Journal of Environmental Science International
26(1); 1~10; January 2017

pISSN: 1225-4517 eISSN: 2287-3503
https://doi.org/10.5322/JESI.2017.26.1.1

ORIGINAL ARTICLE

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/Graphene Oxide Nanocomposite Films: Thermomechanical Properties, Oxygen Transmission Rates, and Hydrolytic Degradation

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Abstract

In this study, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV)/graphene oxide (GO) nanocomposite films containing various content of GO were prepared using solution casting method. The effect of GO content on Young’s modulus and dispersion of GO in PHBV matrix was investigated. Also, the thermomechanical properties, oxygen transmission rates and hydrolytic degradation of PHBV/GO nanocomposite films were studied. The addition of GO into PHBV improves the Young’s modulus and decreases thermal expansion coefficient. The improvement can be mainly attributed to good dispersion of GO and interfacial interactions between PHBV and GO. Furthermore, PHBV/GO nanocomposite films show good oxygen barrier properties. PHBV/GO nanocomposites show lower hydrolytic degradation rates with increasing content of GO.

Key words : Graphene oxide, Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), Hydrolytic degradation, Modulus, Barrier property

1. Introduction

Since polymers derived from petroleum are generally non-degradable, their wastes have an adverse effect on the environment. Tough environmental laws and increasing disposal costs have generated much interest in biodegradable polymers. Recently, sustainability becomes a very important concept for the human well-being and environmental concerns. Therefore, biodegradable polymers based on renewable resources have attracted great interest.

Poly(hydroxylalkanoates) (PHAs) produced as internal carbon and energy storage materials by bacteria grown under nutrient-limited growth conditions are biodegradable polymers based on renewable resources (Rouf and Stoke, 1962). Besides being enzymatically degradable, PHAs possess good mechanical properties that are often compared favorably to petroleum-based thermoplastics. Among PHAs, poly(3-hydroxybutyrate) (PHB) is the most studied. Even though the physical properties of PHB are very close to those of polypropylene (PP), brittle nature and the narrow thermal processing

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Received 17 October, 2016; **Revised** 21 November, 2016;
Accepted 29 November, 2016

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This paper is part of Eun Jung You’s Master’s thesis, which was accepted by Pusan National University.

window of PHB limit its application (King, 1982). To overcome these drawbacks, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) was developed. The copolymer composition has great influence on the physical properties of PHBV (Shogren, 1997; Wang et al., 2005; Cava et al., 2006).

Recently, a lot of studies about polymer nanocomposites have been done in various fields because of their enhanced physical properties (Giannelis, 1996; Lebaron et al., 1999; Alexandre and Dubois, 2000; Ray and Okamoto, 2003; Maniar, 2004; Shafiee et al., 2010; Ataeefard and Moradian, 2011). Especially polymer/graphene nanocomposites have attracted considerable attention due to their superior mechanical, thermal and electronic properties (Stankovich et al., 2006; Kim et al., 2012; Lee et al., 2012; Tapaswi et al., 2015; Tzeng et al., 2015). Graphene Oxide (GO) formed by the Oxidation of graphene can readily exfoliate to form homogeneous colloidal suspensions in water because of oxygen-containing functional groups such as carboxyl, hydroxyl, and epoxide groups. Even though there have been a lot of studies on the blends between PHBV and other polymers (Imam et al., 1998; Avella and Errico, 2000; Chun and Kim, 2000; Godbole et al., 2003; Qiu et al., 2003; Parulekar and Mohanty, 2007), there have been few studies about PHBV/graphene nanocomposites (Wang et al., 2013; Sridhar et al., 2014; Ambrosio-Martín et al., 2015). With addition of graphene into PHBV, improvement of mechanical properties and thermal degradation temperature was reported in the previous studies (Wang et al., 2013; Sridhar et al., 2014). Also, PHBV nanocomposites containing functionalized graphenes showed improved crystallinity, significantly enhanced conductivity and acceleration of the bio-disintegration process in compositing conditions (Ambrosio-Martín et al., 2015; You et al., 2015).

In this work, PHBV/GO nanocomposite films containing various content of GO (0, 0.7, 1, 2 and 5 wt%) were prepared using solution casting method. The effect of GO content on Young's modulus and dispersion of GO in PHBV matrix was investigated. Also, the thermomechanical properties and oxygen transmission rates of PHBV/GO nanocomposite films were studied. The change in the surface morphology and weight of PHBV/GO nanocomposite films with hydrolytic degradation time was examined.

2. Materials and Methods

2.1. Materials and preparation method

Natural graphite powder (< 20 µm), potassium persulfate, phosphorus pentoxide, potassium permanganate, hydrogen peroxide solution (30 wt%), hydrochloric acid (37%) and PHBV containing 12 mol % of hydroxyvalerate were purchased from Sigma Aldrich and used after oven drying at 60°C for 24 h. Sulfuric acid (97%) was purchased from Junsei. Graphite Oxide (GO) was synthesized from graphite powder by the modified Hummers method (Hummers and Offeman, 1958). Detailed preparation method can be found in our previous publication (You et al., 2015).

For the preparation of PHBV/GO nanocomposite films, GO was dispersed in chloroform with stirring for 12 h, followed by ultrasonication for 30 min. PHBV was dissolved in chloroform at 60°C with stirring for 2 h. GO solution was poured into the PHBV solution, and stirring was continued for 2 h. Then, the mixture was sonicated for 30 min to make a well dispersed suspension. In order to examine the effect of GO content on the physical properties of the PHBV/GO nanocomposite films, the nanocomposite films containing various content of GO (0, 0.7, 1, 2 and 5 wt%) were prepared using solution casting method. Finally, samples were dried to constant weight in a vacuum oven at 35°C. The films were peeled off from a substrate for further testing.

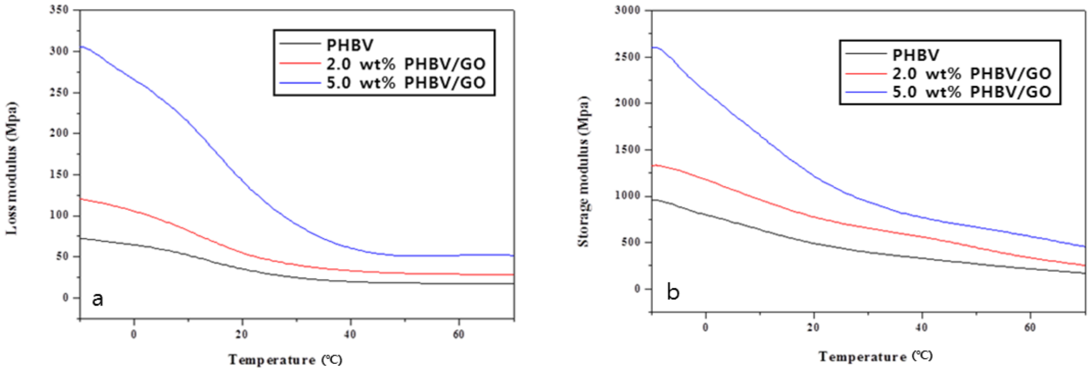


Fig. 1. (a) Loss modulus versus temperature curves and (b) Storage modulus *versus* temperature curves of PHBV/GO nanocomposite films containing 0 wt%, 2.0 wt%, and 5.0 wt% of GO.

2.2. Testing

The storage modulus and loss modulus of the nanocomposite films were measured by Dynamic Mechanical Analyzer (DMA, Perkin Elmer N535 -0001 model) with a heating rate of 10°C/min at 1 Hz. Tensile modulus of PHBV/GO nanocomposite films was measured using a Universal Testing Machine (Model 4466, Instron Co.) at a strain rate of 10 mm/min at room temperature. The sample length and width were 2.5 and 0.5 cm, respectively. All measurements were performed for five replicates of specimens and averaged to get the final result. The morphologies of GO and PHBV/GO nanocomposite films were investigated by field emission-scanning electron microscopy (FE-SEM, JSM-6700F) with an acceleration voltage of 15 kV and energy-filtering transmission electron microscope (EF-TEM, EM-912 Omega, Carl Zeiss). Samples for TEM were prepared by a microtoming method with a focused ion beam (Quanta 3D FEG) at low temperature. Typical tapping-mode Atomic Force Microscopy (AFM) measurements were performed using a Multimode SPM from Digital Instruments. The samples for the AFM were prepared by depositing the homogeneous GO suspension onto a mica substrate in water.

For the oxygen barrier property, an OX-TRAN Model 2/21 (MOCON Inc.) was used with the ASTM protocol D3958. PHBV/GO nanocomposite films were masked with an adhesive aluminum film to expose a circular 5 cm^2 surface area. Thermal Expansion Coefficient (CTE) was measured using a TA Instruments thermomechanical analyzer under nitrogen with a fixed load of 0.05 N from -10 to 140°C with a heating rate of 10°C/ min. PHBV/GO nanocomposite films were weighted and then incubated in 20 mL Phosphate Buffer Solution (PBS) (pH 7.4) in 30 mL glass vial in an incubator at 37°C. The nanocomposite films were retrieved at specified times and air-dried to constant weight. Weight loss was determined gravimetrically.

3. Results and Discussion

Fig. 1 shows the storage and loss modulus of PHBV/GO nanocomposite films measured by DMA. It is obvious that the incorporation of GO into PHBV matrix has a significant influence on the storage and loss modulus. The storage modulus (E') is usually indicative of the elastic modulus of the composites during elastic deformation, and the loss modulus (E'') is indicative of the energy lost due to the friction of polymer chain movement. E′ at 25°C is dramatically increased from 390 MPa for PHBV to 720 MPa and 1060 MPa for PHBV/GO (2 wt%) and PHBV/GO (5 wt%) nanocomposites, respectively. This significant increase of E′ is due to the good dispersion of GO in PHBV matrix, and the good interactions between GO and PHBV, as discussed already in our previous work (You et al., 2015)

The Young's moduli of the PHBV/GO nanocomposites are shown in Fig. 2. Like storage moduli behavior(Fig. 1(b)), the ultimate Young's modulus of the PHBV/GO composite significantly increased by 38% from 1094 Mpa to 1505 MPa. This increase in the modulus with adding GO can be mainly attributed to its good dispersion, as well as the covalent bonding sites which can strong interfacial interactions between the polymer and graphene sheet in the composite. The GO consists of covalently attached oxygen-containing groups such as hydroxyl, carboxyl groups. Between these groups of GO and ester group of PHBV, the composites can form a strong hydrogen bonding, therefore it lead to the mechanical properties in increase (Park et al., 2013).

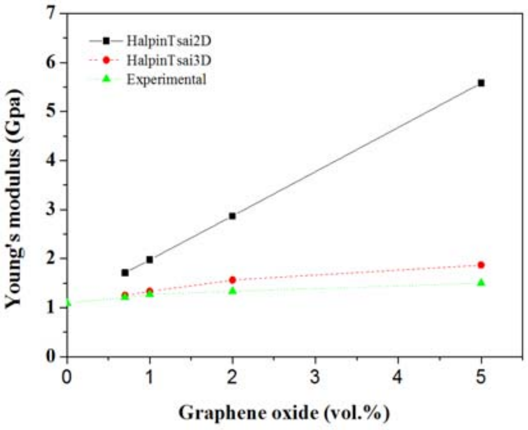


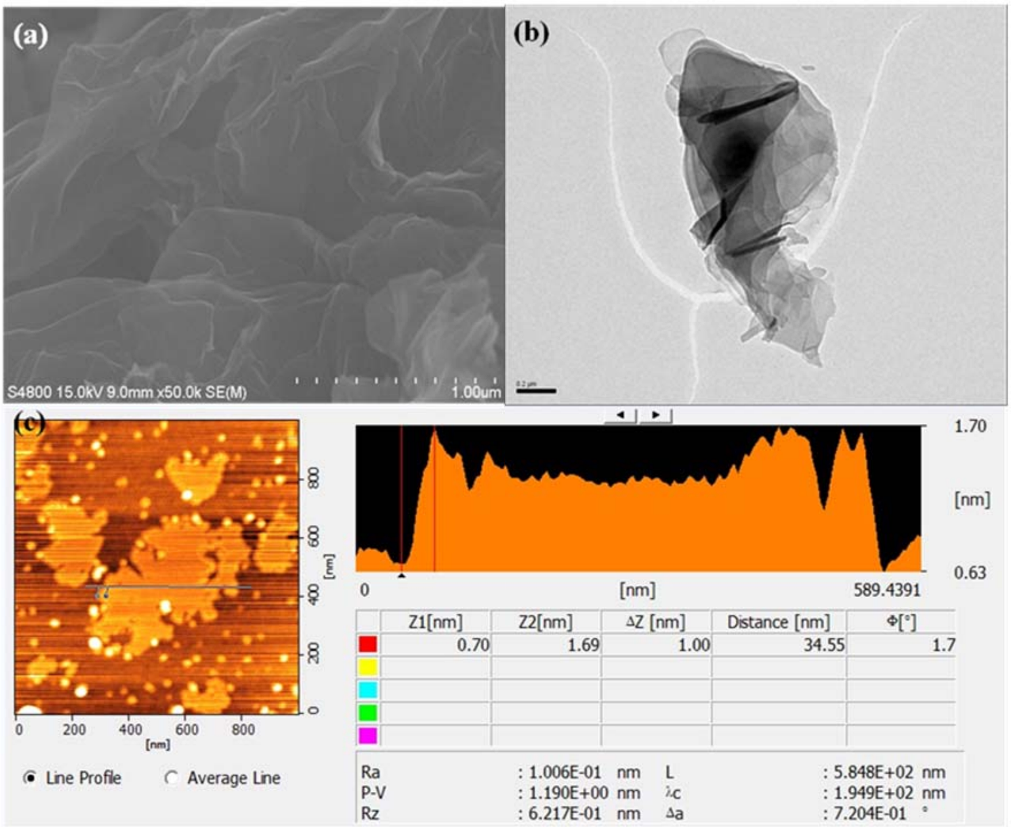
Fig. 2. Experimental Young's modulus of PHBV/GO nanocomposite films and theoretical Young's modulus of the nanocomposite films calculated from the Halpin-Tsai model.

The Young's modulus of composites can be predicted from the Halpin-Tsai theory, a widely used model for predicting the modulus of unidirectionally or randomly oriented filler-reinforced composites (Halpin and Kardos, 1976; Schafer and Justice, 2007; Kim et al., 2012; Lee et al., 2012; Cho et al., 2015). The composite moduli for the randomly and unidirectionally oriented GO sheets in a PHBV matrix are given by the following equations:

$$Ec = E_m \times \left[\frac{3}{8} \times \frac{1 + \frac{(E_g/E_m)-1}{(E_g/E_m)+(2l_g/3t_g)} \times \frac{2l_g}{3t_g} \times V_c}{1 - \frac{(E_g/E_m)-1}{(E_g/E_m)+(2l_g/3t_g)} \times V_c} + \frac{5}{8} \times \frac{1 + 2 \times \frac{(E_g/E_m)-1}{(E_g/E_m)+2} \times V_c}{1 - \frac{(E_g/E_m)-1}{(E_g/E_m)+2} \times V_c} \right] \tag{1}$$

$$E_{ll} = E_m \times \left[\frac{1 + \frac{(E_g/E_m)-1}{(E_g/E_m)+(2l_g/3t_g)} \times \frac{2l_g}{3t_g} \times V_c}{1 - \frac{(E_g/E_m)-1}{(E_g/E_m)+(2l_g/3t_g)} \times V_c} \right] \tag{2}$$

where E_c and E_{ll} represent the Young's modulus of the composites with randomly oriented GO and the aligned GO parallel to the surface of the composite films, respectively. E_g and E_m are the Young's modulus of the GO and the polymer, respectively. The symbols, l_g and t_g refer to the length and thickness of the GO sheet, respectively, whereas V_c refers to the volume fraction of the GO in the composite. The Young's modulus of GO was assumed to be 0.25 TPa based on the literature value for GO (Gomez-Navarro et al., 2008). The Young's modulus of the pure PHBV is 1 GPa. The densities of



● Line Profile ○ Average Line

	Z1[nm]	Z2[nm]	ΔZ [nm]	Distance [nm]	Φ[°]
🟥	0.70	1.69	1.00	34.55	1.7
🟨					
🟦					
🟩					
🟪					

Ra : 1.006E-01 nm L : 5.848E+02 nm
P-V : 1.190E+00 nm λc : 1.949E+02 nm
Rz : 6.217E-01 nm Δa : 7.204E-01 °

Fig. 3. Surface images of GO sheets observed with (a) SEM, (b) TEM, and (c) AFM.

the PHBV and GO were 1.25 and 2.25 g/cm^3, respectively. The statistical averages of the l_g and t_g of the GO sheets were approximately 500 and 1 nm, respectively, according to AFM analysis that are shown later.

The experimental values for Young's modulus of PHBV/GO nanocomposites are compared with the theoretical values (3D random and 2D aligned) predicted from the Halpin-Tsai theory in Fig. 2. The experimental values increase with increasing content of GO. This reinforcement effect from GO can be mainly attributed to its good dispersion and interfacial interactions between PHBV and GO. GO consists of oxygen-containing groups such as hydroxyl and carboxyl groups. A hydrogen bonding can exist between these groups of GO and ester groups of PHBV (Gilje et al., 2007; Park et al., 2013).

Fig. 2 shows that the theoretical values for the random 3D plots are close to the experimental values. Based on this result, the dispersion of GO sheets in PHBV matrix could be mostly random. The surface images of the GO sheets were observed with SEM (Fig. 3(a)) and TEM (Fig. 3(b)), which show flat morphology, with some wrinkles and folding on the surface and edge. AFM is used to determine the length and thickness of the GO sheets. Fig. 3(c) displays a typical tapping-mode AFM image of GO deposited onto a mica substrate from an aqueous dispersion,

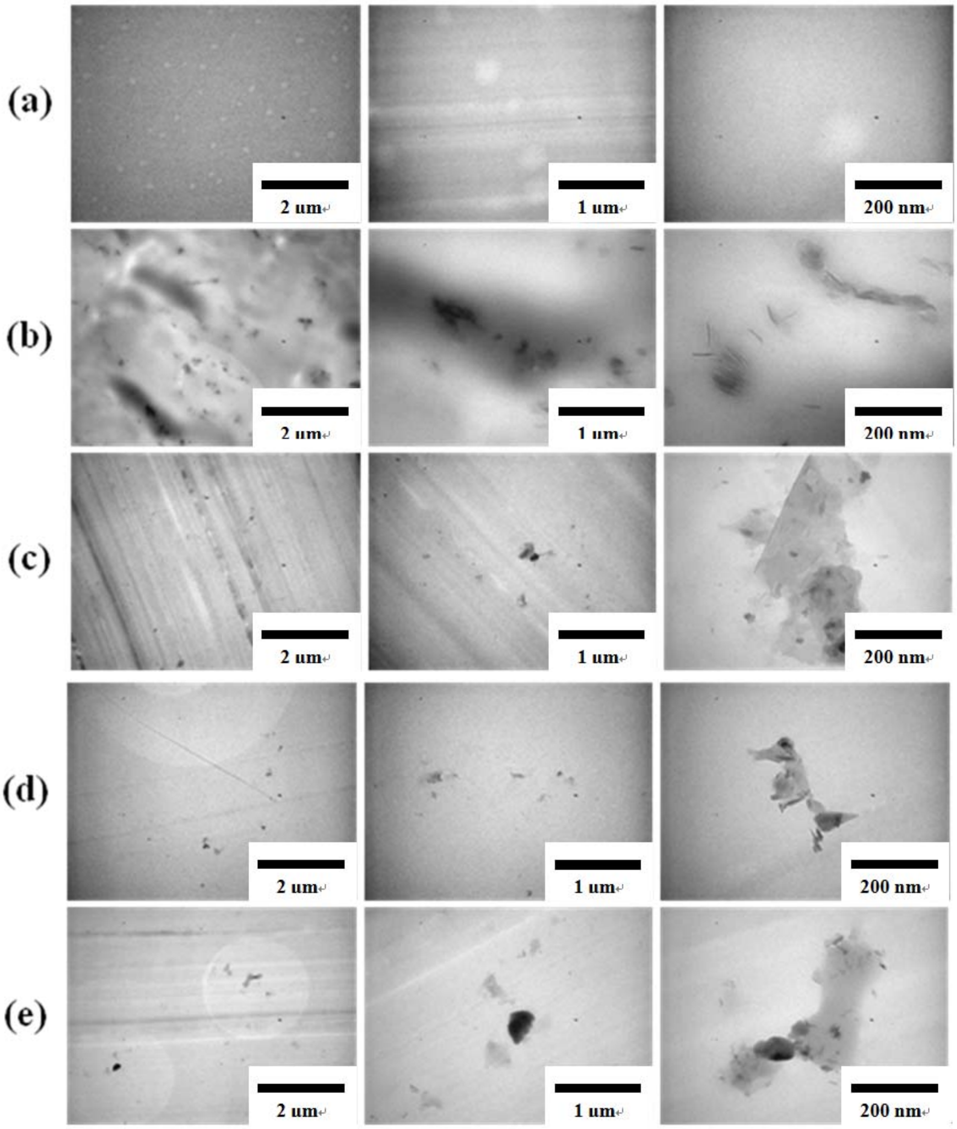


Fig. 4. EF-TEM images of PHBV/GO nanocomposite films containing (a) 0 wt%, (b) 0.7 wt%, (c) 1.0 wt%, (d) 2.0 wt%, and (e) 5.0 wt% of GO.

which shows approximately 500 nm and 1 nm in length and thickness, respectively. Based on this result, the aspect ratio of GO nanosheet is about 500.

Fig. 4 shows the TEM images of PHBV/GO nanocomposite films with various GO weight fractions. GO sheets are randomly dispersed throughout the polymer matrix. Some aggregated sheets are observed in the TEM images. The TEM images of PHBV/GO nanocomposite films are consistent with the result in Fig. 3.

Table 1 shows the oxygen transmission rates

Table 1. Oxygen transmission rates and thermal expansion coefficients of PHBV/GO nanocomposite films

Sample	Oxygen transmission rates $cm^3/(m^2 \cdot day)$	Thermal expansion coefficients μm/(m·°C)
0 wt%	63	271.5
0.7 wt%	51	248.8
1.0 wt%	50	225.5
2.0 wt%	48	202.9
5.0 wt%	45	193.8

of PHBV/GO nanocomposite films, implying much lower oxygen transmission rate compared with commercial polymers such as polyethylene and polypropylene and meaning a desirable oxygen barrier properties for packaging. With increasing content of GO, oxygen transmission rates of PHBV /GO nanocomposite films decrease. Further reduction in the oxygen transmission rates, which is necessary for practical packing uses, may be expected with further increasing GO content due to a tortuous path mechanism by high aspect ratio of GO.

The Thermal Expansion Coefficients (CTEs) for PHBV/GO nanocomposite films are also shown in Table 1. The CTEs were determined from the TMA measurements in the range of -10~140°C. The addition of GO remarkably reduces the CTE of PHBV/GO nanocomposite films. The addition of GO sheets is believed to increase the rigidity, resulting in lower CTE. GO leads to enhanced thermomechanical properties of PHBV/GO nanocomposites.

Hydrolytic degradation of PHBV in an aqueous environment occurs through simple hydrolysis of ester bonds (Casarin et al., 2011). To investigate hydrolytic degradation of PHBV/GO nanocomposites, PHBV and PHBV/GO nanocomposites films were incubated in 20 mL phosphate buffer solution (PBS) (pH 7.4) in 30 mL glass vial in an incubator at 37°C. Fig. 5 shows the morphology of PHBV and PHBV/GO nanocomposites after 30 days of the incubation. Before the incubation, a smooth surface was observed. The micro-holes and cracks on the PHBV film were observed after 30 days of the incubation. The amount of defects decreases for PHBV/GO (0.7 wt%) nanocomposites compared with the pristine PHBV. With increasing

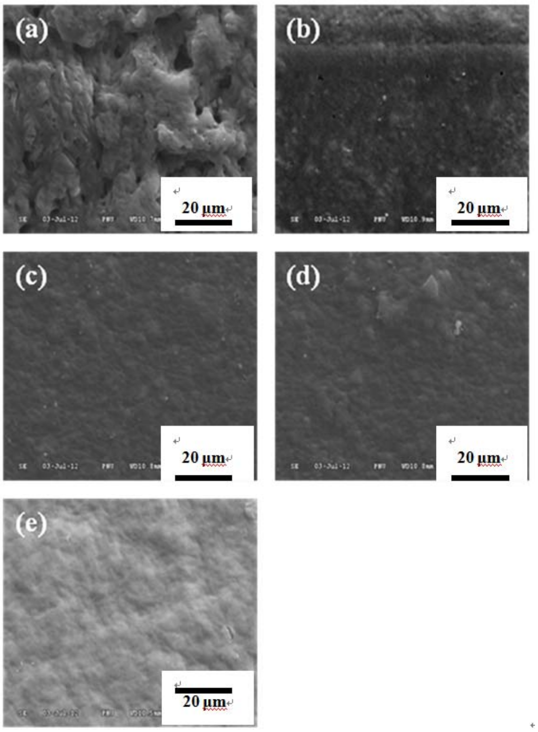


Fig. 5. Morphology of PHBV/GO nanocomposite films with various weight fractions of GO after 30 days of hydrolytic degradation: (a) 0 wt%, (b) 0.7 wt%, (c) 1 wt%, (d) 2 wt%, and (e) 5 wt% of GO.

content of GO, the amount of defects decreases for PHBV /GO nanocomposites. The hydrolytic degradation of nanocomposites decreases with increasing amount of GO.

The weight loss of the nanocomposites as a function of incubation time is shown in Fig. 6. The weight loss is slow in the beginning of the incubation. After 30 days of incubation, PHBV and PHBV/GO nanocomposite samples (0.7 wt%, 1 wt%, 2 wt%, 5 wt%) start losing weight more rapidly. With increasing content of GO, the PHBV/GO samples show lower hydrolytic degradation rates. Therefore, the rates of hydrolytic degradation of PHBV can be controlled using GO.

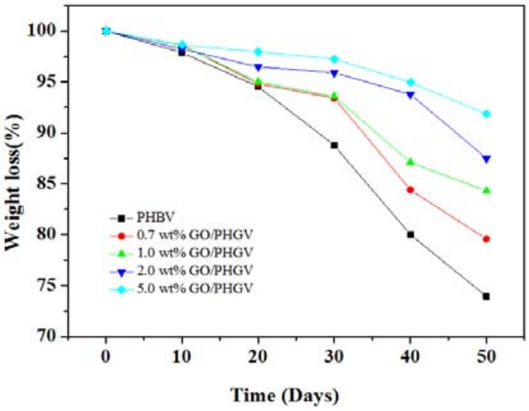


Fig. 6. Weight loss of PHBV/GO nanocomposite films with various weight fractions of GO as a function of hydrolysis time.

4. Conclusions

The addition of 5 wt% GO into PHBV improves the Young's modulus by 38% and decreases thermal expansion coefficient by 29%. The improvement can be mainly attributed to good dispersion of GO and interfacial interactions between PHBV and GO. Furthermore, PHBV/GO nanocomposite films show good oxygen barrier properties. Hydrolytic degradation of PHBV/GO nanocomposite films took place more slowly with increasing GO amounts. Therefore, the rates of hydrolytic degradation of PHBV can be controlled using GO. PHBV/GO nanocomposite films have potential applications in packaging films.

Acknowledgements

The authors thank to the National Research Foundation of Korea through the Ministry of Science, ICT & Future Planning, Korea (Acceleration Research Program (2014R1A2A1110054584); Brain Korea 21 Plus Program (21A2013800002) for financial support.

REFERENCES

Alexandre, M., Dubois, P., 2000, Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials, Mater. Sci. Eng., 28, 1-63.

Ambrosio-Martín, J., Gorrasi, G., Lopez-Rubio, A., Fabra, M. J., Mas, M. C., Lopez-Manchado, M. A., Lagaron, J. M., 2015, On the use of ball milling to develop PHBV – graphene nanocomposites (I) - Morphology, thermal properties, and thermal stability, J. Appl. Polym. Sci.,132, 42101.

Ambrosio-Martín, J., Gorrasi, G., Lopez-Rubio, A., Fabra, M. J., Mas, M. C., Lopez-Manchado, M. A., Lagaron, J. M., 2015, On the use of ball milling to develop poly(3-hydroxybutyrate-co-3-hydroxyvalerate) -graphene nanocomposites (II) - Mechanical, barrier, and electrical properties, J. Appl. Polym. Sci., 132, 42217.

Ataeefard, M., Moradian, S., 2011, Polypropylene/ organoclay nanocomposites: Effects of clay content on properties, Polym-Plast. Technol. Eng., 50, 732-739.

Avella, M., Errico, M. E., 2000, Preparation of PHBV/ starch blends by reactive blending and their characterization, J. Appl. Polym. Sci., 77, 232-236.

Casarin, S. A., Malmonge, S. M., Kobayashi, M., Agnelli, J. A. M., 2011, Study on in vitro degradation of bioabsorbable polymers: Poly(hydroxybutyrate -co-valerate) (PHBV) and poly(caprolactone) (PCL),

J. Biomater. Nanobiotechnol., 2, 207-215.

Cava, D., Gimenez, E., Gavara, R., Lagaron, J. M., 2006, Comparative performance and barrier properties of biodegradable thermoplastics and nanobiocomposites versus PET for food packaging applications, J. Plast. Film Sheet, 22, 265-274.

Cho, H. J., Park, S., Ha, C. S., 2015, Preparation and chacterization of polynorbornene/sepiolite hybrid nanocomposite films, Polym. Int'l., 64, 96-104.

Chun, Y. S., Kim, W. N., 2000, Thermal properties of poly(hydroxybutyrate-co-hydroxyvalerate) and poly (ϵ-caprolactone) blends, Polymer, 41, 2305-2308.

Giannelis, E. P., 1996, Polymer layered silicate nanocomposites, Adv. Mater., 8, 29-35.

Gilje, S., Han, S., Wang, M., Wang, K. L., Kaner, R. B., 2007, A Chemical route to graphene for device applications, Nano Lett., 7, 3394-3398.

Godbole, S., Gote, S., Latkar, M. L., Chakrabarti, T., 2003, Preparation and characterization of biodegradable poly-3-hydroxybutyrate－starch blend films, Bioresource Technol., 86, 33-37.

Gomez-Navarro, C., Burghard, M., Kern, K., 2008, Elastic properties of chemically derived single graphene sheets, Nano Lett., 8, 2045-2049.

Halpin, J. C., Kardos, J. L., 1976, The Halpin-Tsai equations: A Review, Polym. Eng. Sci., 16, 344-352.

Hummers, W. S., Offeman, R. E., 1958, Preparation of graphitic oxide, J. Am. Chem. Soc., 80, 1339-1339.

Imam, S. H., Chen, L., Gordon, S. H., Shogren, R. L., Weisleder, D., Greene, R. V., 1998, Biodegradation of injection molded starch-poly(3-hydroxybutyrate-co-3-hydroxyvalerate) blends in a natural compost environment, J. Environ. Polym. Degr., 6, 91-98.

Kim, G. Y., Choi, M. C., Lee, D., Ha, C. S., 2012, 2D-aligned graphene sheets in transparent polyimide/graphene nanocomposite films based on noncovalent interactions between poly(amic acid) and graphene carboxylic acid, Macromol. Mater. Eng., 297, 303-311.

King, P. P., 1982, An Industrial view, J. Chem. Technol. Biotechnol., 32, 2-8.

LeBaron, P. C., Wang, Z., Pinnavaia, T. J., 1999, Polymer-layered silicate nanocomposites: An Overview, 1999, Appl. Clay Sci., 15, 11-29.

Lee, D., Choi, M. C., Ha, C. S., 2012, Polynorbornene dicarboximide/amine functionalized graphene hybrids for potential oxygen barrier films, J. Polym. Sci. Part A: Polym. Chem., 50, 1611-1621.

Maniar, K. K., 2004, Polymeric nanocomposites: A Review, Polym-Plast. Technol. Eng., 43, 427-443.

Parulekar, Y., Mohanty, A. K., 2007, Extruded biodegradable cast films from polyhydroxyalkanoate and thermoplastic starch blends: Fabrication and characterization, Macromol. Mater. Eng., 292, 1218-1228.

Qiu, Z., Ikehara, T., Nishi, T., 2003, Miscibility and crystallization behaviour of biodegradable blends of two aliphatic polyesters, Poly(3-hydroxybutyrate-*co*-hydroxyvalerate) and poly(butylene succinate) blends, Polymer, 44, 7519-7527.

Ray, S. S., Okamoto, M., 2003, Polymer/layered silicate nanocomposites: A Review from preparation to processing, Prog. Polym. Sci., 28, 1539-1641.

Rouf, M. A., Stoke, J. L., 1962, Isolation and identification of the sudanophilic granules of *Sphaerotilus natans*, J. Bacteriol., 83, 343-347.

Schaefer, D. W., Justice, R. S., 2007, How nano are nanocomposites?, Macromolecules, 40, 8501-8517.

Shafiee, M., Ramazani, S. A. A., Danaei, M., 2010, Investigation of the gas barrier properties of PP/clay nanocomposite films with EVA as a compatibiliser prepared by the melt intercalation method, Polym-Plast. Technol. Eng., 49, 991-995.

Shogren, R., 1997, Water vapor permeability of biodegradable polymers, J. Environ. Polym. Degr., 5, 91-95.

Stankovich, S., Dikin, D. A., Dommett, G. H. B., Kohlhaas, K. M., Zimney, E. J., Stach, E. A., Piner, R. D., Nguyen, S. T., Ruoff, R. S., 2006, Graphene-based composite materials, Nature, 442, 282-286.

Sridhar, V., Lee, I., Chun, H. H., Park, H. H., 2014, c, Express Polym. Lett., 7, 320-328.

Tapaswi, P. K., Choi, M. C., Jeong, K. M., Ando, S., Ha, C. S., 2015, Transparent aromatic polyimides derived from thiophenyl-substituted benzidines with high refractive index and small birefringence, Macromolecules, 48, 3462-3474.

Tzeng, P., Stevens, B., Devlaming, I., Grunlan, J. C., 2015, Polymer－graphene oxide quadlayer thin-film assemblies with improved gas barrier, Langmuir, 51, 5919-5927.

Wang, S., Song, C., Chen, G., Guo, T., Liu, J., Zhang, B., Takeuchi, S., 2005, Characteristics and biodegradation properties of poly(3-hydroxybutyrate -co-3-hydroxyvalerate)/organophilic montmorillonite (PHBV/OMMT) nanocomposite, Polym. Degr. Stab., 87, 69-76.

Wang, B., Zhang, Y., Zhang, J., Gou, Q., Wang, Z., Chen, P., Gu, Q., 2013, Crystallization behavior, thermal and mechanical properties of PHBV/ graphene nanosheet composites, Chinese J. Polym. Sci., 31, 670-678.

You, E. J., Lee, D. B., Ha, C. S., 2015, Preparation and characterization of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/graphene nanocomposites, J. Adhes. Interf., 16, 108-115.