ORIGINAL ARTICLE

Fabrication and characterization of honeycomb-patterned film from poly(ϵ -caprolactone)/poly((R)-3-hydroxybutyric acid)/reduced graphene oxide composite

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A novel biocomposite of poly(ϵ -caprolactone) (PCL) containing poly((R)-3-hydroxybutyric acid) (PHB) and a fixed amount of reduced graphene oxide (RGO) was synthesized. The characterization of the composite by Fourier-transform infrared, ultraviolet–visible spectral analysis, differential scanning calorimetry and thermogravimetric analysis indicates a strong interaction between PCL and PHB/RGO. Honeycomb-patterned thin films with regular structures were fabricated by casting the composite solutions under humid conditions. The temperature-dependent direct current (DC) conductivity of the patterned films was studied over the range of 290–335 K, revealing the semiconducting behavior of the transport properties of the composite films. The presence of the PHB component not only slightly increased the conductivity but also accelerated the biodegradability of the PCL matrix.

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INTRODUCTION

Poly(ϵ -caprolactone) (PCL) is a biodegradable and biocompatible polyester with a number of potential applications, ranging from agricultural use to engineering and biomedical devices.^{1,2} PCL composites that contain conducting materials have many potential applications, such as in biomedical materials, biomedical engineering, biosensors and microparticles for drug delivery.^{3–5} Reported composite materials include PCL/multi-walled carbon nanotubes,^{6,7} PCL/polyaniline^{8,9} and PCL/polypyrrole.^{10,11} PCL/graphene oxide (GO) composites with simple mixing¹² or that have been functionalized with intermediate molecules have also been reported.^{13,14} Recently, Wan *et al.*¹⁵ reported a PCL/GO nanocomposite, prepared by electro-spinning, that showed enhanced hydrophilicity, mechanical properties and bioactivity. However, due to turbulence in the crystal lattice, GO-based polymer composites usually have very low electrical conductivity. To use graphene and its derivatives as a conducting material component in conducting composites, GO must be reduced to reduced graphene oxide (RGO), which is an appropriate alternative.

Poly((R)-3-hydroxybutyric acid) (PHB), which is produced by microorganisms to store carbon as an energy resource, is a promising material for applications that require biocompatibility, non-toxicity and biodegradability.^{16,17} Therefore, the investigation, development and modification of PHB-based materials are of great interest in regenerative medicine. Earlier studies have shown that PHB can be

fabricated into multifilament fibers that have textile properties using high-speed melt spinning and drawing technology. In addition, PHB can be further processed into textile scaffolds and wound-healing patches.^{18–21} In addition to fabricating PHB copolymers with good elastic properties, blending PHB with certain biopolymers also appears to be a reasonable option for application purposes.²² Composites or blended materials produce intermediate or even superior properties while preserving the major characteristics of the pure components. PHB composites have been prepared using several biocompatible and biodegradable polymers, including poly(ethylene oxide), poly(L-lactide), poly(L-lactic acid) and PCL, to improve its weak properties.^{23,24} Therefore, it is promising to combine PCL or a PCL-based composite with a PHB polymer to enhance the degradability of the composite for a variety of purposes.

Honeycomb-patterned thin films, in general, and PCL films, in particular, have attracted considerable attention because of their potential application in various fields, such as in photonic crystals, sensors, membranes, catalyst supports and microreactors.²⁵ Of the many substrates that are available, biopolymers are particularly interesting because of their promising applications in medicine and in environment-friendly industries.

A simple and useful technique for preparing honeycomb-patterned thin films is the breath-figure method.²⁶ In this method, the substrate is completely dispersed in organic solvents, such as chloroform, and

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films are then fabricated by casting these solutions under humid conditions.²⁷ Conducting honeycomb-patterned thin films of bio-compatible polymer composites are suitable candidates for semi-conducting biomaterials for applications.

In this study, a novel biocompatible composite of PCL was synthesized using the *in situ* ring-opening polymerization method of an ϵ -caprolactone monomer in the presence of both RGO and PHB. The spectral characteristics, thermal behavior and degradation of the composite were investigated. Honeycomb-patterned thin films, which were fabricated by casting the composite solution under humid conditions, showed good semiconducting behavior over the temperature range of 290–335 K.

MATERIALS AND METHODS

Materials

ϵ -Caprolactone (99% purity, Aldrich) was purified by recrystallization using absolute methanol and was dried in vacuum at 30 °C. Graphite powder, with an average particle size of 6 μm , poly[(R)-3-hydroxybutyric acid], NaNO_3 , KMnO_4 , concentrated H_2SO_4 , concentrated HCl , a 30% H_2O_2 aqueous solution, benzyl alcohol, tin octoate ($\text{Sn}(\text{Oct})_2$), tetrahydrofuran, methanol, hydrazine hydrate and chloroform, which were all analytical grade, were used as received from Sigma-Aldrich Korea (Seoul, Korea). Deionized water was used in all of the experiments.

Experimental details

Synthesis of PCL/PHB/RGO composite. GO was prepared from the chemical oxidation of graphite powder following a modified Hummers method.²⁸ RGO was obtained using hydrazine hydrate as a reduction agent.²⁹ A total amount of 10 g, including predetermined percentages of RGO, PHB and ϵ -caprolactone, was introduced into a flask and sonicated at room temperature for 3 h.

The mixture reaction was conducted at 160 °C for 24 h in the presence of $\text{Sn}(\text{Oct})_2$ (0.1 g, 1 wt.% of the monomer) as a catalytic agent and of benzyl alcohol (0.015 g) as a co-initiator under a nitrogen atmosphere.³⁰ The resulting polymer composites were dispersed in tetrahydrofuran, precipitated in cold methanol, washed and dried at 40 °C in vacuum. The amount of PHB that was used in the composite preparation varied. The amount was 5, 10 or 20 wt.% with a fixed amount of RGO, 5 wt.%; these samples will be abbreviated as PBR5-5, PBR5-10 and PBR5-20, respectively. The same procedure was used to synthesize the PCL homopolymer without the addition of PHB, RGO and benzyl alcohol for comparison.

Fabrication of honeycomb-patterned thin films. The procedure for the preparation of the patterned PCL and PBR5-5, PBR5-10 and PBR5-20 composite (PBR composites) thin films has been detailed in a previous report.²⁷ Each solution, which contained 0.25 g of the powder samples in 6 ml of chloroform, was sonicated at room temperature for 1 h and then cast onto a glass Petri dish at 25 °C under a relative humidity of 60%. Honeycomb-patterned films were formed by the condensation and deposition of water droplets on the solution surface via evaporative cooling.³¹ The overall experimental scheme for the synthesis of the PBR composite and for the fabrication of the honeycomb-patterned film is shown in Figure 1.

Characterization. The infrared spectra of the PCL, PHB and PBR composite samples, which were pelletized with potassium bromide (KBr), were obtained using an Fourier-transform infrared (FTIR) spectrophotometer (Model 1600, Perkin Elmer, Waltham, MA, USA). Approximately 60 scans were signal-averaged with a resolution of 2 cm^{-1} from 4000 cm^{-1} to 400 cm^{-1} . The ultraviolet–visible (UV–vis) spectra of the samples were obtained using a Shimadzu UV–vis–NIR spectrophotometer (UV-3101PC; Shimadzu, Kyoto, Japan). X-ray photoelectron spectroscopy (XPS) measurements were performed with an XSAM800 (Kratos Company, Manchester, UK) using $\text{AlK}\alpha$

Figure 1 Schematic diagram showing the synthesis of the PBR composite and the formation of the honeycomb-patterned films with the assistance of water droplets. GO, graphene oxide; PCL, poly(ϵ -caprolactone); PHB, poly[(R)-3-hydroxybutyric acid]; RGO, reduced graphene oxide. A full color version of this figure is available at *Polymer Journal* online.

radiation ($h\nu = 1486.6\text{ eV}$). The XPS peak41 software was used to perform curve fitting and to calculate the atomic concentrations. The thermal properties were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The TGA thermograms of the composites were obtained under a nitrogen atmosphere at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from 25 to $800\text{ }^{\circ}\text{C}$ using a TGA Q50 system (TA Instruments, New Castle, DE, USA). DSC thermograms were obtained using a TA Instrument DSC-2010 (TA Instruments) with an autocool accessory under a nitrogen atmosphere. Each sample, which weighed 5 mg, was encapsulated in an aluminum pan, was cooled from room temperature to $-50\text{ }^{\circ}\text{C}$, and was held at this temperature for 5 min. The pan was then heated from -50 to $250\text{ }^{\circ}\text{C}$, isothermally maintained at $250\text{ }^{\circ}\text{C}$ for 3 min, quenched to $-50\text{ }^{\circ}\text{C}$, and reheated from -50 to $250\text{ }^{\circ}\text{C}$ after a 5 min interval. All of the non-isothermal steps were conducted at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The morphology of the obtained patterned films was characterized by scanning electron microscopy (SEM) on a model CX-100 (COXEM, Daejeon, South Korea). DC conductivity measurements were performed on the obtained composite films over the range of 290–335 K using the four-probe technique with a Keithley 224 constant current source and with a Keithley 617 digital electrometer (Keithley Instruments Inc., Cleveland, OH, USA). Biodegradability was determined with a modified Sturm's test³² in accordance with ASTM D5338-98: 100 g of the sample, 600 g of an inoculant medium (humus, dry solids) and 50% distilled water were mixed and used for each experiment. The measurements were interrupted when the CO_2 production of the sample remained approximately the same as that of the control sample for at least 10 days.

RESULTS AND DISCUSSION

Characterization of RGO, PCL and the PBR composites

Figures 2a and b show the SEM image of the RGO sheets and the XPS survey spectra, including the C1s and the O1s spectra of GO and

RGO. The SEM image confirms that the RGO sheets were formed after reducing GO. As observed in the inset figures, the C1s binding energy is approximately 285 eV and that of O1s is approximately 533 eV for GO. The C1s spectra of GO indicate a considerable degree of oxidation within the carbon atoms that belong to five functional groups, that is, to C–H (C–C, C=C), C–OH, epoxide, C=O (carbonyl C) and O=C–OH (carboxylate C).²⁹ In the C1s spectra of RGO, the peaks of the oxygen-containing groups have disappeared.

Table 1 FTIR band assignments of synthesized RGO, PCL and the PBR composites

Assignments	Observed peaks (cm^{-1}) for				
	RGO	PCL	PBR5-5	PBR5-10	PBR5-20
O–H stretching vibrations of the –OH group	3446	—	3441	3442	3444
Asymmetric CH_2 stretching	2925	2950	2948	2947	2947
Symmetric CH_2 stretching	2860	2868	2868	2867	2866
Carbonyl stretching	—	1729	1728	1728	1727
Skeletal vibrations of aromatic C=C	1627	—	—	—	—
C–O stretching	—	1296	1296	1296	1296
	—	—	1283	1283	1283
Asymmetric COC stretching	—	1244	1244	1244	1244
Symmetric COC stretching	—	1175	1175	1175	1175

Abbreviations: FTIR, Fourier-transform infrared; PCL, poly(ϵ -caprolactone); RGO, reduced graphene oxide.

Figure 2 (a) Scanning electron microscopy image of reduced graphene oxide (RGO), (b) the XPS spectra of graphene oxide (GO) and RGO, (c) the Fourier-transform infrared spectra of RGO, poly(ϵ -caprolactone) (PCL) and the PBR composites and (d) the ultraviolet-visible spectra of PCL, poly((R)-3-hydroxybutyric acid) (PHB) and the PBR composites.

The O1s binding energy that is observed in the RGO spectra is the same as that in the GO spectra, but the intensity of the O1s peak is greatly reduced, indicating that most of the oxygen-containing groups

have been reduced by hydrazine. The reduction of GO is confirmed by the fact that the content of the oxygen (O) atoms of RGO is significantly reduced compared with that of GO (the C/O atomic ratio increased from 3.0 for GO to 12.1 for RGO, as calculated in the inset table shown in Figure 2b). The XPS result indicates that some oxygen-containing functional groups were removed and that the sp³-hybridized rings were possibly restored to sp²-hybridized structures.

Figure 2c shows the FTIR spectra, and Table 1 summarizes the major FTIR peaks that were observed for synthesized RGO, PCL and the PBR polymer composites along with their probable assignments. RGO exhibits two strong peaks at 3446 cm⁻¹ (the O–H stretching vibrations of –OH groups) and at 1627 cm⁻¹ (the skeletal vibrations of aromatic C=C from the graphitic domains). In addition, the presence of peaks at 2925/2860 cm⁻¹, which were assigned to methylene stretching, represents the existence of some CH or CH₂ groups in RGO, implying that the sp²-hybridized carbon was not entirely restored by hydrazine hydrate. The FTIR spectrum of RGO indicates that most of the oxide groups of GO were reduced by hydrazine hydrate but that C–OH groups still exist.²⁹

The PCL spectra exhibit main bands at 2950, 2868 and 1729 cm⁻¹, which can be assigned to the stretching vibration of –CH₂ and to the vibration of –C=O bonds. These results are similar to those previously reported.^{8,33} The presence of a fixed amount of RGO and of different concentrations of PHB (in wt.%) in the polymer composites is indicated by the appearance of new peaks that correspond to PHB and RGO and by some shifting of the PCL peaks in the PBR polymer composites.

A new strong absorption emerged at 3441–3444 cm⁻¹ in the composites, which is characteristic of the –OH group of the RGO in the composite matrix. The peak at 1283 cm⁻¹ can be assigned to the stretching of the C–O group in PHB. These results are in good agreement with previously reported PHB FTIR data.³⁴ The PCL peaks at 2950, 2868 and 1729 cm⁻¹ had a slight shift (1–3 cm⁻¹) to a lower wave number in the composites. This result can be attributed to the interaction between PCL and the other materials that form the polymer composite matrix.

Figure 2d shows the UV–vis absorption spectra of PHB, synthesized PCL and the PBR polymer composites. Obviously, the characteristic peaks of PCL were exhibited at 240 and 296 nm, those of PHB were exhibited at 241 and 284 nm. These bands are due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions,⁸ which are attributed to the presence of C–O and C=O in each repeating unit of PCL and PHB, respectively. In the PBR composites, the PCL peak at 240 nm was red-shifted by 1 nm. In

Figure 3 Thermal behavior of poly(ϵ -caprolactone) (PCL), poly((R)-3-hydroxybutyric acid) (PHB) and the PBR composites: (a) thermogravimetric analysis and (b) differential scanning calorimetry curves.

Figure 4 (a) Photographs of reduced graphene oxide (RGO) and the PBR composites dispersed in chloroform at a concentration of 5 mg ml⁻¹ after 5 days of sonication, and (b) photograph of the PBR5-20 patterned film showing stability and flexibility. A full color version of this figure is available at *Polymer Journal* online.

contrast, the UV-vis spectra of the PBR5-5, PBR5-10 and PBR5-20 composites exhibited a slight blue shift of approximately 1–2 nm for the PCL peak at 296 nm. This shift in the polymer composite absorption bands may be due to the interaction between PCL, RGO and/or PHB in the PBR composites. In addition, the appearance of weak peaks at approximately 266 and 366 nm further suggests conjugation between RGO and PCL/PHB in the composites.

The FTIR and UV-vis spectra of the PBR composites confirm an interaction between PCL, RGO and PHB. The chemical bonding between PCL and RGO is achieved via a ring-opening polymerization process in the presence of –OH groups. In this process, the hydroxyl groups on the RGO surface act as initiators for polymerization

and PCL is grafted onto RGO to form a PCL-RGO composite.^{33,35} Physical bonding is obtained via the interaction between the chains of PCL and PHB with RGO and the PCL/RGO network.

Thermal behavior of PCL, PHB and the PBR composites

As can be seen in Figure 3a, the degradation rate of PHB is faster than that of PCL at a given temperature, indicating that PHB has a lower thermal stability. The TGA curve of the PBR composites shows an increase in the thermal stability. The degradation at temperatures ranging from 270 to 350 °C in the PBR composites can be attributed to the presence of the PHB component. The thermal stability of PHB is lower than those of the other materials in

Figure 5 Scanning electron microscopy images of the honeycomb-patterned films prepared from (a) poly(ϵ -caprolactone) (PCL), (b) PBR5-5, (c) PBR5-10 and (d) PBR5-20 (left: top-view, right: cross-sectional view, the pores of the PCL film were deformed during sample preparation because of its flexibility).

the composite. However, despite the PHB concentration in the composite being up to 20 wt.%, the negative effects on the thermal stability of the PBR composite are negligible. By contrast, the presence of RGO in PBR induced a better thermal stability, clearly shifting the degradation starting temperature to higher temperatures.

DSC thermograms of PCL and of the PBR polymer composites are shown in Figure 3b. The crystallization temperature (T_c) was defined as the peak temperature from the first cooling scan curve. The melting temperature (T_m) was determined from the second heating scan curve. The T_c of pure PCL was 31.5 °C and shifted to 32.5, 34.9 and 36.6 °C for the PBR5-5, PBR5-10 and PBR5-20 composites, respectively. The incorporation of RGO and PHB into the PCL matrix resulted in an increase in T_c . This increase in the crystallization temperature implies that the GO/PHB acts as an efficient nucleating agent for the crystallization of PCL; this effect was suggested in previous reports.³⁶ From the second heating scan thermograms, it can be seen that the T_m values of the PBR composites slightly decrease with respect to that of pure PCL. PCL exhibited the highest melting temperature of 54.2 °C; the T_m values of the PBR5-5, PBR5-10 and PBR5-20 composites were 53.8, 52.4 and 50.5 °C, respectively. The lower T_m values that were recorded for the PBR composites are due to the lower melt viscosity of PHB and of RGO.³⁷ In addition, the hydrophilic character of RGO likely leads to poor adhesion with the hydrophobic PCL, which may lead to an enhancement of the molecular mobility of the polymeric chains. The observed shifts in the T_c and T_m values of the PBR composites suggest the formation of interfacial interactions between RGO/PHB and the PCL molecular chain.

Figure 6 Temperature-dependent DC conductivity of poly(ϵ -caprolactone) (PCL) and the PBR composite films over the range of 290–335 K.

Honeycomb-patterned structure of the PCL and PBR polymer composite films

To fabricate honeycomb-patterned films using the breath-figure method, the substrate must be completely dispersed in organic solvents, such as chloroform. Pure RGO exhibits poor dispersibility in common organic solvents. However, the RGO component in the PBR composites was well dispersed in chloroform due to the formation of the composite with PCL/PHB. Stable and homogeneous dispersions were obtained from a lengthy sonication treatment, as shown in Figure 4, leading to a homogeneous dispersion of RGO in the composite film.

Figures 5a–d show typical SEM images of the PCL, PBR5-5, PBR5-10 and PBR5-20 honeycomb-patterned films, respectively. The SEM image of PCL shows a highly regular structure with an average pore diameter of approximately 8.5 μm (Figure 5a), whereas it is impossible to obtain honeycomb-patterned films from RGO and pure PHB. Stable honeycomb structures were obtained with a fairly regular structure for the PBR composite films (Figure 5b–d). As observed in the top-view and cross-sectional view images, the change in the pore diameter with increasing PHB concentration in the composites is negligible, whereas a change in the pore density and a difference in the diameters of the small pores and large pores can be clearly observed. The pore density decreased upon the addition of RGO and PHB to the composite. However, in the PBR composites with a fixed amount of RGO, the distance between the pores only slightly increased with increasing PHB concentration, indicating that RGO has a major role in adjusting the size and density of the honeycomb structures in the PBR composite films. This result may be due to the process that transformed the impossible pattern and to the hydrophilic character of RGO in the PBR composites, which adjusts the hydrophobic property of PCL/PHB in the composites. The SEM images also support the dispersion of RGO in the composite films, which is due to the interaction between RGO and PCL/PHB.

Temperature-dependent DC conductivity of the PBR honeycomb-patterned composite films

The temperature-dependent conductivity of the PCL and PBR composite films with different PHB concentrations was investigated over the temperature range of 290–335 K. As shown in Figure 6 and Table 2, the conductivity value of the PCL homopolymer film is very low and hardly changes with increasing temperature. PCL is not a semiconductor material, so this result is entirely reasonable. By contrast, the conductivity values of the PBR5-5, PBR5-10 and PBR5-20 composite films are much greater than that of PCL. The conductivity increased with increasing temperature. In addition, the conductivity increased with increasing PHB wt.% in the composites. The conductivities were 0.0253 S cm^{-1} for PBR5-5, 0.026 S cm^{-1} for PBR5-10 and 0.030 S cm^{-1} for PBR5-20 at 335 K. The main

Table 2 Conductivity values of PCL and the PBR composites for different temperatures

Samples	Conductivity (S cm^{-1}) at different temperature (K)					
	290	300	310	320	330	335
PCL	7.59×10^{-10}	7.69×10^{-10}	7.84×10^{-10}	8.03×10^{-10}	8.23×10^{-10}	8.24×10^{-10}
PBR5-5	7.73×10^{-4}	0.00161	0.00360	0.0085	0.0192	0.0253
PBR5-10	7.89×10^{-4}	0.00165	0.00375	0.0088	0.0200	0.026
PBR5-20	8.40×10^{-4}	0.00173	0.00405	0.0096	0.0218	0.030

Abbreviation: PCL, poly(ϵ -caprolactone).

Figure 7 CO_2 accumulations (P) of the powder samples of poly(ϵ -caprolactone) (PCL), poly((R)-3-hydroxybutyric acid) and the PBR composites as a function of time.

conductivity values of the PBR5-5, PBR5-10 and PBR5-20 films beyond the 290–335 K range are summarized in Table 2.

The increase in conductivity with increasing temperature indicates the semiconducting behavior of the composites,³⁸ which is primarily due to the introduction of RGO into the polymer composite matrix. In addition, the introduction of PHB into PCL/RGO slightly increases the conductivity of the PBR polymer composites, as shown in Figure 6. This increase can be attributed to the short and linear chain of PHB. These linear chains have a chiral center with an R-stereochemical conformation (isotactic).³⁹ In addition, the mobility of the ions or counter ions of PHB in the composites also cause an increase in the conductivity of the PBR composites. The characterization and SEM studies indicate an interconnection between PHB and PCL/RGO in the composite, which could induce the improved conductivity of the films.

Biodegradability of PHB and the PBR composites

Biodegradation, which is generally measured by either the consumption of oxygen or the formation of carbon dioxide (the Sturm test), is a good indicator of polymer degradability. In this study, the Sturm test was applied to the powders of PCL, PHB and of the PBR5-5, PBR5-10 and PBR5-20 composites. As shown in Figure 7, the decomposition rate of PCL was very slow. PHB showed a maximum degradability in terms of the CO_2 accumulation rate over the same time range. The biodegradability of the PBR composites was better than that of PCL and depended on the PHB concentration in the polymer composite. The composites exhibited an increased CO_2 accumulation rate with increasing PHB concentration. The CO_2 accumulation rate of PBR5-5 was similar to that of PCL, whereas that of PBR5-20 was higher. These results suggest that the increase in the biodegradation rate of PCL was due to the PHB incorporation.

Because PHB was incorporated into the PBR composite networks that contain PCL, the good biodegradability of PHB, which is due to microbes, induced porosity in the polymer composite matrix, leading to the eventual loss of the PCL matrix integrity. This phenomenon enabled the microbes to quickly invade and adhere to the PCL chains. As a result, the PCL in the composite biodegrades more easily than the PCL homopolymer under the same conditions over the same time range. This result is similar to that from a previous report⁴⁰ regarding the biodegradation of PCL/starch blends, indicating that the PHB component played an active role in accelerating the decomposition rate of the PBR composite.

CONCLUSION

Biocompatible PCL/PHB/RGO composites with a fixed RGO wt.% and different PHB wt.% were prepared, and honeycomb-patterned films were fabricated by casting the composite solution under humid conditions. The characterization results from FTIR, UV-vis, TGA and DSC measurements indicate a strong interaction between PCL and PHB/RGO. The temperature-dependent DC conductivity that was obtained for the patterned films exhibited a semiconducting behavior for the composite material. The PCL polymer composite that contained RGO and PHB exhibited good biodegradability, which is similar to that of pure PHB, indicating that the synthesized composite could have potential applications in the areas of biological science, engineering and medicine.

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