the addition of 5 wt % Irgacure 819 and 5 wt % trimethylpropane triacrylate (Aldrich)]. Then, LMWPHB/acrylate intact films with a thickness of about 180 μm were obtained by UV polymerization (365 nm, UV crosslinker XL-1000, Spectronics Co.) of the prepared solutions sandwiched between two poly(ethylene terephthalate) films at room temperature for 10 min (total irradiated UV energy = 3000 mJ/cm^2). The tensile properties of the as-prepared films were measured with an Instron tester (Instron 4202) at a strain rate of 1 mm/min, and we took the average of five specimens.

Biodegradation Test

The photopolymerized films of LMWPHB/HEMA and LMWPHB/MMA-BA were rinsed with stirring with hot water at 80°C and acetone, respectively, in a beaker several times to remove the diluent and residual monomers; they were then soaked in distilled water at room temperature for 24 h so they could saturate. These prepared films (3 $\times$ 3 cm^2, three pieces for each formulation) were then enclosed in mesh plastic bags with mesh sizes of about 0.5 mm to let the films freely contact humid potting soil (purchased from Greenorchids Co., Taiwan, and containing peat moss, perlite, and coconut fibers) but without the loss of small fragments of the films after a long time exposure. The bags were buried vertically in the soil, which was placed in a sealed plastic case with saturated water at 25°C. The buried films were periodically removed, thoroughly cleaned with distilled water, dried in a vacuum oven, and then weighed to determine the weight loss. A scanning electron microscope (JEOL JSM-5600) was used to observe the surface morphology of the films during the biodegradation test.

RESULTS AND DISCUSSION

Characterization of Prepared LMWPHB

The representative FTIR spectrum of LMWPHB is shown in Figure 1. For comparison, the FTIR spectrum obtained from

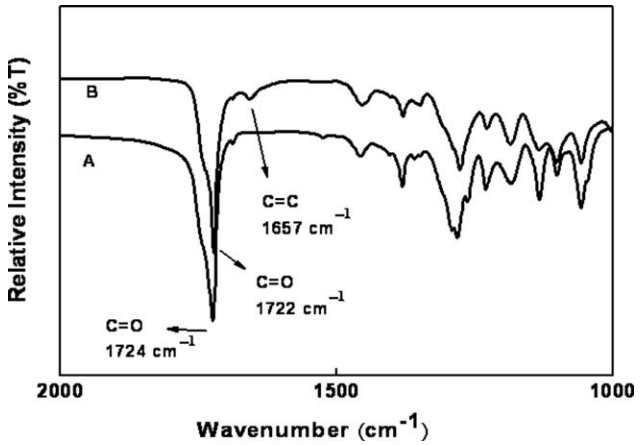


Figure 1. FTIR spectra obtained from (A) PHB and (B) LMWPHB.

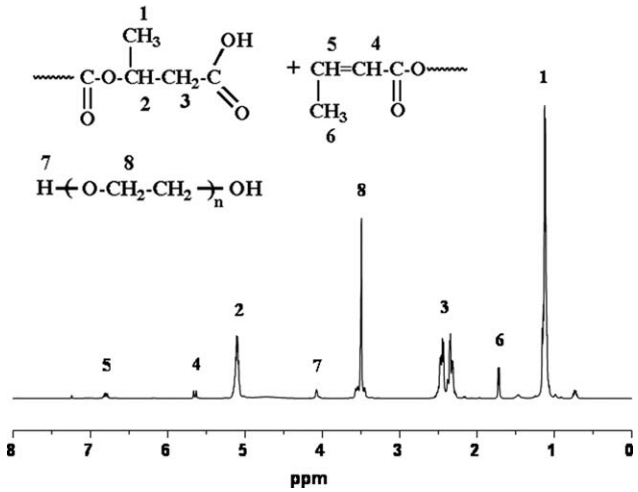


Figure 2. ^{1}H-NMR spectrum of LMWPHB.

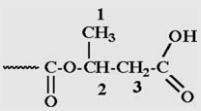
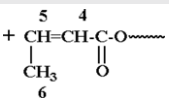
the as-received PHB is also included. As shown, LMWPHB showed characteristic absorption bands of PHB near 1741 cm^{-1} (amorphous ester band), 1724 cm^{-1} (crystalline ester band), 1453 cm^{-1} (methylene band), 1380 cm^{-1} (methyl band), 1278 cm^{-1} (crystalline band), 1230 cm^{-1} (crystalline C—H band from helical chains), 1186 cm^{-1} (asymmetric C—O bending), and 1133 cm^{-1} (symmetric C—O bending) but with different intensities of crystalline bands (e.g., 1724 and 1230 cm^{-1}) than PHB because of the decrease in crystallinity resulting from the significant reduction of the molecular weight (from $M_w \approx$ 750,000 to $M_w \approx$ 1760 g/mol). The decreases in the crystallinity and crystallization rate of LMWPHB were confirmed by differential scanning calorimetry previously.[39] In addition to the differences detected in the crystalline bands, a new absorption band near 1657 cm^{-1} was clearly observed in the FTIR spectrum of LMWPHB, as shown in Figure 1(B). The appearance of this new band was attributed to the unsaturated C=C bonds formed during the high-temperature exposure; these are usually obtained during the thermal degradation of PHB. The chemical composition of LMWPHB was further analyzed by ^{1}H-NMR and is discussed later.

The transformation of the unsaturated LMWPHB was observed from the ^{1}H-NMR spectrum shown in Figure 2. As obtained from the spectrum, the resonances related to the PHB repeating units were observed at $\delta = 1.20$, 5.20, and 2.40–2.55 ppm; these were characteristic of —COO*CH*$_3$CHCH$_2$—, —COOCH$_3$*CH*CH$_2$—, and —COOCH$_3$CH*CH*$_2$—, respectively. In addition, the trans CH$_3$CH=CHCOO— compositions of the formed products could be identified by resonances at $\delta = 5.65$, 6.82, and 1.75 ppm; these were characteristic of trans CH$_3$CH=*CH*COO—, CH$_3$*CH*=CHCOO—, and end *CH*$_3$CH=CHCOO—, respectively. The residual PEG (~10 wt %) in the NMR specimen was also detected at $\delta = 4.05$ [$H(OCH_2CH_2)_n$—OH] and 3.49 ppm [$H(OCH_2CH_2)_n$—OH]. A significant amount of unreacted PEG in LMWPHB was removed by a good water rinse before the reaction with the acrylic monomers. The corresponding assignments of the protons in LMWPHB are listed in Figure 2. The formation of the transformed unsaturated ends in the prepared LMWPHB was confirmed. Similar ^{1}H-NMR spectra and unsaturated end groups were found in PHB under high-temperature degradation in different PEG solvents and in the PHB hydrolyzed in acidic (HCl) and basic (NaOH) solutions.[12,17,22]

The relative concentrations of unsaturated ends and 3-HB repeating units in LMWPB were calculated by a comparison of the relative intensities of the corresponding peaks in the ^{1}H-NMR spectrum shown in Figure 2. The integrated intensities of the assigned peaks are listed in Table I, and the relative concentrations of different protons were obtained as follows: $H_1/H_2/H_3/H_4/H_5/H_6 = 40.6{:}12.2{:}26.3{:}1.0{:}1.0{:}3.0$, where H_4 and H_5 were the references. The ratios of the intensities among different protons were consistent with the proposed chemical compositions, that is, $H_1/H_2/H_3 \approx 3{:}1{:}2$ and $H_4/H_5/H_6 = 1{:}1{:}3$. Henceforth, M_n of LMWPHB was obtained by the calculation of the relative concentrations of H_2 and H_4. We estimated that the M_n values of LMWPHB were about 1118–1204 g/mol with the estimated chemical formula CH$_3$CH=CH(COOCH$_3$CHCH$_2$)$_{12\sim13}$COOH; this result was close to the M_n value of 1200 g/mol obtained from gel permeation chromatography. As expected from the results of the high-temperature degradation of PHB, the M_n of LMWPHB could be changed by the alteration of the temperature and reacting time during the experiments.

The photoreactivity of C=C bonds in LMWPHB was checked by FTIR spectroscopy. In Figure 3, the FTIR spectrum obtained from LMWPHB mixed with 1 wt % photoinitiator (Irgacure

Table I. Relative Concentrations of Different Protons Obtained from ^{1}H-NMR

Functional group		Relative amount (count)
	1	1.48×10^7
	2	4.45×10^6
	3	9.60×10^6
	4	3.64×10^5
	5	3.71×10^5
	6	1.09×10^6

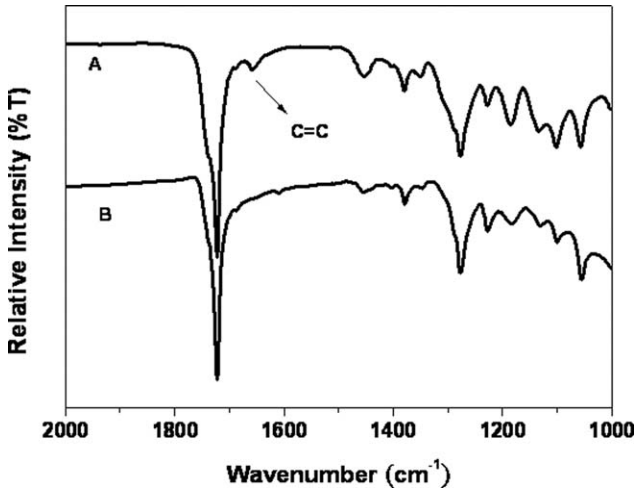


Figure 3. FTIR spectra obtained from LMWPHB (A) before and (B) after UV exposure.

819) after 10 min of UV exposure (3000 mJ/cm^2, 365 nm) is shown. When we compared this to the FTIR spectrum of LMWPHB, shown in Figure 3(A), it was obvious that the characteristic band of C═C near 1657 cm^{-1} became negligible after UV irradiation. Consequently, the promising photoreactivity of LMWPHB was confirmed. As a result, LMWPHB could be applied as a reactive comonomer to prepare various photopolymerized copolymers, and some examples are given later.

The effects of LMWPHB on the tensile properties of various LMWPHB/HEMA specimens were studied with the representative tensile stress–strain curves shown in Figure 4. It was obvious that the ultimate tensile strength (σ_T; kg/cm^2) and elongation at break (ε; %) of LMWPHB/HEMA changed differently with the amount of added LMWPHB. The specimens pHEMA (HEMA polymer), pHEMA-1/7 (i. e., LMWPHB/HEMA solution = 1:7), pHEMA-1/6, pHEMA-1/5, pHEMA-1/4, and pHEMA-1/3 had nominal σ_T values near 12.1, 8.0, 7.5, 6.4, 4.8, and 3.6 kg/cm^2, respectively; these values decreased significantly with increasing LMWPHB content (see Table II). The tensile properties of pHEMA have been studied widely because

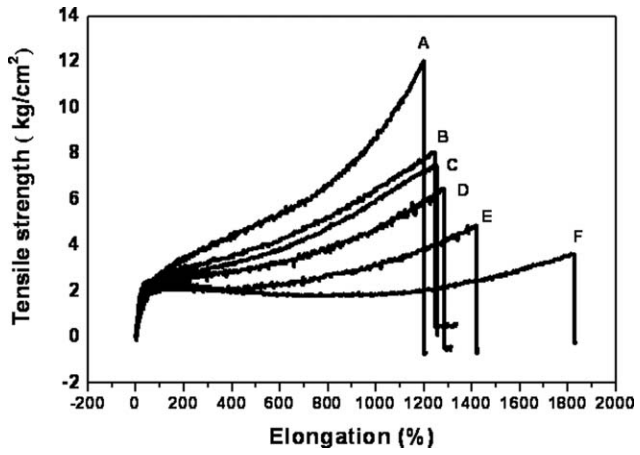


Figure 4. Tensile stress–strain responses obtained from (A) pHEMA, (B) pHEMA-1/7, (C) pHEMA-1/6, (D) pHEMA-1/5, (E) pHEMA-1/4, and (F) pHEMA-1/3.

Table II. Tensile Properties Obtained from LMWPHB Copolymerized with Hydrophilic Acrylic Monomers (HEMA)

Specimen	ε (%)	σ_T (kg/cm^2)
pHEMA	1200 ± 23	12.1 ± 1.9
pHEMA-1/7	1235 ± 35	8.0 ± 0.8
pHEMA-1/6	1257 ± 93	7.5 ± 0.8
pHEMA-1/5	1316 ± 108	6.4 ± 0.8
pHEMA-1/4	1426 ± 57	4.8 ± 0.3
pHEMA-1/3	1831 ± 149	3.6 ± 0.2

of the popular uses of pHEMA hydrogels; for example, it has been shown that pHEMA had σ_T values near 2.6 and 1.5 kg/cm^2 when it contained different water contents of 36.2 (with the crosslinking agent ethylene glycol dimethacrylate) and 41.4 wt % (no crosslinking agent), respectively.[46,47] The results here were reasonable because of the fact that the mechanical properties of pHEMA depend on the types/concentrations of monomers/crosslinkers/initiators, water/diluent contents, and curing conditions.

It was also shown that ε increased in the presence of LMWPHB. In Figure 4 and Table II, it is shown that ε of the six specimens increased with increasing LMWPHB content and followed theorder pHEMA < pHEMA-1/7 < pHEMA-1/6 < pHEMA-1/5 < pHEMA-1/4 << pHEMA-1/3. As obtained, the effect of LMWPHB on improving the flexibility of pHEMA was confirmed, especially in pHEMA-1/3, which contained the greatest concentration (25 wt %) of LMWPHB and exhibited a strain-induced hardening effect in the stress–strain curve shown in Figure 4. The observed changes in σ_T and ε were attributed to the relatively longer chain and greater equivalent molar weights of LMWPHB compared to those of HEMA; this increased the flexibility but decreased the strength of pHEMA noticeably. A similar change in the flexibility was observed in the acrylate materials when monomers with a similar chemical composition but longer chains were used; for example, the acrylate polymerized from butyl methacrylate was more flexible than that from MMA.

In the case of hydrophobic MMA/BA (referred to as ACRY), the addition of LMWPHB had an adverse effect on the tensile properties. As shown in Figure 5 and Table III, σ_T and ε of LMWPHB/ACRY decreased with increasing amount of LMWPHB in ACRY and followed the order ACRY (polymerized MMA/BA with no LMWPHB) > ACRY-1/7 (i. e., LMWPHB–MMA/BA = 1:7) > ACRY-1/6 > ACRY-1/5 > ACRY-1/4 > ACRY-1/3. The decrease in σ_T resulted from the long chains of LMWPHB, as described previously when the decrease in ε was attributed to the relatively increasing content of the crosslinker in specimens containing more LMWPHB because the amount of the crosslinker added was based on 5% of the total weight of the specimen. The abundant crosslinkers could have resulted in a brittle material, and they also decreased the tensile strength. As a result, the crosslinking density in the polymerized films increased, and the flexibility and strength both decreased. The addition of the crosslinker was used to improve the mechanical strength of the prepared LMWPHB/ACRY copolymers because it would be

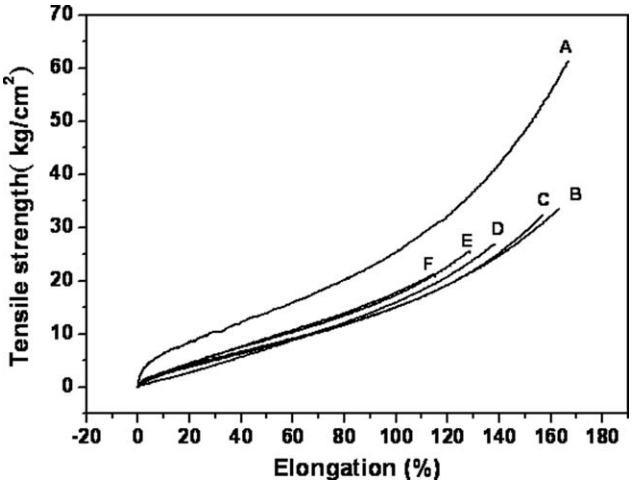


Figure 5. Tensile stress–strain responses obtained from (A) ACRY, (B) ACRY-1/7, (C) ACRY-1/6, (D) ACRY-1/5, (E) ACRY-1/4, and (F) ACRY-1/3.

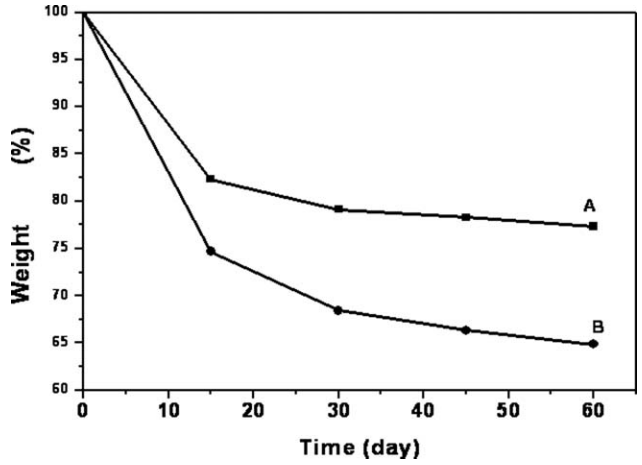


Figure 6. Changes in weight loss from the representative (A) pHEMA-1/5 and (B) pHEMA-1/3 during the biodegradation test.

difficult to form intact films in the absence of the crosslinker. Decreases in the tensile strength and elongation in PMMA were also obtained previously in a study of the formulation of self-curing drug-release materials by the addition of PHB into PMMA.[48] For future industrial applications, the elongation of ACRY/LMWPHB could be modified by the addition of the proper amount or type of crosslinker to a specific formulation.

Although it was indicated previously that the free-radical polymerization via crotonate end groups had difficulties because of steric hindrance and an unwanted chain transfer, the prepared LMWPHB seemed to undergo a satisfactory polymerization reaction in acrylic monomers.[10] To test the unreacted LMWPHB in the cured specimens, the UV-polymerized ACRY-1/3, that is, the specimen with the greatest LMWPHB added, was extracted with chloroform for 24 h, and a negligible weight loss was detected. The result confirmed that the unsaturated LMWPHB had good photoreactivity and could form copolymers with acrylic monomers. In addition to the use of the C═C bonds of LMWPHB to prepare copolymers with MMA, PHB (with higher molecular weights of 14,852, 77,338, and 93,097) could also copolymerize with MMA through atom transfer radical polymerization with chlorinated PHB (PHB-Cl) as the macroinitiator to obtain brush-type PHB-*g*-PMMA graft copolymers.[49]

Despite the effect on the mechanical properties, the presence of LMWPHB could also offer biodegradation properties to acrylate materials. The weight losses of the representative pHEMA/LMWPHB specimens during the biodegradation test are shown in Figure 6. We determined that the total weight loss of the specimens significantly increased with increasing amount of LMWPHB added. The pHEMA-1/5 lost about 22.4 wt % (±1.2 wt %) after 60 days in the humid potting soil at room temperature, whereas pHEMA-1/3 lost a much greater weight of 34.5 wt % (±1.7 wt %) in the same period. This result was expected because the film polymerized with only the HEMA monomer was not biodegradable and should not have shown any weight loss during the test; the addition of LMWPHB caused the pHEMA/LMWPHB specimens to become biodegradable. It is also interesting to note that the weight losses of both specimens were all greater than the amount of LMWPHB added to the specimens (i. e., 22.4 wt % loss > 16.7 wt % LMWPHB in pHEMA-1/5 and 34.5 wt % loss > 25 wt % LMWPHB in pHEMA-1/3). This was attributed to the loss of LMWPHB, which was accompanied by the loss of the adjacent copolymerized pHEMA; this resulted in a weight loss greater than that expected from only LMWPHB. Additionally, not only did the weight loss increased but also the weight loss rate (i.e., the biodegradation rate) increased with the amount of LMWPHB added. The different slopes shown in Figure 6 indicated that pHEMA-1/3 had a greater biodegradation rate than pHEMA-1/5, especially during the first 15 days. This implied that the microorganisms could reach the biodegradable parts in a timely manner because of the great hydrophilic properties of pHEMA and could digest LMWPHB with little initiation time (from a comparison to the relatively long sampling time of 15 days) required. The more LMWPHB was added, the more (and faster) LMWPHB was lost during the biodegradation test. The result was consistent with those reported previously.[39]

Table III. Tensile Properties Obtained from LMWPHB Copolymerized with Hydrophobic Acrylic Monomers (MMA/BA)

Specimen	ε (%)	σ_T (kg/cm^2)
ACRY	166 ± 5	61 ± 3
ACRY-1/7	163 ± 2	33 ± 4
ACRY-1/6	157 ± 4	32 ± 3
ACRY-1/5	138 ± 1	26 ± 2
ACRY-1/4	128 ± 2	25 ± 3
ACRY-1/3	115 ± 1	21 ± 3

The surface morphology of the pHEMA/LMWPHB specimens before and after the attack of microorganisms was obtained from the scanning electron microscopy (SEM) micrographs shown in Figures 7 and 8. From Figure 7, in pHEMA-1/5 after 0, 15, and 45 days in the humid potting soil, it was clear that the surface of pHEMA-1/5 was eroded to form irregular deep holes with dimensions near 100 μm; this indicated that the

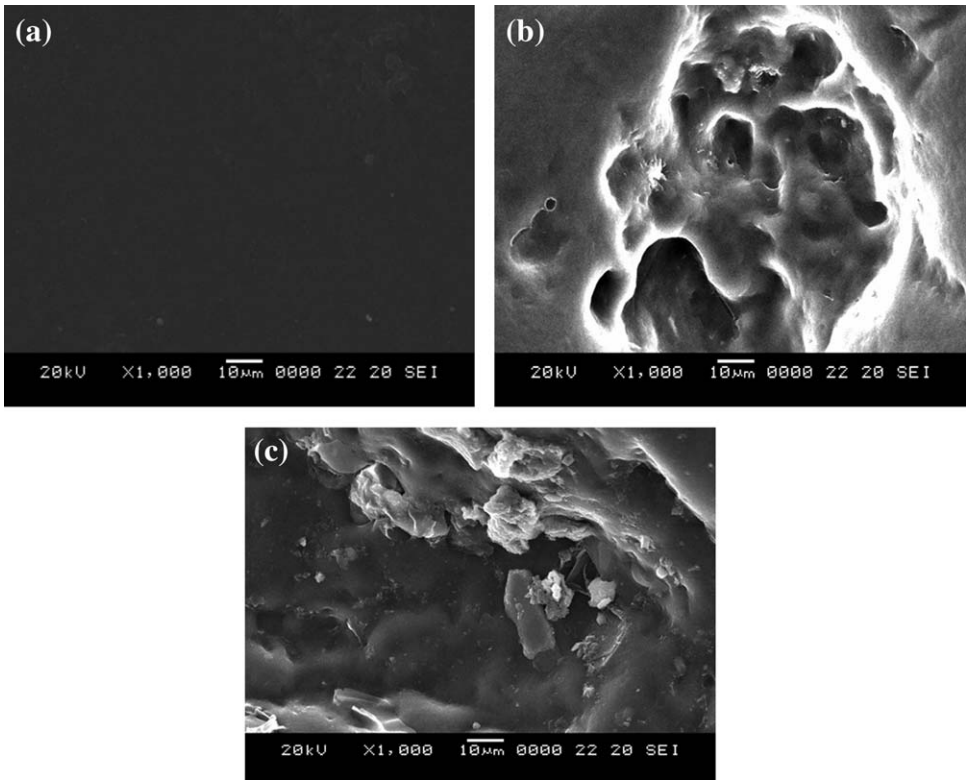


Figure 7. SEM micrographs obtained from pHEMA-1/5 (A) before and after (B) 15 and (C) 45 days of biodegradation.

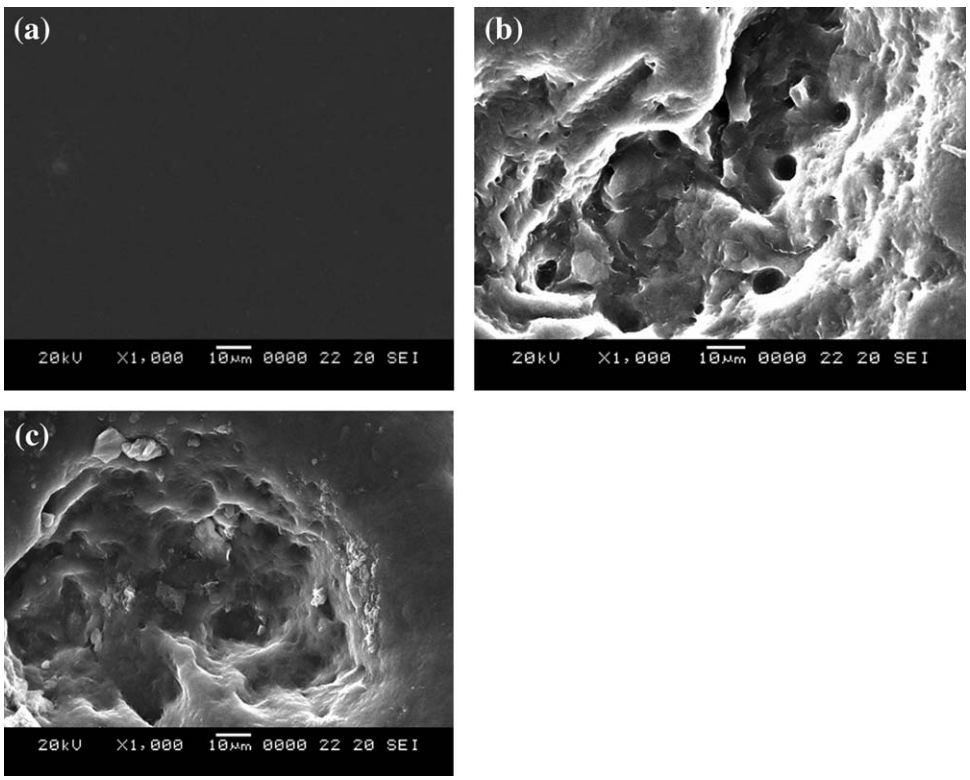


Figure 8. SEM micrographs obtained from pHEMA-1/3 (A) before and after (B) 15 and (C) 45 days of biodegradation.

microorganisms penetrated into the material fast. For pHEMA-1/3, a similar surface morphology but with more severe eroded marks was obtained from the SEM micrographs shown in Figure 8 because of a greater weight loss compared to that of pHEMA-1/5.

The biodegradation properties of ACRY/LMWPHB were also tested and were demonstrated to be different from those of pHEMA/LMWPHB. It is shown in Figure 9 that the weight losses of the representative ACRY/LMWPHB specimens also changed with the content of added LMWPHB; that is, the total weight loss of the specimen ACRY-1/3 was much greater than that of ACRY-1/5. Also, ACRY-1/3 lost about 15.1 wt % (±1.3 wt %) after 60 days in the humid potting soil, whereas ACRY-1/5 lost a much smaller amount of 8.8 wt % (±0.7 wt %) in the same period; these values were all much smaller than the amount of LMWPHB added to the specimens. The result was different from those obtained from pHEMA/LMWPHB and was attributed to the hydrophobic nature of MMA/BA in the ACRY/LMWPHB specimens with regard to the penetrating and attacking speeds of microorganisms and led to the small weight loss obtained. Consequently, although the weight loss rates or the biodegradation rates of ACRY/LMWPHB increased with the LMWPHB content, they were also much smaller than those of pHEMA/LMWPHB and changed less drastically during the testing period, especially in the first 15 days. The results indicate that the biodegradation properties of various acrylate/LMWPHB copolymers could be modified and controlled by changes in the hydrophilic properties of the acrylic constituents and could generate many diversified applications, such as artificial skin manufacturing/dressings, marrow/spinal cord cell regeneration, drug delivery, scaffolds for cell adhesion and artificial cartilage production, and bone cements, as mentioned previously.[28,40–48] The studied materials with the combined mechanical and biodegradation properties not only could result in bioactive and biodegradable second-generation biomaterials but could also further result in third-generation materials capable of stimulating specific cellular responses at the molecular level for new biomedical applications.[50,51]

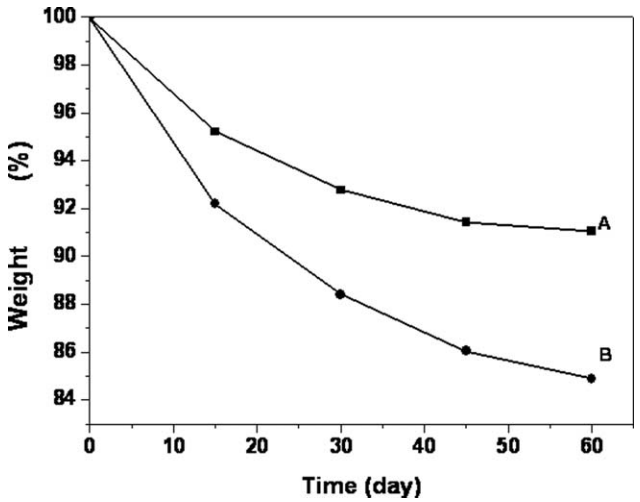


Figure 9. Changes in weight loss from the representative (A) ACRY-1/5 and (B) ACRY-1/3 during the biodegradation test.

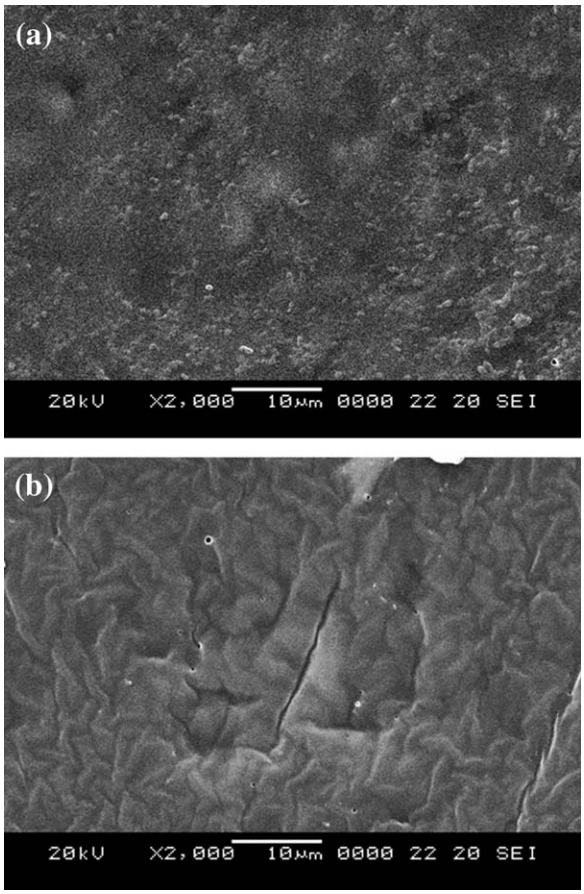


Figure 10. SEM micrographs obtained from ACRY-1/5 after biodegradation for (A) 15 and (B) 45 days.

The surface morphology of the ACRY/LMWPHB specimens after the biodegradation test is also shown in Figures 10 and 11. From Figure 10, it is obvious that ACRY-1/5 had a much different surface shape than pHEMA-1/5 after 15 and 45 days in the testing soil. The surface of ACRY-1/5 seemed to remain intact and showed no digested holes like those observed in Figure 7 because a relatively small weight loss resulted from the hydrophobic nature of ACRY. However, a clear irregular canyonlike morphology was obtained after the surface was biodegraded to a noticeable extent. A similar surface type was observed in the SEM micrographs of pHEMA-1/3 shown in Figure 11, where a more distinct canyonlike morphology was obtained after only 15 days of biodegradation than in Figure 10 because of the significant loss of LMWPHB.

CONCLUSIONS

The structure of the prepared LMWPHB and the properties of LMWPHB photopolymerized with hydrophilic and hydrophobic acrylic monomers were obtained. The prepared LMWPHB had transformed unsaturated ends and was UV-reactive. The tensile strengths of the LMWPHB/acrylates decreased, but the biodegradation rates increased with increasing content of LMWPHB. In addition, the flexibility and biodegradation rate of the LMWPHB/hydrophilic acrylates were much greater than those

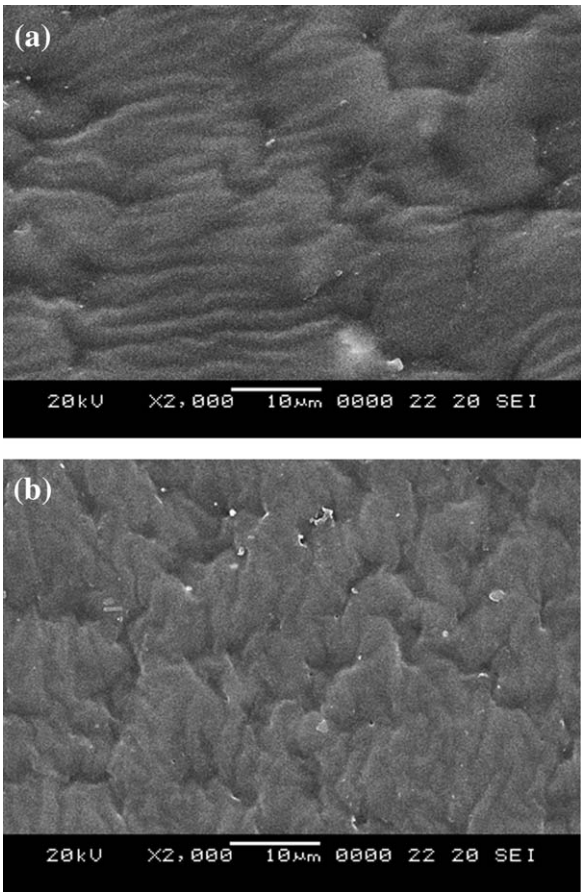


Figure 11. SEM micrographs obtained from ACRY-1/3 after biodegradation for (A) 15 and (B) 45 days.

of the LMWPHB/hydrophobic acrylate. We demonstrated that the prepared LMWPHB could offer biodegradation properties to acrylates, control the biodegradation rate of acrylates, and then potentially find wide applications in biomedical fields.

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