

## PREPARATION AND CHARACTERIZATION OF BIODEGRADABLE THIN FILM GELATIN GRAFTED VINYL ACETATE-METHYLEMETHACRYLATE NANOCOMPOSITE

U. FATIMA<sup>a</sup>, S. SHAHID<sup>a\*</sup>, S. NADEEM<sup>a</sup>

<sup>a</sup>*Department of Chemistry, School of Science, University of Management & Technology, Lahore, 54770, Pakistan*

Thought to make the environment green and restrict fossil sources is increasing day by day. Renewable sources are helpful in production of green materials as they are biodegradable and non-toxic to living being and atmosphere. Our main concern is to from biodegradable polymeric product from non biodegradable product. Graft copolymerization was used to prepare biodegradable gelatin grafted vinyl acetate methylmethacrylate nanocomposite. Gelatin backbone used as biodegradable material and grafted with vinyl acetate Methylmethacrylate. This polymer was fully characterized by Fourier transform Infrared (FTIR), Thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC) and Scanning electron microscopy (SEM). The polymer nanocomposite was prepared by adding the suitable amount of Ni doped ZnO nanoparticles. Biodegradability was checked by soil burial method. Percent weight loss was measured as a function of number of days and results showed that degradability increase with the number of day's up to 44.39%. Degradation studies showed that Gelatin-Grafted-Vinyl Acetate-Methylmethacrylate is more degraded as compare to Gelatin-Grafted-Vinyl Acetate-Methylmethacrylate nanocomposite. Results showed that the grafting was a flexible tool to impart biodegradation to non biodegradable polymers. Addition of nanoparticles gave them a resistance against microbes up to an extent. Therefore this nanocomposite can be used successfully as biodegradable food packaging material.

(Received February 20, 2017; Accepted June 1, 2017)

*Keywords:* Gelatin; Graft copolymerization; Ni doped ZnO nanocomposites; Thin films

### 1. Introduction

Most food packaging materials are non degradable and main cause of pollution. These non degradable materials are producing burden on environment. Different biopolymer have been reported that used as environment and health friendly food packaging material. However these biopolymers can't be used freely because of limited resources [1]. The thought to make the environment green and control the sources of fossil is increasing day by day. Scientists are taking interest in producing green materials from renewable sources as they are biodegradable and non-toxic to living being and atmosphere. Now a day's a lot of interest have been seen in production of natural based polymers so that we can save fossil fuels and reserved these materials. Bio-nanocomposites provide a chance to produce new, useful and best performance eco friendly nanocomposites. These nanocomposites can replace the traditional non biodegradable material into biodegradable material and can give better response in technological terms, particularly in thermal, mechanical and barrel properties of polymer.

Production of synthetic polymers is the main focus of new generation of research world. But this is also true that these synthetic non biodegradable polymers creating a dangerous condition for a hale and hearty life. The alteration in natural polymers has capability to formed novel materials. In few years, great deal of attention has been seen in the modification of

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\*Corresponding author: sammia.shahid@umt.edu.pk

natural based biodegradable nanocomposites [2-4]. Backbone of vinyl monomers provides an efficient approach to modify natural polymer through Graft polymerization [5-7].

Proteins are extensively spread in nature and obtained from animals in the form of collagen, keratin, gelatin etc, and a small number from plants for example Soya. Generally, protein polymers have high molecular weight and insoluble in inorganic solvents.

Gelatin is a fibrous protein. It is a self-assembled, nontoxic, biodegradable and inexpensive material. It is mostly used in pharmaceutical [8], food, photographic industries [9] and as a stabilizer [10] etc. Moreover, peptide units show high selectivity to interact with metal oxide [11] and can produce porous material through the traditional synthetic methods. Conversely, toughness and brittleness of gelatin films caused difficulty in synthesis. Gelatin has double bonds and it is believed that these double bonds provide an easy mode to introduce the polymers into the gelatin units via copolymerization of gelatin and alkenes through radical initiation.

Commonly studied bio nanocomposites are derivatives of protein [12], starch, chitosan [13], cellulose [14] and gelatin [15] with a lot of synthetic polymers such as polylactic acid (PLA), polyhydroxybutyrate (PHB) and polyvinyl acetate (PVA). The mainly synthesized man-made porous polymers comprise of poly (glycolic acid) [16], poly (D,L-lactic acid) [11,17] and poly(methylmethacrylate) (PMMA) [18].

In this study our main concern to form a novel biodegradable Ni doped ZnO Gelatin-Grafted-Vinyl Acetate-Methylmethacrylate nanocomposite through a non-biodegradable methyl methacrylate.

## **2. Materials and Methods**

### **2.1. Synthesis of Gelatin-Grafted-Vinyl Acetate-Methylmethacrylate (Gelatin-g-VA-MMA):**

Synthesis of Gelatin-g-VA-MMA was carried out as described before [13]. 1.0 g of gelatin was dissolved in 50 ml of distilled water into the three-neck reaction flask equipped with a mechanical stirrer, a condenser and thermometer. Nitrogen purging was started from the start of reaction. The reaction flask was immersed in a thermo state water bath preset at 80 °C temperature. When a clear solution of gelatin was obtained 0.5 g of luntensol XL- 100 and potassium persulphate was added and stirred for 10 min. A mixture of vinyl acetate and methylmethacrylate with the ratio of 6:1 was added to gelatin solution at the rate of 1.0 ml/min. After complete addition of monomer, the reaction content kept at constant 80 °C for 90 min.

### **2.2. Preparation of Ni doped ZnO/ Gelatin-Grafted-Vinyl Acetate-Methylmethacrylate Nanocomposite (Gelatin-g-VA-MMA-NA):**

0.5 g of gelatin and 0.25g potassium persulphate was dissolved in 25 ml of distilled water into the three necked flask. A temperature of 80 °C was attained to dissolve the gelatin. When a clear solution of gelatin was obtained 0.5 ml of luntensol XL- 100 was added and allowed to mix for 5 min. A mixture of vinyl acetate and methylmethacrylate with the ratio of 6:1 and sodium sulphite was added to gelatin solution at the rate of 1.0 ml/min. Temperature was maintained at 80 °C for 3.0 hr. At the end nickel doped zinc oxide nanoparticles were added (2.0% weight of all the polymeric emulsion) and stirrer for 20 min, then form a thin film [13].

### **2.3. Biodegradable study**

Biodegradation of prepared Gelatin-g-VA-MMA and Gelatin-g-VA-MMA-NA was checked by soil burial method. Soil has microbes specially bacteria and fungi. These microbes helped in degradation of the polymer samples present in soil. Prepared polymer sample was poured over a glass plate, spread it by an applicator. When thin film of polymer was dried cut it into rectangular strips of specific size. The average weight of strips was found to be 0.301 g. Three different pots were selected having approximately 1 kg soil. The pre weighted strips of Gelatin-g-VA-MMA and Gelatin-g-VA-MMA-NA were covered with of Teflon net and placed into the soil carefully. Soil covered all the corners of sample completely. Now the pots were covered with

aluminium foil and kept at room temperature. Loss in mass after fixed interval (10 days) of time was determined by using Eq. (1):

$$\% \text{ mass loss} = \frac{\text{Initial mass of sample} - \text{mass after number of days passed}}{\text{initial mass of the sample}} \times 100 \quad (1)$$

Further analysis of gelatin-g-VA-MMA and gelatin-g-VA-MMA-NA was carried out by FTIR analysis performed by Equinox 55 spectrometer. Thermal stability was characterized by thermal gravimetric analysis and differential scanning calorimeter on SDT Q600 V20.9 Build 20. Morphology of gelatin-g-VA-MMA nanocomposite was confirmed by scanning electron micrographs. SEM analysis was performed by JEOL-6380LV, Japan.

### 3. Results and discussion

#### 3.1 Infrared spectroscopic Studies of Gelatin:

Fourier transform infrared spectroscopic technique was used to confirm the grafting of gelatin-g-VA-MMA and gelatin-g-VA-MMA-NA. IR spectrum of gelatin-g-VA-MMA showed different bands as compare to gelatin. The band observed at 1645 cm<sup>-1</sup> was due to stretching of amide carbonyl group, 3306 cm<sup>-1</sup> was due to NH stretching while band at 1548cm<sup>-1</sup> was due to NH bending.

#### 3.2. Infrared spectroscopic Studies of gelatin-g-VA-MMA:

IR spectrum of grafted gelatin-g-VA-MMA showed characteristic band at 1645 cm<sup>-1</sup> due to presence of stretching of amide carbonyl group of gelatin. The asymmetric stretching band of primary NH was observed at 1558 cm<sup>-1</sup>. Intensity of peak decreased at 3445 cm<sup>-1</sup> confirmed that most of amide group were used in grafting.

#### 3.3. Infrared spectroscopic Studies of gelatin-g-VA-MMA-NA:

IR spectrum of gelatin-g-VA-MMA-NA with nickel doped ZnO nanoparticles showed characteristic band at 1641 cm<sup>-1</sup> due to presence of stretching of amide carbonyl group of gelatin. The asymmetric stretching band for primary NH was observed at 1540 cm<sup>-1</sup> and intensity of peak decreased at 3336 cm<sup>-1</sup> confirmed that most of amine group were used in grafting.

#### 3.4. Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetric (DSC) Results of gelatin-g-VA-MMA:

Thermal properties of gelatin-g-VA-MMA and gelatin-g-VA-MMA-NA films were determined by differential scanning calorimeter (universal V4.7A T instrument). The transition temperature of thin films was determined from endothermic peak of DSC thermo gram. The scan of gelatin-g-VA-MMA showed two endothermic peaks at 125 °C and 330 °C while the scan of gelatin-g-VA-MMA-NA also showed two endothermic peaks at 355 °C and 450 °C. In both samples peaks were disappeared when the samples were re-heated and cooled rapidly. First transition peak was due to the volatilization of absorbed water while the second transition temperature was because of relative amount of gelatin-g-VA-MMA and gelatin-g-VA-MMA-NA [19]. DSC results of gelatin-g-VA-MMA and modified gelatin-g-VA-MMA-NA have shown different behavior. Gelatin-g-VA-MMA-NA increased the thermal stability as compare to parent polymer of gelatin-g-VA-MMA.

The onset of thermal decomposition was estimated through thermo gravimetric analysis (TGA). TGA analysis also showed in Fig.1 and 2 respectively. The minimum thermal stability of gelatin-g-VA-MMA is observed at 265 °C while modified gelatin-g-VA-MMA-NA at 275 °C. The decomposition of gelatin-g-VA-MMA and gelatin-g-VA-MMA-NA were started from 200 °C (which is a considerable value) by removal of water and moisture bounded with sample surface while the higher thermal decomposition of gelatin-g-VA-MMA has been seen at 265 °C while gelatin-g-VA-MMA-NA showed at 275 °C. The final change in mass was observed at 410 °C for gelatin-g-VA-MMA and 450 °C for gelatin-g-VA-MMA-NA with remaining mass of

residual carbon and others. It was concluded from the results that modified gelatin-g-VA-MMA-NA shifted towards higher temperature and showed more thermal stability and strong interaction with gelatin matrix as compare to gelatin-g-VA-MMA. TGA and DSC curves suggested that gelatin films of nanoparticles enhanced their thermal stability up to 275 °C.

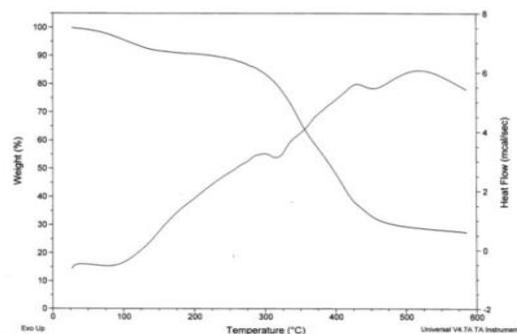


Fig.1.TGA and DSCResults of gelatin-g-VA-MMA thin film annealed at 600 °C

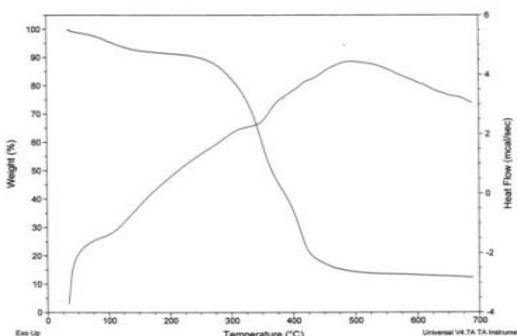


Fig. 2.TGA and DSC Results of gelatin-g-VA-MMA-NA annealed at 700 °C.

### 3.5.Biodegradable study:

Biodegradation of gelatin-g-VA-MMA and gelatin-g-VA-MMA-NA were determined after 10 days of interval and shown in Fig. 3. Percent weight loss as a function of days was noted. Three samples of each sample were under observation. Result showed better degradation of gelatin-g-VA-MMA as well as gelatin-g-VA-MMA-NA. After ten days weight was increased due to the absorption of water and after ten days a rapid weight loss has been seen. After 40 days degradation of gelatin-g-VA-MMA was 44.39% while gelatin-g-VA-MMA-NA degrade up to 35.50%. Gelatin-g-VA-MMA-NA showed the decreased in degradation due to antibacterial effect of nanoparticles as compared to gelatin-g-VA-MMA. The results suggested that this gelatin-g-VA-MMA-NA can be used as antibacterial agent up to and extend.

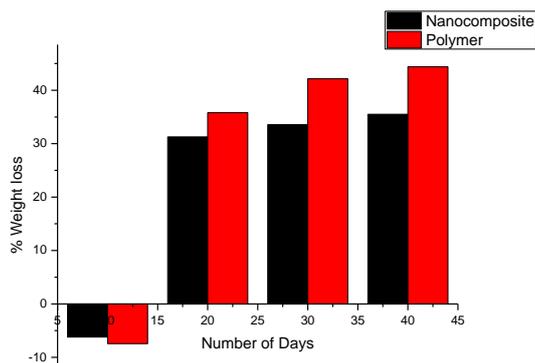


Fig. 3. Percent Weight Loss of Gelatin-g-VA-MMA and Gelatin-g-VA-MMA-NA after ten days of interval.

### 3.6. Scanning electron micrographs of degraded gelatin-g-VA-MMA and Gelatin-g-VA-MMA-NA:

SEM images of Gelatin-g-VA-MMA-NA and degraded gelatin-g-VA-MMA and Gelatin-g-VA-MMA-NA were shown in Fig. 4, 5 and 6 respectively. The results clearly showed that Gelatin-g-VA-MMA-NA appeared as a uniform homogenous surface deposited on polymer and after degradation this has been reduced to spotted film. These results showed Gelatin-g-VA-MMA and Gelatin-g-VA-MMA-NA degraded during the soil burial method.

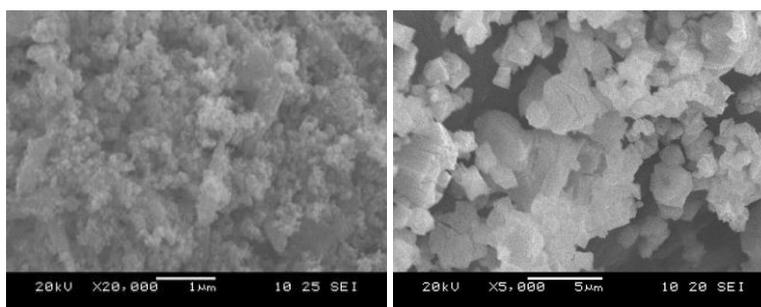


Fig. 4. Scanning Electron Micrograph of Fig. 5. Scanning Electron Micrograph of degraded Gelatin-g-VA-MMA-NA at x20,000 magnification. Gelatin-g-VA-MMA at x5,000 magnification.

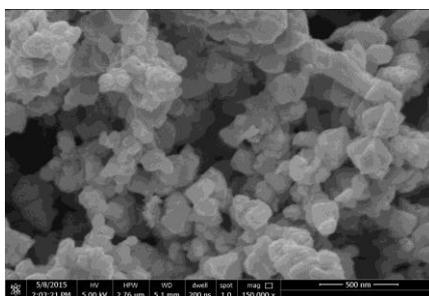


Fig. 6. Scanning Electron Micrograph of degraded Gelatin-g-VA-MMA-NA at x150,000 magnifications

## 4. Conclusions

In the present study, we have investigated a biodegradable polymer of protein with vinyl acetate methylmethacrylate and its nanocomposite with nickel doped Zinc oxide nanoparticles.

Gelatin backbone used as biodegradable material for grafting with vinyl acetate monomer. After that gelatin backbone was grafted with copolymer Methylmethacrylate. This polymer was fully characterized by FTIR, SEM, TGA and DSC. All the results were encouraging and sufficient to justify further studies. The nanocomposite was also prepared by adding the suitable amount of nanoparticles (Ni doped ZnO nanoparticles). The DSC results confirmed that Gelatin-g-VA-MMA and Gelatin-g-VA-MMA-NA both were amorphous, with a minimum thermal stability of 200 °C.

Thermal stability of Gelatin-g-VA-MMA-NA was increased after incorporation of 2% nanoparticles by weight as compare to Gelatin-g-VA-MMA film. FTIR analysis showed that most of the amide group was used in grafting. Biodegradation of gelatin-g-VA-MMA and Gelatin-g-VA-MMA-NA was also studied by soil burial method using range of 40 days. An initially weight increased due to moisture absorption and then decreased in weight was noted. Gelatin-g-VA-MMA-NA of Ni doped ZnO showed a decreased in biodegradation because of antibacterial effect. The degradation of Gelatin-g-VA-MMA and Gelatin-g-VA-MMA-NA increased up to 44.39% and 35.50% respectively. The results showed that the grafting was a flexible tool to impart biodegradation to non biodegradable polymers. The addition of nanoparticles gave them resistance against microbes up to an extent. Therefore this nanocomposite can be used successfully as biodegradable food packaging material.

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