Int. J. Bio-Inorg. Hybr. Nanomater., Vol. 3, No. 3 (2014), 169-173
ISSN Print: 2251-8533
ISSN Online: 2322-4142

International Journal of Bio-Inorganic Hybrid Nanomaterials

Preparation and Rheological Property Evaluation of LDPE/ Zinc Oxide Nanocomposite Films for Food Packaging Application

Mehri Mohammadizadeh[1*], Aryou Emamifar[2]

[1] *Instructor, Department of Food Science and Technology, Kurdistan Science and Research Branch, Islamic Azad University, Sanandaj, Iran*

[2] *M.Sc., Department of Food Science and Technology, University of Kurdistan, Iran*

Received: 26 May 2014; Accepted: 2 August 2014

ABSTRACT

Nowadays, nanoscale innovations in the forms of pathogen detection, active packaging, antimicrobial packaging and barrier formation are poised to elevate food packaging to new heights. Antimicrobial nanocomposite LDPE films containing ZnO nanoparticles at different concentrations (e.g. 1%, 3%, 5% and 3% nano-ZnO pulse 10% polyethylene grafted maleic anhydride (PE-g-MA), w/w pure LDPE), were prepared by melt-mixing process and followed by compression molding using hot press machine. Dispersion quality of antimicrobial nanoparticle distribution within the polymer matrix has been assessed by Transmission Electron Microscopy analysis (TEM). The mechanical properties of the films prepared were characterized by using stress-strain analysis. Rheological properties of nanocomposites were determined using rotational rheometers. Rheological properties demonstrate that the rheological moduli of the nanocomposite increases with increasing the nanofiller concentration so that the high frequency region is more benefited by this effect.

Keyword: Zinc oxide; Antimicrobial activities; LDPE; Rheology; Mechanical properties.

1. INTRODUCTION

Today, among fresh fruits and vegetables, strawberries are especially interesting because of their fragility and mold sensitivity that causes high depreciation in sales at retailing point [1]. The use of active antimicrobial compounds incorporated in packaging material is getting more attention as a microbial control in food packaging system. It ensures microbial food safety for consumer, and can be useful for the extension of shelf life of the products [2]. In recent years much attention has turned to the field of nanotechnology in the quest to improve antimicrobial packaging [3]. Nano food packaging with antimicrobial properties represents a new generation of active packaging based on metal nanocomposites. Inorganic materials such as metals and metal oxides have been the focus of nanotechnology research [4]. In nanocomposite polymers in

(*) Corresponding Author - e-mail: mmohammadzadeh7@yahoo.com

comparison with conventional composites there is a better interaction between polymer matrix and filler. The uniform distribution of nanoparticles in the polymer matrix, will lead to an increase in the contact surface of the matrix and the particles and this follows mechanical, thermal and preventive improvement [5]. Zinc oxide is an inorganic compound which is greatly used in everyday applications and as generally recognized as Safe (GRAS) by the Food and Drug Administration (21CFR182.8991) [6]. However, given their reduced cost, recent research efforts have focused on the use of ZnO nanoparticles [7] has been recognized and antimicrobial activity against food-borne pathogens has been previously demonstrated [8]. The purpose of this study was to investigate the capabilities of ZnO nanoparticles filled LDPE nanocomposite packaging as a new approach to preservation and prolonging shelf life of the fresh strawberries.

2. EXPERIMENTAL

Materials and methods

2.1. Preparation of antimicrobial nanocomposite films

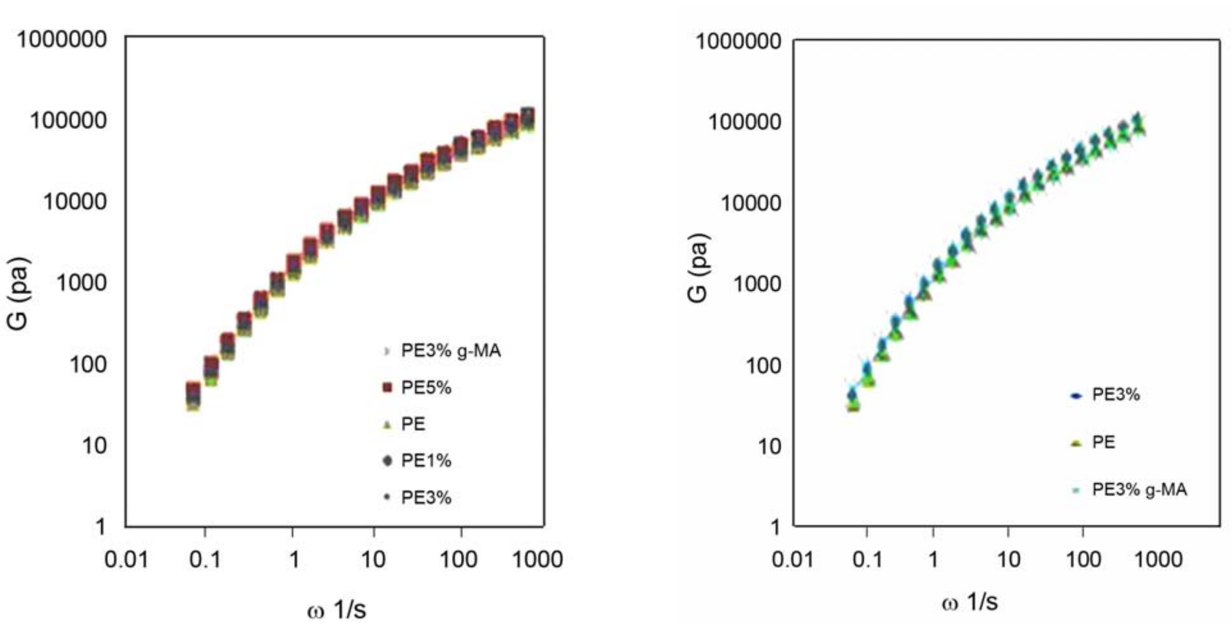
Low density polyethylene granules (LF0200, MFI 2 g/10 min , density 0.92 g/mL, softening point 94°C) and antimicrobial compounds include zinc oxide powder particles with an average diameter of 10-30 nm sections 20-60 m^2/g are prepared from Iranian Pishgaman Nanomaterial Company a product by US NANO. Also, Synox antioxidants powder and polyethylene graft malic anhydride containing 1% malic anhydride as compatible factor have been used. Preparing master batch granules made from low density polyethylene style and containing of antimicrobial have been mentioned and antioxidant. In addition the polyethylene graft maleic only 3% nano-ZnO nanocomposite through direct melt mixing and using Brabender (GMBH 8 CO.KG). Nanocomposites with different percentages of antimicrobial compounds (1, 3, 3 g-ma, 5) were prepared. In the case of pure polyethylene it melts at 170°C for 8 minutes and then slowly antioxidants are added to melt but in nanocomposite samples after adding antioxidant within 1 minute to 30 seconds we add Nano zinc oxide. Then, the materials are being mixed in Berbeder for about 7 minutes at 60 rpm. After this process, hot press (Polystat 200T) with an attached water cooling system has been used to fabricate the final nanocomposite film spacements (0.09 mm thick) with the desired nanomaterial concentrations (1, 3 and 5% for nano-ZnO, 3% nano-ZnO pulse 10% polyethylene-grafted maleic anhydride as a compatilizer and pure LDPE as a control). The compression molder was heated to 180°C for 30 min prior to use. The material was first pressed at low pressure for 4 min followed by a high pressure cycle at 150 psi for 6 min, and the samples were then cooled under pressure (70 psi) for 5-7 min. Film thickness was measured using a micrometer (Mitutoyo, Japan) and reported as the average of five readings taken at five different points on the film sample.

2.2. Melt rheology

Rheometer RMS (Model MCR 301) of Anton Paar Company made of Austria. Using 25 mm diameter parallel plates at 180°C were used. Testing sample disks with a thickness of 0.7 mm and a diameter of 2.5 mm were prepared by compression molding of the extruded pellets at 180°C for 2 min. $\gamma(t) = \gamma_0 \sin(\omega t)$ where γ_0 is strain amplitude, ω is oscillatory frequency and t is time, was imposed on the samples Rotation mode measurements were conducted within a shear rate range of 0.01-1000 s^{-1} [9]. To ensure the reliability of rheological data all measurements were conducted under nitrogen atmosphere to minimize oxidative degradation of the polymer. It is important to point out that range should be selected very low to avoid the failure of structure.

2.3. Mechanical properties

Mechanical properties (Young's modulus and Elongation at break) of the LDPE (control) and LDPE nanocomposite films were investigated using ASTM D882 method, with an universal material testing machine (Zwik Roell Zolo Testing Instruments Inc., China) at 25°C and 40% relative humidity (RH). Five identical specimens were tested for each sample. Specimens for the mechanical property measurements were in shape of strip with about 50 mm in length, 10 mm in width and thickness about 0.05 mm. The speed of the moving clamp was 500 mm min^{-1}. Dispersion quality of

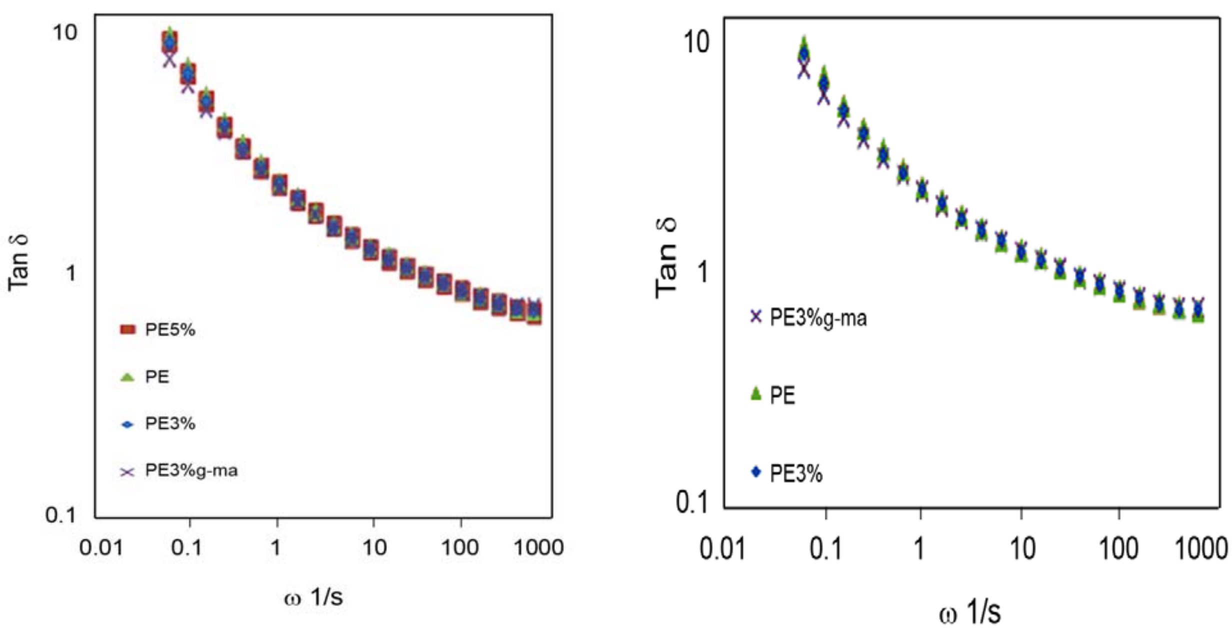


(a) (b)

Figure 1: *Dynamic modulus, (a) of PE/ nano-ZnO composites prepared with different concentration of nanoparticles and (b) PE With composites concentration PE/ 3% ZnO and PE/ nano-ZnO concentration 3% ZnO and Maleic anhydride grafted polyethylene prepared.*

nanomaterials into the polymer matrix film was monitored using the Transmission Electron Microscope (Zeiss EM10C 80 KV, The Germany).

This research was administered in a factorial experiment based on a completely randomized design with three replications.



(a) (b)

Figure 2: *Tan δ of PE/ nano-ZnO composites prepared with different concentration of nanoparticles and (b) PE With composites concentration PE/ 3% ZnO and PE/ nano-ZnO concentration 3% ZnO graft maleic prepared.*

2.4. Transmission electron microscopy analysis

Dispersion quality of nanomaterials into the polymer matrix film was monitored using the Transmission Electron Microscope (Zeiss EM10C 80 KV, The Germany).

2.5. Statistical method

Analysis of variance was carried out using the SAS statistical software release 6.12 (SAS Institute, Cray, NC) based on completely randomized designs. Significant differences among the data were represented as $p < 0.05$.

3. RESULTS AND DISCUSSION

3.1. Melt dynamic rheology

Rheometry is a powerful tool for inspecting the internal microstructure of polymer nanocomposites containing nanoparticles. The rheological moduli against frequency of PE/ ZnO nanocomposites and pure PE are presented in Figures 1 and 2. As can be directly seen, the moduli of nanocomposites increased with increase in nanofiller concentration; however this increase was greater in the high frequency region. Compare these results with findings of other researchers.

3.2. Effect of ZnO nanoparticles on mechanical property

For comparison, the mechanical property of pure LDPE films and ZnO-doped LDPE films prepared using LDPE coatings were measured. Figure 3 shows the tensile stress–strain curves of the LDPE films and the mechanical parameters are listed in Table 1. It can be seen that the Young's modulus and tensile strength increase first and then decrease with the increase of ZnO

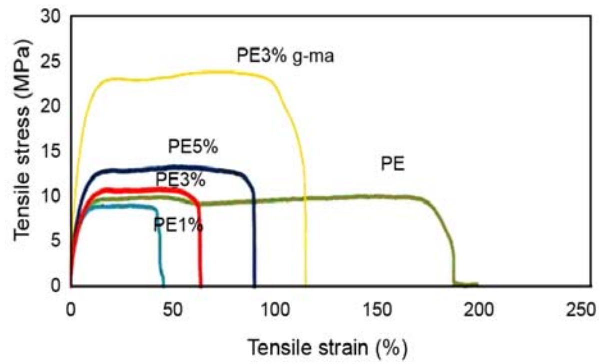


Figure 3: *Tensile stress–strain curves of different ZnO LDPE films.*

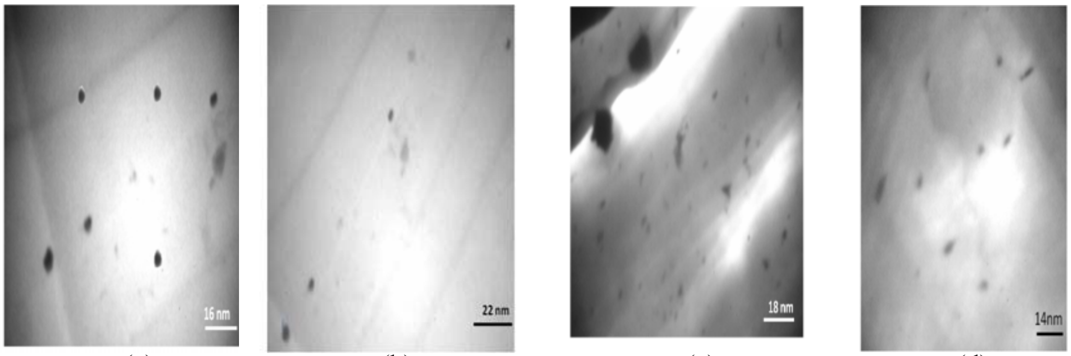
content and the optimal ZnO content for the Young's modulus and tensile strength is obtained at 3.0 PE g-ma wt%. However, the elongation at rupture goes inversely relating to the Young's modulus and tensile strength. Repeated tests show that the filled ZnO nanoparticles can enhance the strength but not the flexibility of the composite films. Compare these results with findings of other researchers. The elevation of Young's modulus and tensile strength of the composite films may be due to the limit of moving scale of chain segments of the LDPE matrix with the addition of ZnO. Moreover, when ZnO nanoparticles are filled into the interstice of LDPE chains, an interactive force against the LDPE chains may be generated. Therefore, when an external force is applied onto the two ends of the dumb-bell-shaped LDPE film, the film goes to rupture easily due to the strong interaction force generated between ZnO nanoparticles and LDPE chains.

3.3. Transmission electron microscope

Figures of polyethylene films containing ZnO nanoparticles are shown in Figure 4 (a, b, c, and d). These Figures show that the ZnO nanoparticles were spherical shape and a diameter of Nanoparticles is be-

Table 1: *Mechanical property of the LDPE films filled with different ZnO content.*

ZnO (%)	Young's modulus	Tensile strength	Elongation ratio
0	260.09	4.45	100.58
1	332.23	3.91	19.88
3	233.29	5.12	40.26
3 g-ma	626.76	9.57	63.69
5	371.62	5.06	40.11



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

Figure 4: *TEM micrograph of antimicrobial nanocomposites LDPE film a: LDPE 1% ZnO, b: LDPE 3% ZnO, c: LDPE 3% ZnO and PE g –MA, d: LDPE 5% ZnO.*

tween 10-30 nm. They demonstrate a relative uniform distribution in nanocomposite films (except for Figure 4). Relative uniform distribution and lack of agglomeration of nanoparticles in the polymer matrix increased strength has a direct relation with an increase of antimicrobial polymer levels due to an increase of surface contact with micro-organisms. According to Figure 4 (a, b, c and d), Zinc nanoparticels with a diameter approximately 20-30 nm are distrusted in Polymer matrix. With an increase in Zinc nanoparticels' density up to 5%, agglomeration will increase, too (Figure 4d). Compare these results with findings of other researcher.

4. CONCLUSIONS

In this study, the rheological and mechanical behavior of low density polyethylene filled with different amounts of ZnO nanoparticles was analyzed and observed respectively in which by increasing the amount of nano-zinc oxide, Young's modulus is increased, but it decreased the elongation at break. Increasing the amount of ZnO nanoparticles, up to 5% leads to agglomeration of nanoparticles and reduction in the level of nanofillers. As a result, it can also reduce the interactions between the nanoparticles and the matrix.

ACKNOWLEDGEMENT

We gratefully acknowledge everyone who helps us in this research.

REFERENCES

1. Cagnon T., Mery A., Chalier P., Guillaume C. and Gontard N., *Innov. Food Sci. Emerg. Technol.*, **20** (2013), 288.
2. Cho I.J., Lee H.S., Lim S.J., Koh J.Y., Kwak S.H. and Hwang G.I., *Food Sci. Biotechnol*., **20** (2011), 525.
3. Cushen M., Kerry J., Morris M., Cruz-Romero M. and Cummins E., *Trends in Food Sci. Tech.*, **24** (2012), 30.
4. Panea B., Ripoll G., Gonzalez J., Fernandez-Cuello A., Albertl P., *J. Food Eng.*, **123** (2013), 104.
5. Choudalakis G., Gotsis A., *A review, Eur. Polym. J.*, **45** (4) (2009), 967.
6. Food and Drug Administration's (FDA's), 2003. Electronic Code of Federal Regulations. Title 21. Part 182- Substances generally recognized as safe. Available at: http://ecfr.gpoaccess.gov/cgi/t/text/text-idx.
7. Tankhiwale R. Bajpai S.K., *Colloids Surf. B: Biointerfaces*, **90** (2012), 16.
8. Espitia P., Soares, N.D.F., Coimbra J.S.D.R., Andrade N.J., Cruz, R.S. and Medeiros E.A.A., *Food and Bioprocess Tech.*, **5** (2012), 1447.
9. Mohagheghian M., Ebadi-Dehaghani H., Ashouri D., Mousavian S., *Compos. Part B. Eng.*, **42** (2011), 2038.