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TENSILE AND THERMAL BEHAVIOURS OF POLY(LACTIC ACID)/ LIQUID NATURAL RUBBER BLEND MATRIX INCORPORATED NICKEL ZINC FERRITE NANOPARTICLES

(Sifat Regangan dan Terma Matriks Adunan Asid Polilaktik/Cecair Getah Asli Diperkuat Nanozarah Nikel Zink Ferit)

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Abstract

Magnetic polymer nanocomposites (MPNCs) based on poly(lactic acid)/liquid natural rubber (PLA/LNR) (90:10) blend and nickel zinc (NiZn) ferrite magnetic nanoparticles were fabricated via melt-blending technique. The effect of NiZn ferrite nanofiller concentration (1 – 5 wt.%) on the tensile and thermal properties of PLA/LNR/NiZn ferrite nanocomposites was investigated. Tensile tests showed that as the tensile strength and modulus increased with the increase of nanofiller concentration until the optimum values of nanofiller concentration was achieved. The thermal behaviour of MPNCs including degradation temperature and its shiftment as well as the remaining residues after complete degradation were determined by thermogravimetric analysis (TGA) measurement. As the NiZn ferrite nanofiller concentration increased, it was noted that the T_{end} of nanocomposites at low amount of nanofillers (1 – 2 wt.%) was higher than neat PLA/LNR and nanocomposites containing high concentration of nanofillers. The current work proves that NiZn ferrite could be served as an excellent reinforcement filer in PLA/LNR matrix. The improved tensile properties and thermal stability of PLA/LNR composites achieved at 2 – 3 wt.% NiZn due to the good dispersion of NiZn ferrite within the PLA/LNR matrix and strong filler-matrix interfacial adhesion, as can be confirmed by the scanning electron micrograph (SEM).

Keywords: biopolymer, polymer blend, nanocomposite, magnetic particles, melt blending

Abstrak

Nanokomposit polimer magnetik (MPNC) berasaskan adunan asid polilaktik/cecair getah asli (PLA/LNR) (90:10) dan nanozarah magnetik nikel zink ferit (NiZn) dihasilkan melalui teknik pengadunan leburan. Kesan kandungan NiZn ferit (1-5 wt.%) terhadap sifat regangan dan terma nanokomposit PLA/LNR/NiZn telah dikaji. Ujian regangan menunjukkan bahawa peningkatan kekuatan dan modulus regangan dengan peningkatan kandungan pengisi nano sehingga nilai optimum tercapai. Tingkah laku terma bagi MPNCs termasuk suhu degradasi (T_{end}) dan anjakannya serta baki sisa selepas degradasi lengkap telah ditentukan melalui analisis termogravimetri (TGA). Apabila kandungan NiZn ferit pengisi nano meningkat, didapati T_{end} bagi nanokomposit berpengisi nano dalam kandungan kecil (1 – 2 wt.%) adalah lebih tinggi daripada PLA/LNR dan nanokomposit terkandung pengisi yang banyak. Hasil kajian ini membuktikan bahawa NiZn ferit boleh bertindak sebagai pengisi pengukuhan yang baik dalam matriks PLA/LNR. Penambahbaikan sifat regangan dan kestabilan terma komposit PLA/LNR tercapai pada 2 – 3 wt.% NiZn disebabkan penyebaran NiZn ferit yang baik dalam matriks PLA/LNR dan lekatan antaramuka pengisi-matriks yang kuat, seperti yang disahkan oleh mikrograf elektron imbasan (SEM).

Kata kunci: biopolimer, polimer adunan, nanokomposit, zarah magnetic, pengadunan leburan, morfologi

Introduction

In recent years, the development research works based on the use of biodegradable materials such as poly(lactic acid) (PLA) which served as biopolymer, have been attracted lots of attention from academic and industrial area. Due to the renewability issue and comparable properties with petroleum based polymers, PLA is gaining its popularity [1]. However, as well-established, high brittleness is the main weakness for PLA to be applied in most of the commercial applications [2]. As for that, toughening of PLA by blending with rubber is an applicable method, as a result of the ductility properties imparted by natural rubber (NR). Another advantage could be, NR is derived from renewable sources. Therefore, blending of PLA and NR such as liquid natural rubber (LNR) which is a low molecular weight version of NR, could be a good choice to enhance the toughness of PLA without affecting its biodegradability [1,2]. Somehow, PLA based blending does not provide any high end performance, for examples, electrical, magnetic, conductivity properties and etc. In which these limit its applications in various high performance fields and industries.

Magnetic polymer nanocomposites (MPNCs) are known as materials consisted of an inorganic magnetic component with at least one dimension in the nanometer scale whether in the form of fibers, particles, or lamellae that embedded in an organic polymer [3]. By combining the polymeric matrix materials that are non-magnetic properties with the magnetic nanoparticles as fillers, a new composite material that possesses magnetic properties can be produced and its applications and usefulness can be further expanded. The combination of organic and inorganic materials in magnetic polymer nanocomposites (MPNCs) has produced new properties that could not be obtained by single organic or inorganic material. The applications for MPNCs can be extended from the fields related to the environment [3, 4] until medical field [5]. For instances, technological fields have recently getting more and more attention in the market, especially, in the microwave, electronics and telecommunication industries such as microsensors, magnetic refrigeration, microelectromechanical system, controlling drug delivery and etc. [3, 6].

As well-known, nickel zinc (NiZn) ferrite is soft magnetic material which possesses versatile properties such as high saturation magnetization, electrical resistivity, mechanical hardness, thermal conductivity and chemical stability as well as low coercivity and dielectric losses [7, 8]. In actual sense, not much researchers have studied the use of NiZn ferrite in PLA/LNR matrix [9]. The selection of PLA and LNR to form blend matrix was made because of their biodegradability and cost effectiveness as well as high strength and modulus. Instead of magnetic properties, the objective of this current work is to investigate the effect of NiZn ferrite as nanoparticles on the tensile, thermal and morphological behaviours of nanocomposites based on poly(lactic acid)/liquid natural rubber (LNR) blend.

Materials and Methods

Raw materials

The chosen thermoplastic resin, a commercial poly(lactic acid) with the trade name of Natureworks Ingeo Biopolymer 3251D, density of 1.24 g/cm^3 and melt flow index of 30 – 40 g/10 min (190 °C/2.16 kg), was obtained from Unic Technology Ltd, China. SMR-L grade natural rubber (NR) which supplied by Malaysian Rubber Board (MRB) was used to synthesize the liquid natural rubber (LNR) via photosensitized chemical oxidation technique. The nanofiller used in this study, nickel zinc (NiZn) ferrite nanoparticles powder with the chemical formula of $Ni_{0.5}Zn_{0.5}Fe_2O_4$, 98.5% purity and 10 – 30 nm particle size was purchased from Nanostructured & Amorphous Materials Inc, USA.

Preparation of nanocomposites

Prior to mixing, PLA was dried in the oven at 100 °C for 24 hours to eliminate trapped moisture in PLA. PLA/LNR blend and PLA/LNR/NiZn ferrite nanocomposites were melt-blended using an internal mixer machine (Haake Rheomix 600P) at 180 °C, 100 rpm and complete mixing time of 15 minutes. Indirect mixing technique (IDT) was applied to prepare nanocomposites, by pre-mixing the NiZn ferrite powder into LNR before being introduced in the mixer. The ratio of PLA and LNR was mixed at 9:1, whereas the NiZn ferrite nanoparticles was varied from 1 to 5 wt.%. PLA was first introduced into the internal mixer for melting about 3 minutes, then the pre-mixture of LNR and NiZn ferrite was added. The whole mixing process was completed for 15 minutes. In order to produce the composite specimens for characterization, compression molding was carried out via hot/cold pressing process. The temperatures of the upper and lower plates were applied at 180 °C, whereas the pressure was set at 6.9 MPa. The preheating of 4 minutes, venting of 4 minutes, full pressing of 5 minutes and cold pressing of 3 minutes were applied.

Characterization

Tensile testing was conducted using Testomeric tensile machine (Model Testomeric M350-10CT) with load cell of 5 kN and at a crosshead speed of 50 mm/min using 1 mm thickness test specimens in accordance with ASTM 412. At least five replicate specimens were tested for each formulation. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using Mettler Toledo TGA/SDTA851^e and DSC 882^e, respectively. For TGA, samples were tested at a heating rate of 10 °C/min from 100 °C to 500 °C. The surface morphology of tensile-fractured specimen was analysed using scanning electron microscope (SEM) (Philips XL 30). Energy dispersive X-ray spectroscopy (EDX) was carried out to determine the elemental composition of the nanocomposites containing different NiZn ferrite concentrations.

Results and Discussion

The effect of NiZn ferrite loadings on the tensile strength and Young's modulus of PLA/LNR nanocomposites is described in Table 1. The tensile results indicates that both tensile strength and Young's modulus exhibited the same trend, that is the increasing concentration of NiZn ferrite increased the tensile properties until an optimum level of nanofillers, and then decreased for higher nanofiller concentrations. Neat PLA/LNR blend possessed 29.93 MPa of tensile strength and 5.29 GPa of Young's modulus. Comparing to that, the highest tensile strength (40.90 MPa) and Young's modulus (7.50 GPa) were achieved at nanocomposite incorporated with 2 wt.% NiZn ferrite, which are increased by 36.65% and 41.78%, respectively. This could be ascribed to the good interfacial interaction between the PLA and NiZn ferrite as a result of the enhanced nanofiller dispersion [2]. When NiZn ferrite nanoparticles added at above 2 wt.%, the tensile strength and Young's modulus decreased gradually from 3 to 5 wt.%. The possible reason is the presence of nanoparticles' agglomerates within the matrix when the content of NiZn ferrite exceeded the optimum level.

Table 1. Tensile strength and Young's modulus of PLA/LNR nanocomposites with various NiZn ferrite loadings

Sample (wt.% NiZn Ferrite)	**Tensile Strength (MPa)**	**Young's Modulus (GPa)**
PLA/LNR		
0	29.93 ± 0.81	5.29 ± 0.04
1	36.70 ± 2.51	7.34 ± 0.34
2	40.90 ± 1.61	7.50 ± 0.17
3	38.01± 1.50	7.14 ± 0.45
4	36.96 ± 1.65	6.90 ± 0.04
5	35.45 ± 2.13	6.78 ± 0.04

Thermogravimetric analysis (TGA) has been carried out to study the mass changes the increase temperature. The mass loss of sample was due to the vaporization process occurred when the temperature increased until a certain high temperature. Figure 1 presents TGA curves of PLA/LNR nanocomposites with various NiZn ferrite loading. Table 2 summarizes the data obtained from TGA testing for all investigated formulations, including temperature of weight loss at 3% (T_3) and 50% (T_{50}), final degradation temperature (T_{end}) as well as residue left after 400 °C. The results of weight loss at 3% (T_3) are important to understand the thermal behaviour at initial stage and to determine the thermal stability of nanocomposites. Based on Figure 1, neat PLA/LNR blend and PLA/LNR/NiZn ferrite nanocomposites experienced a dramatic weight loss at around 300 – 350 °C. This represents the degradation of PLA/LNR blend components, as reported by Bijarimi et al. [2]. It was found that PLA/LNR nanocomposites incorporated with 1 and 2 wt.% NiZn ferrite underwent the degradation process at higher temperature.

As compared to neat PLA/LNR blend (T_3 = 283.98 °C, T_{50} = 324.75 °C and T_{end} = 396.69 °C), nanocomposite with 1 wt% NiZn ferrite exhibited T_3 = 285.29 °C, T_{50} = 325.44 °C and T_{end} = 412.78 °C while nanocomposite with 2 wt% NiZn ferrite demonstrated T_3 = 285.35 °C, T_{50} = 326.79 °C and T_{end} = 401.91 °C. These phenomenons suggest the improved thermal stability by adding nanofiller in small amount. Similar results were observed for thermoplastic natural rubber (TPNR)/NiZn ferrite nanocomposites [8]. Further increasing the concentration of NiZn ferrite in the PLA/LNR blend matrix, the weight loss curves seemed to be similar (3 and 4 wt.%) and shifted to the left (5 wt.%), as depicted in Figure 1 and Table 2. This might be due to the agglomeration of nanofillers (as shown by 4 wt.% NiZn ferrite in Figure 2(c)) which negatively affects the dispersion and distribution of NiZn ferrite within the PLA/LNR matrix. As the agglomerated NiZn ferrite poorly distributed within the PLA/LNR matrix, the heat transfer from matrix to filler is restricted or delayed in the inhomogenous parts of the composites, and thus, induces the reduced thermal stability of nanocomposites. As the temperature reached to about 400 °C, the change in weight loss as a function of temperature can be considered negligible as a result of the complete degradation of PLA/LNR matrix into carbonaceous products. Therefore, the obtained weight percentages of residues could imply the remaining non-decomposed magnetic nanofillers [8]. As expected, the residues increased with the concentration of NiZn ferrite added from 1 to 5 wt.%.

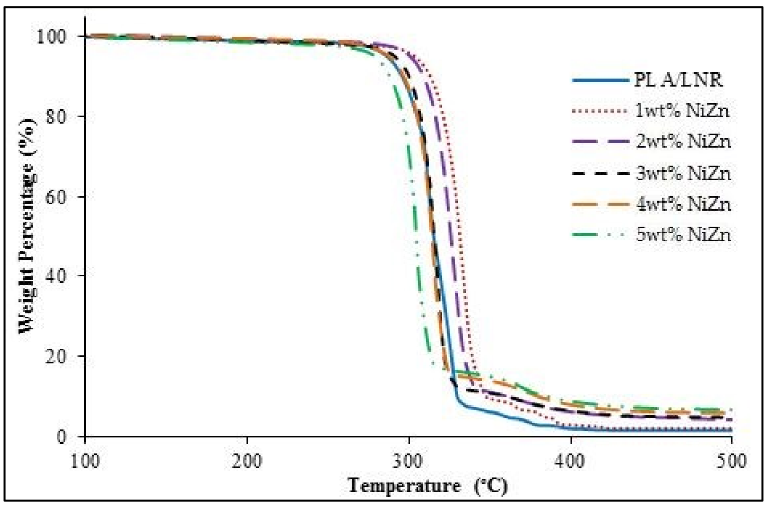

Figure 1. TGA curves of PLA/LNR nanocomposites with various NiZn ferrite loadings

Table 2. TGA data of PLA/LNR nanocomposites with various NiZn ferrite loadings

Sample (wt.% NiZn ferrite)	**T_3 (°C)**	**T_{50} (°C)**	**T_{end} (°C)**	**Residue (%)**
PLA/LNR				
0	283.98	324.75	396.69	1.46
1	285.29	325.44	412.78	1.96
2	285.35	326.79	401.91	3.35
3	270.33	313.06	396.57	4.19
4	250.41	312.89	386.53	5.27
5	235.15	302.90	381.88	5.73

Figure 2 illustrates the SEM micrograph of PLA/LNR with (a) 0 wt.%, (b) 2 wt.% and (c) 4 wt.% NiZn ferrite nanoparticles. In Figure 2(a), the neat PLA/LNR blend (without NiZn ferrite nanoparticles) showed a one-phase

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surface morphology with the existence of holes that indicates rubber particles in the PLA matrix. For Figure 2 (b), the presence of holes seemed getting lesser as filled by homogenous dispersion of NiZn ferrite nanoparticles. At higher concentration of NiZn ferrite, for instance at 4 wt.% (Figure 2 (c)), there were many agglomerations of nanoparticles within the matrix, as shown in white circle, and the holes were visible. This observation indicates the poor dispersion of NiZn ferrite nanofillers when the nanofiller concentration exceeds the optimum level, which resulting in the decrease of mechanical and thermal properties. As described in Table 3, the presence of NiZn ferrite in the PLA/LNR matrix was proven by the existence of Ni, Zn and Fe elements in the nanocomposites. It was interesting to observe that the percentage changes in these elements seemed to be inconstant, in which the increase for 3 – 4 wt.% NiZn ferrite was getting larger as compared to low amount (1 to 2 wt.%) and a sudden decrease for 5 wt.% NiZn ferrite. This might be due to (1) the agglomeration of NiZn ferrite within the polymeric matrix, and (2) the EDX analysis had been done in a spot area of morphology.

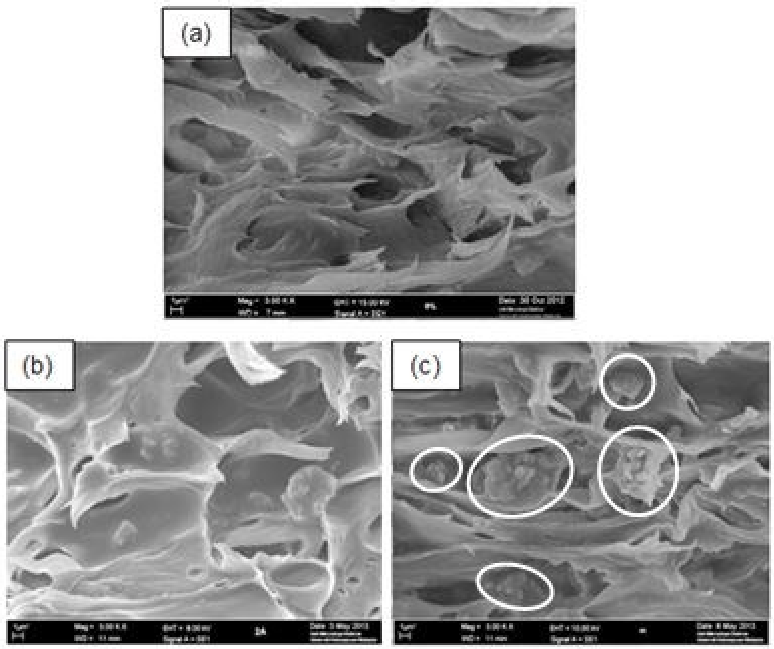

Figure 2**.** SEM micrograph of PLA/LNR with (a) 0 wt.%, (b) 2 wt.% and (c) 4 wt.% NiZn ferrite

Table 3. Weight and atomic percentage of elements presented in nanocomposites with different concentration of NiZn (obtained from EDX)

NiZn Ferrite (wt.%)	**Weight Percentage of Element (%)**				
	C	**O**	**Ni**	**Zn**	**Fe**
1	54.14	44.98	0.24	0.04	0.60
2	53.11	44.40	0.94	0.43	1.12
3	50.15	41.56	1.61	0.93	5.75
4	47.20	35.28	4.11	1.26	12.15
5	47.05	43.14	2.05	0.78	6.17

Conclusion

Nanocomposites PLA/LNR embedded with NiZn ferrite at different concentrations were prepared using internal mixer. In overall, the incorporation of NiZn ferrite nanoparticles resulted in positive effect to the mechanical and thermal properties of nanocomposites based on PLA/LNR blend. As the NiZn ferrite nanofiller increased from 0 to 2 wt.%, the tensile strength and modulus of nanocomposites increased up to 36 – 42%. By adding small amount of NiZn ferrite into biodegradable matrix, the thermal stability of nanocomposites enhanced significantly. Once higher NiZn ferrite was introduced, > 2 wt.%, tensile properties and thermal behavior reduced due to the agglomeration of NiZn ferrite, as shown in SEM micrograph. The residues after complete degradation increased accordingly with the filler concentration.

Acknowledgement

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