Preparation of UV-protective kefiran/nano-ZnO nanocomposites: Physical and mechanical properties

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A B S T R A C T
In this study, we investigated the effect of ZnO nanoparticles (ZN) as a UV-protective agent of kefiran biopolymers. Our results showed that with increasing ZN content, the tensile strength, elongation at break, and tensile energy to break the kefiran film and nanocomposites also increased. Kefiran nanocomposites with a ZN content higher than 2% produced a UV-protective film with good visual properties, low sensibility to water, and low water-vapor permeability. The thermal properties of all specimens, analyzed by DSC, showed that the ZN content had a negative effect on Tg and a positive effect on nanocomposites' melting point. TEM, SEM micrography and XRD spectrum analysis confirmed the hypothesis that ZNs act like a ball bearing, making movement of kefiran chains easier and increasing elongation at break, while simultaneously decreasing the Tg of kefiran nanocomposites.

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1. Introduction

Polymers from renewable resources have attracted ever-increasing attention over the past two decades, predominantly for three reasons: environmental concerns, the realization that petroleum resources are finite [1], and the cost of petroleum-based polymers. In recent years, increasing oil prices have added to these reasons; hence, there is growing attention to biodegradable polymers as gas and moisture barriers to increase the shelf life of foods. Some interesting film-forming ingredients are carbohydrate polymers such as starch [2] and kefiran [3].

The fermentation of kefir from dairy products produces kefiran, a water-soluble microbial polysaccharide consisting of approximately equal proportions of galactose and glucose residues [4]. Kefiran has functional properties such as antimutagenic activity and antimicrobial activity [5] and has recently attracted much interest as a high-performance biodegradable polymer with good mechanical, physical, and visual properties compared to other biopolymers [3,6,7]. After introducing kefiran as filmogenic agent, further studies have investigated modifications to this biopolymer, such as adding plasticizers [8,9] or determining its composition with other polysaccharides [7].

Recently, nanoparticles with large specific surface areas have attracted much attention in polymer science as a reinforcing agent [10]. These particles lead to a very large matrix/filler interfacial area, which changes the molecular mobility, relaxation behavior, and consequently thermal and mechanical properties of the material [10]. Hence, nanoparticles have been used to modify the weak point of carbohydrate-based polymers [2,11–13]. The modification of kefiran by nanomaterials has not yet been reported in the literature.

Zinc oxide nanoparticles (ZNs) have been used for particular applications based on their semiconducting, piezoelectric, and pyroelectric properties [14], antimicrobial activity [15], reinforcing properties, and UV-protective activity [11–13,16].

Oxidation alters the flavor and decreases the nutritional quality of foods and produces toxic compounds, all of which can make foods less acceptable or unacceptable to consumers. Singlet oxygen, produced by UV irradiation from sun light, is the fastest cause of lipid oxidation, resulting in drastically increased rates of oxidation even at very low temperatures, which in turn lowers the quality of foods during processing and storage [17]. Hence, the use of
UV-protective food-packaging material can decrease the consumption of synthetic antioxidants. The main purpose of this work is the production of a UV-protective kefirian bionanocomposite using ZN and the evaluation of its physical and mechanical properties.

2. Materials and methods

2.1. Starter culture

Kefir grains, used as a starter culture in this study, were obtained from a household in Tehran, Iran. The grains were kept in skimmed milk at 25 °C for short periods and the medium was exchanged daily for new culture to maintain the grains’ viability.

2.2. Kefiran and ZNs

Kefir grains were dissolved in boiling water (1:10) for 30 min. After centrifuging at 10,000 x g for 30 min, nearly all undissolved portions of grain were decanted. Then, polysaccharides were precipitated by mixing with chilled ethanol (1:1) at −18 °C overnight. This purification procedure was followed by centrifuging at 10,000 x g for 30 min at 4 °C and washing three times with water to remove water-soluble impurities [7]. The resulting white precipitated polysaccharide is hereafter called kefirian. The total polysaccharide content of kefirian was 92% according to the phenol–sulfuric method [18]. ZNs prepared from Tecnán (Tecnología Navarra de Nanoproductos S.L., Spain) were used as received. According to the producer’s catalogue, the average size and specific surface area of ZNs were 20–30 nm and 35–50 m²/g, respectively (Fig. 1e).

2.3. Film preparation

An aqueous solution of 2 wt% kefirian was prepared and 40 wt% (dry base) glycerol was added to it as a plasticizer. ZN was dispersed in distilled water by sonication for 30 min at room temperature. Different concentrations of ZN dispersion (1, 2, and 3 wt% (dry base)) were added to the aqueous solution of kefirian and mixed for 10 min. After degassing, the film-forming solutions were cast by pouring the mixture onto Teflon plates, which were then dried at 25 °C in an oven at room relative humidity. The dried films were peeled off the casting surface. All the film specimens were conditioned inside desiccator containing a saturated calcium nitrite (Merk Co., Germany) solution to ensure a relative humidity of 55% at 25 ± 1 °C for 48 h.

2.4. Microstructure

Microstructural analysis of the cross-sections and surface area of the dried films were conducted by SEM (Cam Scan MV2300, Canada). The film specimens were sputtered with gold using a KVKY-SBC-12 sputter coater (KVKY, China). All cross-sections and surface-area specimens were examined using an accelerating voltage of 19.0 kV.

2.5. Measurements

2.5.1. Thickness

The thickness of specimens was measured by a hand-held micrometer with an accuracy of 0.01 mm at 13 random positions for each film.

2.5.2. Moisture content

The moisture content of the specimens was determined (in three replicates) by measuring the weight loss of films before and after drying in a laboratory oven (Shimaz Co., Iran) at 105 ± 1 °C until constant weight.

2.5.3. Moisture absorption

Moisture absorption (MA) was measured according to the method of Almasi et al. [2]. In brief, the dried sheets of 20 × 20 mm² were first conditioned at 0% RH (prepared by dried calcium sulfate) for 24 h. After weighing, they were conditioned in a desiccator containing a saturated calcium-nitrite solution at 25 °C to ensure a relative humidity of 55%. The specimen was weighed at desired intervals until an equilibrium state was reached. The moisture absorption of the specimen was calculated with Eq. (1):

\[
MA = \frac{w_e - w_0}{w_0} \times 100
\]

where \(w_e\) and \(w_0\) are the weights of the specimen after equilibration at 55% RH and the initial weight of the specimen, respectively. All measurements were performed in three replicates.

2.5.4. Solubility

Solubility in water (SW) is defined as the ratio of the water-soluble dry matter of film that is dissolved after immersion in distilled water [3]. A 20 × 20 mm² specimen was cut from each film, dried at 105 ± 1 °C to constant weight in a laboratory oven (Shimaz, Iran), and weighed to determine the initial dry weight (\(m_1\)). The solubility in water of the specimen was measured from immersion assays in 50 ml of distilled water with periodic stirring for 6 h at 25 °C. After that period, the remaining film pieces were taken out and dried at 105 ± 1 °C until constant weight (\(m_2\)). The SW of the specimens was calculated using Eq. (2):

\[
SW = \frac{m_1 - m_2}{m_1} \times 100
\]

2.5.5. Color

Film color was determined using a colorimeter (Labscan XE, Hunterlab, USA). Film specimens were placed on a white standard plate and the lightness (L) and chromaticity parameters a (red-green) and b (yellow-blue) were measured. All colors can be described by L values ranging from 0 (black) to 100 (white); negative values of a (greenness) to positive values (redness); and negative values of b (blueness) to positive values (yellowness). All measurements were performed in five replicates. The total color difference (\(\Delta E\)) and whiteness index (WI) were calculated using Eqs. (3) and (4) [3]:

\[
\Delta E = \sqrt{(L^* - L)^2 + (a^* - a)^2 + (b^* - b)^2}
\]

\[
WI = 100 - \sqrt{(100 - L)^2 + a^2 + b^2}
\]

where \(L^*, a^*, b^*\) are the color-parameter values of a standard \((L^* = 93.7, a^* = -1.13, \text{ and } b^* = 1.24)\) and \(L, a, \text{ and } b\) are the color-parameter values of the specimen.

2.5.6. Water-vapor permeability

The water-vapor permeability (WVP) of films was measured gravimetrically according to ASTM E96 standard [19] and corrected for the stagnant air gap inside the test cups [20]. Special glass vials with a diameter of 12.62 mm and a volume of 10 ml were used as test cups. The area of the vial mouth was 1.25 × 10⁻⁴ m², and the depth was 43 mm. The vials contained calcium-chloride desiccant (0% RH, assay cup) or nothing (control cup). Each vial was covered with a film specimen, which was sealed to the vial mouth using paraffin. Each vial was placed in a desiccator maintained at 75% RH with a saturated solution of sodium chloride (Dr Mojalali Co., Iran). The difference in RH corresponded to a driving force of 1753.55 Pa, expressed as water-vapor partial pressure. After the films were mounted, the weight gain of the whole assembly was periodically
recorded (with an accuracy of 0.0001 g) every 1 h during the first 10 h and finally after 25 h. The slope (S) of the weight-versus-time plot \( (R^2 \geq 0.986) \) was divided by the effective film area \( (A) \) to obtain the water-vapor transmission rate \( (WVTR) \), as shown in Eq. (5). This was multiplied by the thickness of the film and divided by the pressure difference between the inner and outer surfaces to obtain the WVP, as shown in Eq. (6):

\[
WVTR = \frac{S}{A} \quad (5)
\]

\[
WVP = \frac{WVTR \times X}{\Delta P} \quad (6)
\]

where \( x \) is the average film thickness (m) and \( \Delta P \) is the driving force (1753.55 Pa).

### 2.6. Mechanical properties

Tensile strength (TS), elongation at break (EB), and tensile energy to break (TEB) were evaluated by Machine M350-10CT (Testometric Co., Ltd., Rochdale, Lancs., UK) according to ASTM standard method D882-02 [21]. Films were cut in rectangular ribbons of 100 mm long by 10 mm wide. All specimens were conditioned at 50 ± 5% relative humidity for 48 h in a desiccator containing a saturated calcium-nitrate solution. The ribbons were fixed with an initial grip separation of 50 mm and stretched at a cross-head speed of 10 mm/min. Three replicates were run for each film specimen. TS, EB, and TEB were calculated using Eqs. (7)–(9):

\[
TS = \frac{F_{\text{max}}}{A_{\text{min}}} \quad (7)
\]

\[
EB = \frac{L_{\text{max}}}{L_0} \times 100 \quad (8)
\]

\[
TEB = \frac{A_{\text{Stress-Strain}}}{V} \quad (9)
\]

where \( F_{\text{max}} \) is the maximum load, \( A_{\text{min}} \) is the minimum cross-section area, \( L_{\text{max}} \) is the extension at the moment of rupture, \( L_0 \) is the initial length of specimen, \( A_{\text{Stress-Strain}} \) is the area under the stress–strain curve, and \( V \) is the volume of the original gage region.

### 2.7. UV-Vis spectroscopy

The UV–visible spectra of the kefiran-ZN nanocomposites were recorded using a UV-2600 spectrophotometer (Shimadzu Scientific Co., Japan) from 200 to 800 nm.

### 2.8. X-ray diffraction

The X-ray diffraction (XRD) profiles of the film specimens were taken using a Bruker Advance D8 (Karlsruhe, Germany). The specimens were irradiated by Cu Kα (\( \lambda = 0.15418 \) nm) at 40 kV and 30 mA with a symmetric reflection geometry in the range of \( 2\theta = 5^\circ - 80^\circ \) with a step of 0.02°.

The crystallite size of the polymer specimens was estimated by Scherrer’s equation (Eq. (10)):

\[
D = \frac{\lambda}{\beta \cos \theta} \quad (10)
\]

where \( D \) is the crystallite size, \( \lambda \) is the X-ray wavelength (0.15418 nm), \( \theta \) is the diffraction angle for the first peak, and \( \beta \) is the corrected integral width [22]. D-spacing between the crystalline layers of the polymer chain was estimated using the Bragg diffraction equation (Eq. (11)):

\[
d = \frac{\lambda}{2 \sin \theta} \quad (11)
\]

where \( d \) is the \( d \)-spacing between layers.
The films' thermal properties were determined using DSC equipment (Metler Toledo, USA) according to ASTM standard method D 3418-08 [23]. A film specimen of approximately 6 mg was cut and placed into a pan of the DSC equipment. Each specimen was then scanned at a heating rate of 10°C/min between a temperature range of −50 and 160°C. Nitrogen was used as the purge gas at a flow rate of 20 ml/min. The glass-transition temperatures (T_g) of the different films were determined from the resulting thermograms as the midpoint temperature of a step-down shift in baseline, due to the discontinuity of the specific heat of the specimen. The melting point (T_m) was calculated as the temperature where the peak of the endotherm occurs. All these properties were determined in duplicate and the results averaged.

2.10. Statistical analysis

Statistics were analyzed on a completely randomized design with the analysis of variance (ANOVA) procedure using SPSS software (Version 11.5; SPSS Inc., USA). Duncan’s multiple range tests were used to compare the difference among mean values of film specimens’ properties at the level of 0.05.

3. Results and discussion

3.1. Microstructure

Fig. 1a–d shows the morphological properties of the surface and cross-sections of kefiran film and kefiran nanocomposites. As shown in Fig. 1e, the average size of ZN was calculated at 20–30 nm, but the particles were agglomerated in nanocomposites (Fig. 1b–1, c–1, and d–1). This is due to the high surface energy of ZN [24]. The surface appearance of a nanocomposite becomes rougher with increased ZN content. The result showed a lack of good affinity between ZN and kefiran. Previous researchers have also shown that ZN cannot disperse well in composites of polypropylene and soluble starch [11] and pea starch [13].

3.2. XRD

Fig. 2 shows the X-ray diffraction profiles of kefiran film and ZnO–kefiran nanocomposites. In the XRD profile of kefiran and those of the nanocomposites, there is a clear and sharp peak around 2θ of 7°, which has also been reported in previous studies [8,25]. This peak was used to calculate all crystallography properties of the kefiran polymer (Fig. 2). The intensity of peak and crystallite size increased with increasing ZN content, whereas the d-spacing increased up to 2% ZN and then decreased for larger ZN percentages. This may be due to the penetration of kefiran polymer between ZNs making a bigger crystalline structure. At the highest concentration of ZN, the ZNs were agglomerated, making a thicker crystallite size (11.42 nm), but this particle caused the polymer chain to exit from d-spacing, thus decreasing the crystallite size. This phenomenon was confirmed by the SEM micrograph (Fig. 1b–1, c–1, and d–1). Moreover, the strongest peaks of ZN (at 2θ = 32°, 34°, and 36°) also appeared in the nanocomposites’ profiles, and their intensity increased with an increase in ZN content.

3.3. Thickness, moisture content, water-absorption, and solubility

Table 1 shows the thickness, moisture content, water absorption, and solubility of film specimens. The thickness of the film decreased with the addition of ZN to the filmogenic solution. Previous studies have shown different results; in some, the polymer thickness decreased [26], but in others it was stable or increased with increase in nanoparticles [27]. It seems that these changes depend on polymer and nanoparticle type.

The calculation of the films’ moisture content showed that the addition of ZN to kefiran resulted in no significant changes in the moisture content. Similarly, the water-absorption values were not significantly affected by ZN.

Unlike moisture content and water absorption, solubility was inversely affected by ZN content (Table 1). This is attributed to the creation of hydrogen bonds between the kefiran’s hydroxyl groups and oxygen atoms in the ZN, which improved the cohesiveness of the biopolymer matrix and decreased the water sensitivity; a similar result has also been reported by Almasi et al. [2].

3.4. Visual properties

Table 2 presents the values of hunter color (L, a, and b), ΔE, and WI of kefiran films as a function of nano-ZnO concentration. Although L, a, and b factors changed with increase in ZN content, ΔE and WI, as the most important color parameters [28], did not show any significant differences.

3.5. Water-vapor permeability

WVP is often used to study the moisture transport through the film and is of interest in almost all research into the characterization of biopolymers, because it is a key factor in food packaging to support food against water adsorption and desorption. Table 1 shows the WVP values of the specimens. WVP decreased with increasing ZN content, except for a ZN content of 1%. These results indicate that the addition of ZN had a positive effect on the WVP of the kefiran matrix. This is attributed to the fact that kefiran is able to form hydrogen bonds with the oxygen atoms of the ZN, making a strong structure, and resulting in reduced diffusion of water molecules in the polymer matrix. Also, WVP loss depends on the hydrophilic character of ZN and the morphology of nanocomposite structures (macro-voids, free volumes, crystallite size, and degree of crystallinity) [2]. As discussed, the XRD results (Fig. 2) confirmed that with increasing ZN content, the crystallinity of all nanocomposite specimens increased. Moreover, it is clear that using ZN produced a tortuous pathway and also increased the length of free way for vapor uptake. Similar results have also been obtained by the other researchers [2,12,13].

3.6. Mechanical properties

Interfacial interaction between the fillers and matrix was an important factor affecting the mechanical properties of the nanocomposites. Table 3 shows the results for mechanical properties. The TS of the nanocomposite specimens increased with increasing ZN content, but this modification was not significant.
up to 3% ZN content in the kefiran matrix. This phenomenon has also been observed in previous studies [12,13,16]. The EB of specimens was positively affected by ZN contents of 1 and 2%, reaching 221 ± 48%, but the corresponding value of nanocomposite containing 3% ZN dropped to 100 ± 47%. However, in other studies [11,12,16], EB decreased with an increase in nanoparticle content. The mechanical properties of nanocomposite depend on the properties and morphology of nanoparticles and polymer properties. According to the result of this present study, there is a significant difference between the EB of nanocomposite and that of kefiran film. This can be attributed to the fact that the nanoparticle (ZN) is like a ball bearing, make the movement of polymer chains easier than that for polymer chains in pure kefiran film. This hypothesis is confirmed by this study’s DSC and SEM data. According to the results (Table 3), the TEB of nanocomposites increased with increase in ZN content up to 2%, reaching 2285 ± 292 MJ/m², and then decreased with the addition of more ZN. However, in all nanocomposites, the TEB was at least 16 times greater than that of pure kefiran film. The SEM micrograph of specimen containing 1% ZN (Fig. 1b) showed that ZN dispersed well, but the particles were smaller than the reception capacity of the biopolymer. Although this amount of ZN (1%) had a significant effect on the TEB, its effect was not as much as that of 2% ZN content. Also, at the highest ZN percentage (3%), TEB decreased again as the result of the agglomeration of ZN.

3.7. UV–Vis spectroscopy

Fig. 3a shows kefiran nanocomposite film (containing kefiran and 2 wt% ZN). The nanocomposite possesses excellent transparent and visual properties. Based on our experiences in other experiments, the visual properties of kefiran nanocomposites containing ZN are superior to those prepared from nanoclay and nanoTiO₂ (unpublished data).

### Table 1

Physical properties and WVP of kefiran film and ZnO–kefiran nanocomposites incorporated with various concentrations of nano-ZnO content.\(^a,\(^b\)

<table>
<thead>
<tr>
<th></th>
<th>Thickness (mm)</th>
<th>Moisture content (%)</th>
<th>Water absorption (%)</th>
<th>Solubility (%)</th>
<th>WVP (× 10(^{-10}) g (^{-1}) s (^{-1}) Pa(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kefiran</td>
<td>0.08 ± 0.01a</td>
<td>13.81 ± 2.82a</td>
<td>8.04 ± 2.14a</td>
<td>32.47 ± 1.64a</td>
<td>2.19 ± 0.00a</td>
</tr>
<tr>
<td>ZnO(1%)</td>
<td>0.07 ± 0.00b</td>
<td>15.35 ± 1.12a</td>
<td>8.58 ± 0.67a</td>
<td>27.19 ± 0.73b</td>
<td>2.34 ± 0.18a</td>
</tr>
<tr>
<td>ZnO(2%)</td>
<td>0.07 ± 0.00b</td>
<td>12.22 ± 0.78a</td>
<td>8.37 ± 1.10a</td>
<td>24.77 ± 1.96b</td>
<td>1.83 ± 0.00b</td>
</tr>
<tr>
<td>ZnO(3%)</td>
<td>0.07 ± 0.00b</td>
<td>13.50 ± 1.88a</td>
<td>7.46 ± 0.63a</td>
<td>22.08 ± 1.61c</td>
<td>1.81 ± 0.18b</td>
</tr>
</tbody>
</table>

\(^a\) Means within each column with same letters are not significantly different (P < 0.05).
\(^b\) Data are means ± SD.

### Table 2

Hunter color values (L, a, and b), total color difference (ΔE), and whiteness index (WI) of kefiran film and ZnO–kefiran nanocomposites as a function of nano-ZnO concentration.\(^a,\(^b\)

<table>
<thead>
<tr>
<th>ZnO concentration (%)</th>
<th>L</th>
<th>a</th>
<th>b</th>
<th>ΔE</th>
<th>WI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kefiran</td>
<td>89.64 ± 0.74b</td>
<td>−0.14 ± 0.03a</td>
<td>1.00 ± 0.00b</td>
<td>6.40 ± 1.28a</td>
<td>89.59 ± 0.74a</td>
</tr>
<tr>
<td>Kefiran + ZnO(1%)</td>
<td>90.21 ± 0.70a</td>
<td>−0.86 ± 0.05b</td>
<td>4.07 ± 1.14a</td>
<td>7.30 ± 1.09a</td>
<td>89.31 ± 0.88a</td>
</tr>
<tr>
<td>Kefiran + ZnO(2%)</td>
<td>90.36 ± 1.01a</td>
<td>−1.07 ± 0.27b</td>
<td>4.07 ± 0.62a</td>
<td>7.13 ± 1.13a</td>
<td>89.47 ± 1.01a</td>
</tr>
<tr>
<td>Kefiran + ZnO(3%)</td>
<td>90.16 ± 0.85a</td>
<td>−1.07 ± 0.35b</td>
<td>4.29 ± 0.99a</td>
<td>7.23 ± 1.19a</td>
<td>89.42 ± 1.05a</td>
</tr>
</tbody>
</table>

\(^a\) Means within each column with same letters are not significantly different (P < 0.05).
\(^b\) Data are means ± SD.

### Table 3

Effect of various concentrations of nano-ZnO on the mechanical properties of kefiran film and ZnO–kefiran nanocomposites.\(^a,\(^b\)

<table>
<thead>
<tr>
<th>ZnO concentration (%)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Tensile energy to break (MJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.40 ± 2.62b</td>
<td>18.35 ± 3.76c</td>
<td>19.77 ± 7.83c</td>
</tr>
<tr>
<td>1</td>
<td>7.42 ± 1.88b</td>
<td>80.30 ± 10.89bc</td>
<td>360.95 ± 95.70b</td>
</tr>
<tr>
<td>2</td>
<td>7.11 ± 0.64b</td>
<td>221.46 ± 48.11a</td>
<td>2295.47 ± 292.17a</td>
</tr>
<tr>
<td>3</td>
<td>13.12 ± 2.05a</td>
<td>100.36 ± 47.13b</td>
<td>319.24 ± 64.06b</td>
</tr>
</tbody>
</table>

\(^a\) Means within each column with same letters are not significantly different (P < 0.05).
\(^b\) Data are means ± SD.

**Fig. 3b** shows the UV-visible absorption spectra of kefiran film and ZnO–kefiran nanocomposites. The UV absorbance of the nanocomposite polymers increased as ZN content increased. An absorption peak was found at 363 nm for the nanocomposite polymers, and the intensity of the peak increased with increasing ZN content. Nevertheless, this peak was not observed in the nanocomposite with 1% ZN; therefore, ZN content greater than 1% was necessary to induce UV filtration in kefiran biopolymer. This result has also been shown in previous studies [13,16]. The observation of this peak is due to a bandgap of ZnO bulk material at around 3.3 eV (corresponding to 376 nm). The absorption peak at 363 nm for the polymers embedded with ZN indicated some blue-shift phenomenon due to the quantum size effect of ZN [16].

3.8. DSC

**Fig. 3c** and **d** shows the results for thermograms and thermal properties of pure kefiran and kefiran nanocomposite specimens. The Tg—the temperature at which the material undergoes a structural transition from an amorphous solid state (glassy state) to a more viscous rubbery state—of nanocomposites decreased with increasing ZN content. Below Tg, films are rigid and brittle, whereas above Tg they become flexible and pliable [29]. Hence, ball-shaped ZN acted as lubricant for polymer chains at lower temperatures, leading to Tg loss, as shown in (Fig. 1b–d). However, the other studies have demonstrated that with increasing ZN, free volume decreases and Tg increases [12,13]. This difference may be due to the size of the nanofiller, the chemical properties at interface of the filler and polymer matrix, and the dispersion of filler particles [30]. Tm increased with increasing ZN content, but this change was not significant for the lowest percentage (1%) of ZN. However, the increase in Tm in the other specimens was rarely significant. Also, other studies have shown that Tm is not significantly affected by ZN content [11].
4. Conclusions

According to the results of this study, kefiran/nano-ZnO nanocomposites readily form a new bionanocomposite film. The mechanical, physical, and WVP properties—which are crucial parameters in food packaging—were improved significantly by increasing ZN content in the nanocomposites, but thermal properties, especially T<sub>m</sub>, dramatically decreased. On the other hand, T<sub>m</sub> slightly increased. Ball-bearing effect of ZN on polymer chain is an applicable hypothesis to justify the mechanical and thermal properties of kefiran/nano-ZnO nanocomposites. The hypothesis confirmed by TEM, SEM micrograph and DSC analysis. XRD analysis showed that the crystallinity and crystallite size increased with increasing ZN content. Kefiran/nano-ZnO nanocomposites not only possessed good transparency and other visual properties, but were also good UV filters. This is a unique property for kefiran/nano-ZnO nanocomposite films and useful for increasing the shelf life of food products. Most functional properties of kefiran were improved by adding ZN. However, to intensify the positive effect of ZN on polymer properties, it is highly recommended to modify ZN surface properties due to weak affinity between it and kefiran.

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