Asian Journal of Chemistry; Vol. 27, No. 3 (2015), 979-983

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17839

Preparation and Characterization of Poly(3-hydroxybutyric acid)/Poly(vinyl acetate) Blend Films

Olla Sharhan[1,*], Abdul Hamid Yahaya[1] and Mohamed Mahmoud Nasef[2]

[1]Chemistry Department, University of Malaya, 50603 Kuala Lumpur, Malaysia
[2]Institute of Hydrogen Economy, University Teknologi Malaysia, 54100 Kuala Lumpur, Malaysia

*Corresponding author: Tel: +60 172087769; E-mail: olla_sh@yahoo.com

Received: 17 April 2014; *Accepted*: 6 June 2014; *Published online*: 19 January 2015; AJC-16708

Modification of poly(3-hydroxybutyric acid) (PHB) films by blending with poly(vinyl acetate) (PVAc) was investigated. The variation effect of poly(vinyl acetate) proportions in PHB/PVAc blend on the chemical structure, thermal stability, melting and phase morphology and crystallization behaviour were studied. The structure was characterized by Fourier transform infrared, thermogravimetric analysis, X-ray Diffraction (XRD) and field emission scanning electron microscopy. The properties of poly(3-hydroxybutyric acid) were found to be improved by blending with poly(vinyl acetate) and the level of improvement is a function of the proportion of poly(vinyl acetate) in the blend. The thermal stability for the blending was more stable than the pure polymers. The TGA results of the prepared polymers showed three-step decomposition assigned to the thermal degradation of poly(3-hydroxybutyric acid) hard and poly(vinyl acetate). For the XRD, the crystallization rate was decreased by blending poly(3-hydroxybutyric acid) with poly(vinyl acetate).

Keywords: Poly(3-hydroxybutyric acid), Poly(vinyl acetate), Blend, FTIR, DSC, TGA, SEM.

INTRODUCTION

Poly(3-hydroxybutyric acid) (PHB) is a thermoplastic polyester which has high crystallinity (more than 65 %), with a melting temperature of 175-180 °C. It has a glass transition temperature between 4-7 °C, like those of polypropylene (PP), but different mechanical properties. However, poly(3-hydroxybutyric acid) has numerous inherent deficiencies to be used as an engineering material and practical polymer materials; these include brittleness due to its thermal instability near its melting point and high crystallinity. Usually poly(3-hydroxybutyric acid) mixture with polymers that has degradability and good mechanical properties can be a solution to get additional environmental friendly biodegradable polymers[1-3].

Poly(3-hydroxybutyric acid) is of the typical natural polyesters produced by some bacteria and microorganisms. It is biodegradable in the environment by either hydrolytic degradation *via* variety of bacteria[2,4-9]. It is been well known that poly(3-hydroxybutyric acid) has similar thermal and mechanical properties to polypropylene (PP). It is not always well suited for certain applications as a commodity plastic because it is stiff and thermally unstable due to the high melting temperature[10].

In general poly(3-hydroxybutyric acid) has some properties, such as its thermal instability and high degree of crystallinity. It has physical properties and chemical structure fairly similar to petroleum synthetic polymers[11]. It has many advantages including biocompatibility and biodegradability. Nevertheless, the practical application of poly(3-hydroxybutyric acid) has been limited by its stiffness and brittleness and the enzymatic degradability of poly(3-hydroxybutyric acid) must be controlled in order to enable utilization[12]. Several used different materials were obtained based on blending poly(3-hydroxybutyric acid) with poly(vinyl acetate) in different proportion. This result in improving the general physical properties of poly(3-hydroxybutyric acid) and reducing the excess brittleness. In addition, poly(vinyl acetate) (PVAc) is usually used as paper finishing agents, binders and adhesives[13]. Poly(3-hydroxybutyric acid) is grafting with poly(vinyl acetate) and the surfaces of these PHB-g-PVAc films were completely covered with graft chains and the enzyme poly(3-hydroxybutyric acid) depolymerize could not attack the poly(3-hydroxybutyric acid) substrate[12].

There is an increasing request for biodegradable polymers as a solution to problems about the biomedical applications and overall environmental applications. Polymers are still produced in large commercial amount because of its production process characterized by less cost unlike poly(3-hydroxybutyric acid) that is still difficult to process and high brittleness[3]. Poly(3-hydroxybutyric acid) has high crystallinity, brittle and stiffness because it has been the matter of general studies as an environmentally friendly polymeric substance[7]. However, there are numerous experiences to blend poly(3-hydroxybutyric acid) with other low molecular weight plasticizers or flexible polymers to turn poly(3-hydroxybutyric acid) into substances with developed properties in impact strength, processing, biodegradability, film formation, biocompatibility and mechanical strength[14-16]. It was reported that, poly(3-hydroxybutyric acid) is grafting with poly(vinyl acetate)[12] and it is miscible with poly(methyl methacrylate) (PMMA), (cyclohexyl methacrylate) (PCHMA)[17], poly(epichlorohydrin)[18], poly(ethylene oxide)[19], dendrimers[2], Poly(vinyl alcohol)[20,21] and poly(vinylidene fluoride)[22]. Poly(vinyl acetate) (PVAc) is a type of thermoplastic which belong to the poly-(vinyl esters) family. Poly(vinyl acetate) has good adhesion to textiles, glass, leather, wood and paper[23]. In recent years, blending polymers are an economic technique to improve new polymeric substances, because the last properties of the blend depend on the properties of its polymeric components, its composition and mainly on the miscibility of the polymers[24]. In addition, blending polymers with low concentration of poly(vinyl acetate) may enhance the physical properties of the polymers.

Poly(3-hydroxybutyric acid), is a well-known biodegradable thermoplastic polyester with a high degree of crystallinity. Therefore, to improve these material properties, various poly(3-hydroxybutyric acid) blend have already been examined. Blending of poly(3-hydroxybutyric acid) seems to decease the melting temperature[4], there by implying an improved process ability at a lower temperature to avoid or limit degradation. The aim of this research was to seek the possibility of improving the thermal, mechanical properties and process ability of poly-(3-hydroxybutyric acid) *via* the addition of poly(vinyl acetate).

EXPERIMENTAL

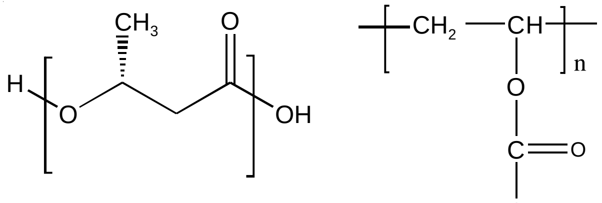
Bacterial poly(3-hydroxybutyric acid) was purchased from Sigma Aldrich (average M.W = 150,000) powder, natural origin. Poly(3-hydroxybutyric acid) was dissolved in chloroform, then poured into a mixed solvent of methanol and *n*-hexane (1:1v/v %). poly(vinyl acetate) was purchased from Sigma Aldrich (average m.w. = 100,000 by GPC), beads and used as receive without further purification.

Procedure: Poly(3-hydroxybutyric acid) was dissolved in chloroform and poured into a mixed solvent of *n*-hexane and methanol (1:1 v/v %). Poly(3-hydroxybutyric acid) and poly(vinyl acetate) were weighted and dissolved in chloroform and followed by moderate stirring and heating at around 55 °C for 48 h. PHB/PVAc blended solutions were prepared by adding the poly(vinyl acetate) gradually drop by drop to the poly(3-hydroxybutyric acid), after that, kept on the homogenizer under magnetic stirrer, at around 55 °C. Then the PHB/PVAc mixtures were stirred at thin speed for 1 h. Details are shown in Table-1.

The range of the added poly(vinyl acetate) to poly(3-hydroxybutyric acid) was with different ratios and stirring for 1h after blending. Blending films of solutions were obtained by casting onto glass dishes followed by drying at 60 °C for 48 h. Similar films from pure polymers were prepared using the same casting processes. Structure details (PHB and PVAc) are shown in Fig. 1.

TABLE-1
PREPARATION OF POLY(3-HYDROXYBUTYRIC ACID) AND POLY(VINYL ACETATE) BLENDS

Solution blends	V_{PHB} (v/v %)	V_{PVAc} (v/v %)
PHB/PVAc (100/0)	100	0
PHB/PVAc (0/100)	0	100
PHB/PVAc (90/10)	90	10
PHB/PVAc (80/20)	80	20
PHB/PVAc (70/30)	70	30



Poly(3-hydroxybutyric acid)

Poly(vinyl acetate)

Fig. 1. Structure details of reaction between poly(3-hydroxybutyric acid) and poly(vinyl acetate)

Fourier transform infrared spectroscopy: The FTIR spectrum of polymer thin film was recorded on a spectrometer [Perkin Elmer, 2000, USA]. The spectra were obtained at room temperature in the range of 4000-400 cm^{-1}.

X-ray diffraction analysis: The XRD analysis is a convenient tool to determine the crystallization and structure of the polymer[25]. XRD measurements of polyester sample was made on a PAN alytical diffractometer system (High Score Plus) using CuK$_{\alpha}$ radiation (40 mA; λ = 0.154 nm; 40 kV) and The XRD patterns of polyesters were recorded at room teamperature in the range of 2θ = 5° to 80° at a scan speed of 98 sec[2,26,27]. The percentage of crystallinity was calculated from diffracted intensity data.

Thermogrvmetric analysis: TGA analysis was done on a Perkin Elmer Pyris Diamond TG/DTA thermal instrument (TGA 4000-USA) in the temperature range 50-700 °C, under N_2 at a flow rate of 10 cm^3 min^{-1} and scan rate of 20 °C min^{-1} to temperature well above the degradation temperature of the polymers.

Field emission scanning electron microscopy: FESEM analysis was used to study the morphology of the blend samples. The FESEM (Quanta FEG 450, EDX-OXFORD) measurement was carried out to study the surface morphology and to study the compatibility of the blended films. The film surface image was observed atvoltage of 10 KV.

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy analysis: Fig. 2 shows the spectrum of pure poly(3-hydroxybutyric acid), poly(vinyl acetate) thin film and their blends show a broad peak at 3434 cm^{-1} which is due to the O-H stretching[28]. The peaks at wave numbers 2900-2800 cm^{-1} in all samples spectrum are the combination of CH_2, CH_3 asymmetric and symmetric stretching modes. The poly(3-hydroxybutyric acid) shows a strong and sharp absorption peak at wave number 1734 cm^{-1} assign to C=O and in pure poly(vinyl acetate) at 1738 cm^{-1}, but in their blends shown broad peak and decrease the value[4,28] (Table-2).

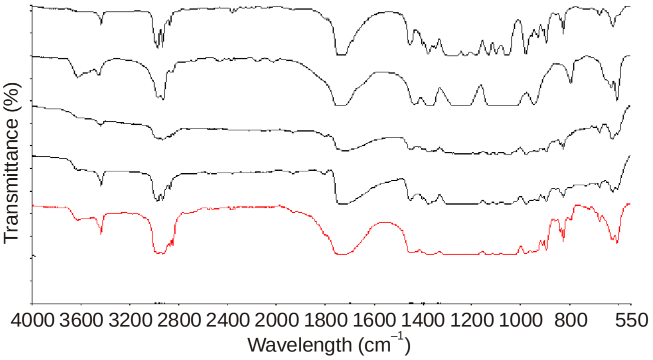


Fig. 2. Typically FTIR spectra of pure poly(3-hydroxybutyric acid), poly(vinyl acetate) and their blends shown the decreasing in C=O when increasing PVAc

X-ray diffraction analysis: Fig. 3 shows typical X-ray diffraction patterns of pure polymers and their blends. The XRD pattern of the pure poly(3-hydroxybutyric acid) showed that it has a semi crystalline nature, which is in good agreement with the results reported earlier[4]. The XRD pattern of pure poly(vinyl acetate) is shown to have low crystallinity or amorphous nature[7,24,29]. The diffraction patterns of physical mixtures showed varied peaks which is similar to that in pure form, indicating that the crystallinity of poly(3-hydroxybutyric acid) and poly(vinyl acetate) was not changed[2,25-27,30].

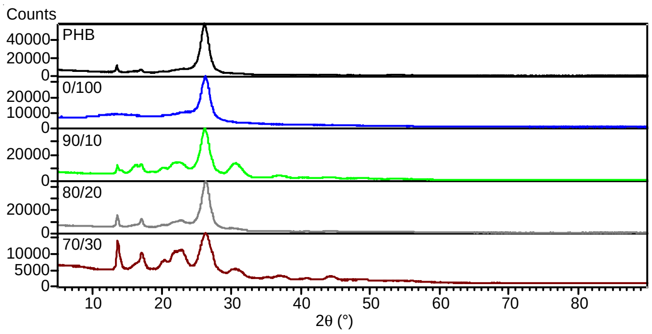


Fig. 3. Typical XRD of pure poly(3-hydroxybutyric acid), poly(vinyl acetate) and their blends

The crystallinities decrease from 73.6 to 50 % as the poly(vinyl acetate) fraction was increased from 10 to 30 mL %[26]. The crystal structures were not affected by the addition of poly(vinyl acetate) to poly(3-hydroxybutyric acid)[7,30]. While by the addition of poly(vinyl acetate), the curves present a better resolution for peaks than that of poly(3-hydroxybutyric acid). Moreover, the intensities of the crystalline peaks of the blending obviously increased, thereby appear small peaks[4].

Thermogravimetric analysis: The TGA results profiles of poly(3-hydroxybutyric acid), poly(vinyl acetate) and their blends shown in Fig. 4. There was no mass loss up 200 °C for all polymers. Fig. 4 showed TGA curves were obtained in the range of temperature between 50 to 700 °C for poly(3-hydroxybutyric acid), poly(vinyl acetate) and their blends. The real weight percentages of blends in composites were determined from these curves[31]. The TGA data analysis also provided thermal degradation temperatures of the composites (Table-3). It was evident that intended compositions had been achieved for the composites. The pure poly(3-hydroxybutyric acid) thin film degrades thermally in one stage with weight loss around 97.57 % at 276 °C[1,4,32, 33]. The pure poly(vinyl acetate), whose thermal degradation takes place as two stages with weight loss around 67.4 % at 315 °C[34]. The first stage is due to acetic acid at 280 °C, known as deacetylation and in the second stage is due to the structural degradation of the polyene backbone occurs, leading to the evolution of benzene, toluene and aliphatic hydrocarbon at 423 °C[13,35]. On the other hand, degradation of blend polymers thin film sample stake place *via* three stages. In the first peak decomposition of poly(3-hydroxybutyric acid), in the second peak corresponds to deacetylation of poly(vinyl acetate) and the third smaller stage corresponds to structural breakage of polyolefinic backbone of poly(3-hydroxybutyric acid) and poly(vinyl acetate).

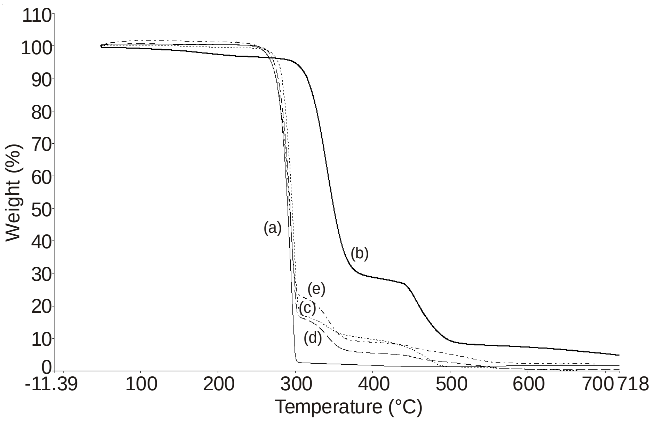


Fig. 4. TGA curves for (a) pure poly(3-hydroxybutyric acid) PHB; (b) poly(vinyl acetate) PVAc, (c) 90/10, (d) 80/20 and (e) 70/30. PHB degrades in single stage; PVAc degrades in two stages and their blends in three stages

Field emission scanning electron microscopy (FESEM): Study on the morphology of the blends was carried out using field emission scanning electron microscopy (FESEM) and it was observed on the surface of pure poly(3-hydroxybutyric acid), pure poly(vinyl acetate) and their blends are shown in Fig. 5. Poly(3-hydroxybutyric acid) was semi-crystalline and poly(vinyl acetate) was amorphous. It presents the micrograph of the pure polymer and their blends and an increase

TABLE-2
FTIR CHARACTERISTIC BANDS OF POLY(3-HYDROXYBUTYRIC ACID)/POLY(VINYL ACETATE) (PHB/PVAc) BLENDED THIN FILMS WITH DIFFERENT RATIOS AND THEIR PURE COMPONENTS

Perpetration	O-H	C-H	C=O	CH_3
PHB/PVAc (100/0)	3436	2976, 2934,2874	1734	1379
PHB/PVAc (0/100)	3457	2960,2926, 2851	1738	1378
PHB/PVAc (90/10)	3436	2975, 2934, 2875	1732	1379
PHB/PVAc (80/20)	3436	2976, 2928, 2876	1715	1372
PHB/PVAc (70/30)	3436	2976, 2934, 2874	1738	1396

TABLE-3
THERMAL PROPERTIES OF POLY(3-HYDROXYBUTYRIC ACID)/POLY(VINYL ACETATE) (PHB/PVAc) BLENDED FILMS WITH DIFFERENT PROPORTION

	$T_{(decommission)}$ (°C)	T_1 (%)	T_2 (%)	T_3 (%)
Pure PHB	276	97.57 % 238-311 °C	-	-
Pure PVAc	315	67.4 % 280-404 °C	10.8 % 423-535 °C	-
PHB/PVAc (90/10)	282	82.4 % 254-315 °C	6.1 % 316-377 °C	7.4 % 434-501 °C
PHB/PVAc (80/20)	279	83.891 % 254-312 °C	10.135 % 313-380 °C	3.137 % 434-480 °C
PHB/PVAc (70/30)	274	78.7 % 239-315 °C	12.9 % 315-383 °C	3.5 % 382-490 °C

in the porosity of the samples can be seen when the proportion of poly(vinyl acetate) is increased[11]. The pure poly(3-hydroxybutyric acid) surface was homogenous and has pores even though it is quite brittle[6,36] while pure poly(vinyl acetate) was strap surface. In the pure poly(vinyl acetate) had strap surface and also their blends shown pores and smooth surface[11]. In the blends, the degree of crystallinity of poly(3-hydroxybutyric acid) remains relatively constant for blends having a large amount of poly(3-hydroxybutyric acid), but as the poly(vinyl acetate) volume in the blend increases, the degree of crystallinity of the blend decrease in proportion to the weight fraction of poly(vinyl acetate)[13].

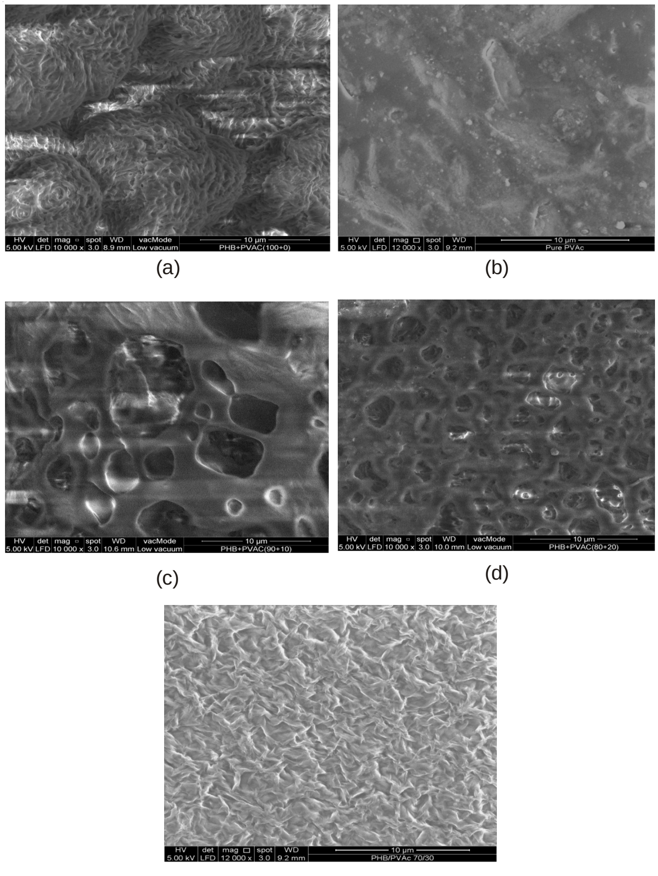

(a) (b) (c) (d) (e)

Fig. 5. Field emission scanning electron micrographs: (a) pure poly(3-hydroxybutyric acid); (b) poly(vinyl acetate), (c) PHB/PVAc 90/10, (d) PHB/PVAc 80/20 and (e) PHB/PVAc 70/30

Conclusion

The mechanical properties and thermal degradation of poly(3-hydroxybutyric acid), poly(vinyl acetate) and their blends made by solution and mechanical blends were investigated. With increasing poly(vinyl acetate) content in the PHB/PVAc blends, the C=O for the blends decreased from 90 to 70 for the pure polymers. Properties of poly(3-hydroxybutyric acid) were modified by blending with different ratios of poly(vinyl acetate). The results of TGA showed that the addition of the poly(vinyl acetate) improved the thermal stability of poly(3-hydroxybutyric acid) component. Thermal stability for the blending were more stable than the pure polymers[4]. For the XRD, the crystallization rate was decreased by blending poly(3-hydroxybutyric acid) with poly(vinyl acetate). In the addition of poly(vinyl acetate) to poly(3-hydroxybutyric acid) does not affect the crystal structure .The decrease in crystallinity is an indication of miscibility.

ACKNOWLEDGEMENTS

This study was financially supported by the research grant (PG075-2012B) and the authors are thanking and grateful to University of Malaya for supporting this research project. The authors thank Dean, Faculty of Science and Head of Dapartment of Chemistry, University of Malaya for providing all the necessary facilities to carry out this work. The first author thanks Prof. Dr. Abdul Hamid Yahaya and Prof. Dr. Mohamed Nasef for helpful discussions.

REFERENCES

1. G.R. Saad and H. Seliger, *Polym. Degrad. Stab*., **83**, 101 (2004).
2. S. Xu, R. Luo, L. Wu, K. Xu and G.-Q. Chen, *J. Appl. Polym. Sci*., **102**, 3782 (2006).
3. L. Wang, W. Zhu, X. Wang, X. Chen, G.-Q. Chen and K. Xu, *J. Appl. Polym. Sci*., **107**, 166 (2008).
4. S.T. Lim, Y.H. Hyun, C.H. Lee and H.J. Choi, *J. Mater. Sci. Lett*., **22**, 299 (2003).
5. G.Q. Chen, Q. Wu, K. Zhao, H.P. Yu and A.C. Chan, *Chin. J. Polym. Sci*., **18**, 389 (2000).
6. P. Greco and E. Martuscelli, *Polymer*, **30**, 1475 (1989).
7. S.A. Madbouly, A.A. Mansour and N.Y. Abdou, *Eur. Polym. J*., **43**, 3933 (2007).
8. E. Chiellini and R. Solaro, Biodegradable Polymers and Plastics 2003, Proceedings of The 7th World Conference on Biodegradable Polymers & Plastics, Springer, USA, pp. 389, June 4-8 (2002).
9. B. Immirzi, M. Malinconico, G. Orsello, S. Portofino and M.G. Volpe, *J. Mater. Sci*., **34**, 1625 (1999).
10. H. Sato, J. Dybal, R. Murakami, I. Noda and Y. Ozaki, *J. Mol. Struct.,* **744-747**, 35 (2005).
11. D.S. Dias, M.S. Crespi, M. Kobelnik and C.A. Ribeiro, *J. Therm. Anal.Calorim*., **97**, 581 (2009).
12. Y. Wada, N. Seko, N. Nagasawa, M. Tamada, K.-i. Kasuya and H. Mitomo, *Radiat. Phys. Chem*., **76**, 1075 (2007).
13. G. Sivalingam, R. Karthik and G. Madras, *Polym. Degrad. Stab*., **84**, 345 (2004).
14. C. Zhijiang and W. Zhihong, *J. Mater. Sci*., **42**, 5886 (2007).
15. W.M. Choi, T.W. Kim, O.O. Park, Y.K. Chang and J.W. Lee, *J. Appl. Polym. Sci*., **90**, 525 (2003).

16. S. Wong, R. Shanks and A. Hodzic, *Macromol. Mater. Eng*., **287**, 647 (2002).
17. N. Lotti, M. Pizzoli, G. Ceccorulli and M. Scandola, *Polym. J*., **34**, 4935 (1993).
18. E.D. Paglia, P.L. Beltrame, M. Canetti, A. Seves, B. Marcandalli and E. Martuscelli, *Polymer*, **34**, 996 (1993).
19. M. Avella and E. Martuscelli, *Polym. J*., **29**, 1731 (1988).
20. Y. Azuma, N. Yoshie, M. Sakurai, Y. Inoue and R. Chujo, *Polym. J*., **33**, 4763 (1992).
21. E.A. El-Hefian, M.M. Nasef and A.H. Yahaya, *E-J. Chem*., **7**, 1212 (2010).
22. A. Kaito, *Polym. J*., **47**, 3548 (2006).
23. D. Feldman and A. Barbalata, Synthetic Polymers: Technology, Properties, Applications, Springer (1996).
24. M.S. Khan, U. Khalil and G. Nasar, *J. Pak. Mater. Soc*., **3**, 22 (2009).
25. R. Baskaran, S. Selvasekarapandian, N. Kuwata, J. Kawamura and T. Hattori, *Solid State Ion*., **177**, 2679 (2006).
26. Y. Doi, S. Kitamura and H. Abe, *Macromol*., **28**, 4822 (1995).
27. G. Wu, B. Su, W. Zhang and C. Wang, *Mater. Chem. Phys*., **107**, 364 (2008).
28. H.S. Mansur, C.M. Sadahira, A.N. Souza and A.A.P. Mansur, *Mater. Sci. Eng. C*, **28**, 539 (2008).
29. E.G. Crispim, I.T.A. Schuquel, A.F. Rubira and E.C. Muniz, *Polym. J*., **41**, 933 (2000).
30. Y. An, L. Dong, P. Xing, Y. Zhuang, Z. Mo and Z. Feng, *Eur. Polym. J*., **33**, 1449 (1997).
31. L.J. Chen and M. Wang, *Biomaterials*, **23**, 2631 (2002).
32. S.N. Lee, M.Y. Lee and W.H. Park, *J. Appl. Polym. Sci*., **83**, 2945 (2002).
33. E.A. El-Hefian, M.M. Nasef and A.H. Yahaya, *E-J. Chem*., **8**, 91 (2011).
34. G. Sivalingam and G. Madras, *J. Appl. Polym. Sci*., **93**, 1378 (2004).
35. S. Zulfiqar and S. Ahmad, *Polym. Degrad. Stab*., **71**, 299 (2001).
36. H.-J. Chiu, H.-L. Chen, T.-L. Lin and J.S. Lin, *Macromol*., **32**, 4969 (1999).