

Synthesis and analysis of environment friendly gelatin grafted biodegradable polymer

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Abstract: Polymers are extensively used in human life with a serious problem of disposal. The non-biodegradable polymers cause severe environmental concerns therefore synthesis of biodegradable green polymer was targeted in this study. Gelatin based grafted copolymer was synthesized with vinyl acetate and acrylonitrile monomers by the use of free radical polymerization technique with potassium per sulfate as initiator. The polymer was characterized by the use of Fourier Transform Infrared Spectroscopy (FTIR), Thermo Gravimetric Analysis and Differential Scanning Calorimetry (TGA-DSC). FTIR proved the grafting of monomers on the backbone of the gelatin. TGA-DSC analyzed the degradation and melting of the copolymer and nanocomposite polymer. The nanocomposite biopolymer was prepared with the incorporation of suitable quantity of Nickel doped nanoparticles. Soil burial method was used for the study of biodegradation of this polymer for 60 days. The degradation study of the two prepared samples W-1 (copolymer) and W-2 (nanocomposite biopolymer) showed degradation percentage of 29.9% and 11.05% respectively. Initially, weight of the W-1 increased due to the absorption of moisture from the soil but after 20 days the weight of polymer decreased constantly due to degradation. The W-2 sample showed resistance against the biodegradation with slower degradation rate and was also less moisture absorber. Results depicted that the blended nanoparticles imparted resistance against the fungi and bacteria, therefore these nanocomposite biopolymers are more suitable for biodegradable packing.

Keywords: Biodegradable polymer; Gelatin; Graft polymerization; Nanocomposite; TGA-DSC.

Introduction

Polymers have been the integral part of our world right from the very beginning of life. The synthesis of first manmade polymer from natural raw materials in nineteenth century was followed by enormous research and development in this field [1]. Synthetic polymers, used for packaging and medical field, are mostly non-degradable and responsible for enormous increase in debris. Such debris is difficult to dispose off and hence cause serious environmental concerns. Even if these polymers are degraded artificially, they give toxic products which themselves are pollutants. Non-degradable polymeric waste has been badly effecting all marine or terrestrial organisms but is most abundant in marine debris. Many species of marine animals die from suffocation due to this polymeric waste which do not decompose even after the death of animals and get ingested again and again. The biodegradable polymers (BPs) are being preferred since they meet the biocompatibility requirement by decomposing into almost non-toxic degradation products. However, they are still less common in use because of their limitations of physical strength, dimensional stability, molding and cost [2], [3]. Natural resources are now widely used for the preparation of BPs for carbon sequestration and hence greening of the process. BPs are mostly utilized for packaging [4], surgical biomaterials [5] and drug delivery systems [6].

A lot of research interest have been observed these days to blend BPs with renewable and nonrenewable resources to enhance their mechanical properties and slow their microbial degradation resulting in longer shelf life. Such successful blending include the incorporation of metal nanoparticles into the natural polymeric films to produce nanocomposites biopolymers (NBPs). These blended NBPs are the latest generation of polymers which possess high stability, rigidity and solvent resistance than original polymers [7]. Nanoparticles get immersed uniformly in the polymers and increase the surface area resulting in enhancement of their thermal and mechanical properties. Some of reported NBPs are blends of starch, proteins, cellulose and gelatin with polymers like polyvinyl acetate (PVA),

polylactic acid (PLA) and polyhydroxyalkanoate (PHA) and metal nanoparticles such as AgO, MgO and ZnO [8], [9], [10], [11], [12].

Mostly medical chemists focus on PLA because of relatively low degradation rate and lower cost [13]. However some drawbacks of this biopolymer include low hydrophilicity, low thermal stability and poor soft tissue compatibility [14]. The polymers which have hydrophilic segments in their backbone chain (e.g; polyacrylic acid, polyethers and polyvinyl alcohol) are much more degradable as hydrophilicity helps the microorganisms to secrete enzymes. Therefore, grafting of natural polymers by vinylic monomers is an efficient way of enhancing the degree of biodegradation along with increase of mechanical and thermal strength [15], [16].

Gelatin being a fibrous protein swells up on absorbing water and its biodegradability increases [17]. It has triple helix type 1 structural conformation made up of heterogeneous mixture of many single and multi-stranded polypeptides [18]. Moreover, it is an abundant, nontoxic and inexpensive biomaterial. It can selectively react with metal oxides through its peptide units due to its amphoteric nature [19], [20]. Synthesis of BPs by employing graft polymerization of different monomers on such natural-based polymer via free radical mechanism is an effective method to modify their backbone [17]. Successful grafting of gelatin by using different vinyl monomers like ethyl acrylate, methyl acrylate and ethyl methacrylate and acrylamide in the presence of ammonium persulfate as an initiator has already been reported [21], [22].

The present study aimed to study the biodegradability of a copolymer synthesized by grafting gelatin with acrylonitrile and vinyl acetate monomers using potassium per sulfate as initiator. Further goal was to prepare a nanocomposite by blending nickel doped zinc oxide nanoparticles with synthesized copolymer and examine the effect of blending on biodegradability.

Materials and methods

Chemicals and instruments. Vinyl acetate monomer (VAM), Acrylonitrile, Gelatin, Lutensol XL-100, Potassium Per Sulfate, Nickel doped ZnO nanoparticles were purchased from Merck. All the chemicals and solvents used in this research work were of analytical grade. Mechanical stirrer used was RZR 2021 Heidolph. The FTIR studies were performed on Bruker FTIR Spectrometer having scanning range of 4000-650 cm^{-1} . TGA and DSC analysis was carried out on SDT Q600 V20.9 model of TA Instruments.

Synthesis of gelatin grafted copolymer (W-1). Gelatin-g-poly (vinyl acetate-co-acrylonitrile) copolymer was synthesized by the general procedures reported by Ali et al., 2015 [23] and Soleimani et al., 2012 [17] with some modifications. Sample W-1 was synthesized in the three necked reactor fitted with mechanical stirrer assembly and adjusted on the water bath. Gelatin (1.0 g) was added to the reactor with double distilled water (50 ml) and heated with stirring till clear solution was obtained at 70°C. Lutensol XL-100 (0.50 g) was added in the clear solution as emulsifier. After 2 min, potassium per sulfate (0.10 g) was added in the reactor as an initiator and mixture was stirred for 5 min. A mixture of VAM (23 ml) and acrylonitrile monomer (3 ml) was prepared in separate beaker. This 26 ml mixture of monomers was added in the reactor continuously at the rate of 1 ml/min. After the complete addition of monomers, the reaction was continued for 90 min at 80°C to ensure maximum completion of reaction. The liquid polymer product was obtained which was poured into the petri dish. After cooling for 30 min the liquid polymer was applied on the glass sheet with the help of applicator. A thin film sheet of copolymer was obtained that was analyzed by FTIR and TGA-DSC.

Preparation of nanocomposites biopolymer (W-2). NBP was prepared by same procedure as described above for sample W-1. But after the completion of reaction 0.040 g nickel doped ZnO nanoparticles were added in the reactor and the reaction was allowed to proceed further for 15 min. A thin film of this liquid polymer blend was spread as plastic sheet with the help of applicator and analyzed further.

FTIR analysis. Sample W-1 was taken as strip by cutting the plastic sheet prepared. The strip of W-1 as well as reactants were analyzed by FTIR spectrometer one by one. The FTIR spectra were obtained in transmittance mode and samples were scanned by setting the scanning range between 4000 cm^{-1} - 500 cm^{-1} .

Thermal degradation studies by TGA-DSC analysis. The sample strips (W-1 and W-2) were then analyzed by TGA-DSC for degradation studies. The samples were subjected to controlled heating and measurements were continued till 600°C. Results were obtained as a graph between weight loss (%) with temperature (°C). Temperatures of melting and crystallization of the polymers were also included.

Biodegradation studies by soil burial method. The sheets of polymers were cut into strips of equal size for both samples W-1 and W-2. Each strip were 2.0 cm wide, 10.0 cm long and had a thickness of 0.10 cm. Initial weight of each strip was noted. Two pots were filled with soil (1 kg each). Pre weighted W-1 and W-2 sample stripes were carefully wrapped in Teflon net and then placed in the soil. Both pots were covered with aluminum foil, placed at in

lab at room temperature. Weight loss of each strip was noted daily for 50 days. %Weight loss was calculated by following equation:

$$\% \text{ Weight Loss} = \frac{\text{initial weight of sample} - \text{Weight after number of days passed}}{\text{Initial weight of sample}} \times 100$$

Results and discussion

Characterization by FTIR. The grafting of monomer on gelatin backbone polymer was confirmed by comparing the FTIR spectra of monomers with polymer samples. The IR spectra proved the success of grafting process by as the bands of reacting functional groups which were present in reactants were found to be absent in products and new bands appeared demonstrating the new bonds produced. Al et al., 2008 [24] used FTIR to determine the grafting of starch acrylic acid hydrogels and their Na nanocomposites.

IR studies of reactants. The IR spectrum of pure gelatin is shown in Fig. 1. Gelatin has carboxamide groups which is confirmed by the C=O stretching band at 1634 cm^{-1} . Fig. 2 represent the IR spectrum of VAM which has the dominant carbonyl stretching band at 1739 cm^{-1} and a C=C stretching band at 1650 cm^{-1} . The -O-C- ester functional group of VAM gave characteristic band at 1188 cm^{-1} . Fig. 3 elaborate the FTIR spectrum of acrylonitrile. The band at 1430 cm^{-1} was confirmed for the C=C stretching whereas band at the 2249 cm^{-1} showed the -C≡N group of the acrylonitrile.

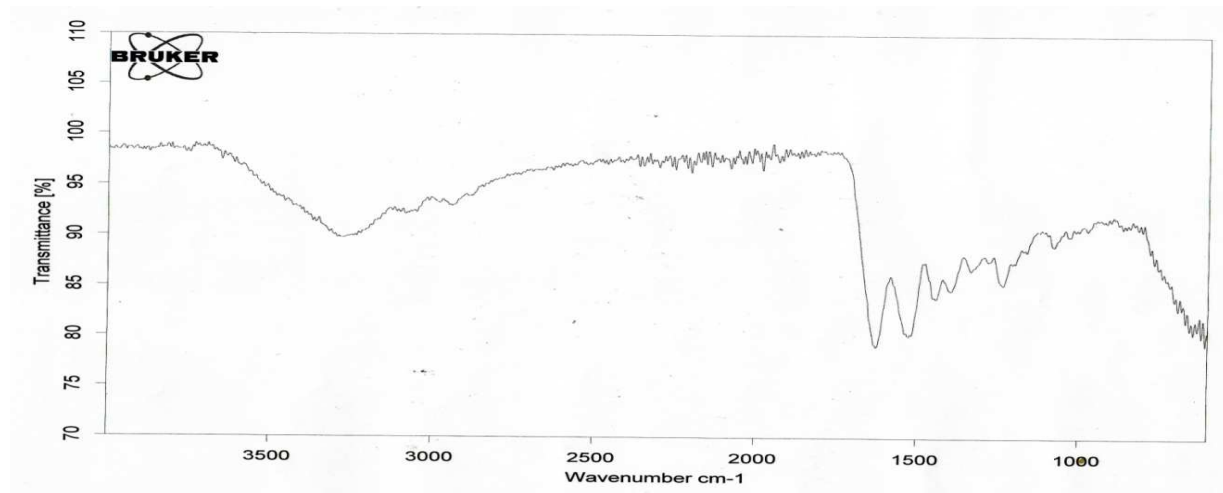


Figure 1: FTIR spectrum of gelatin

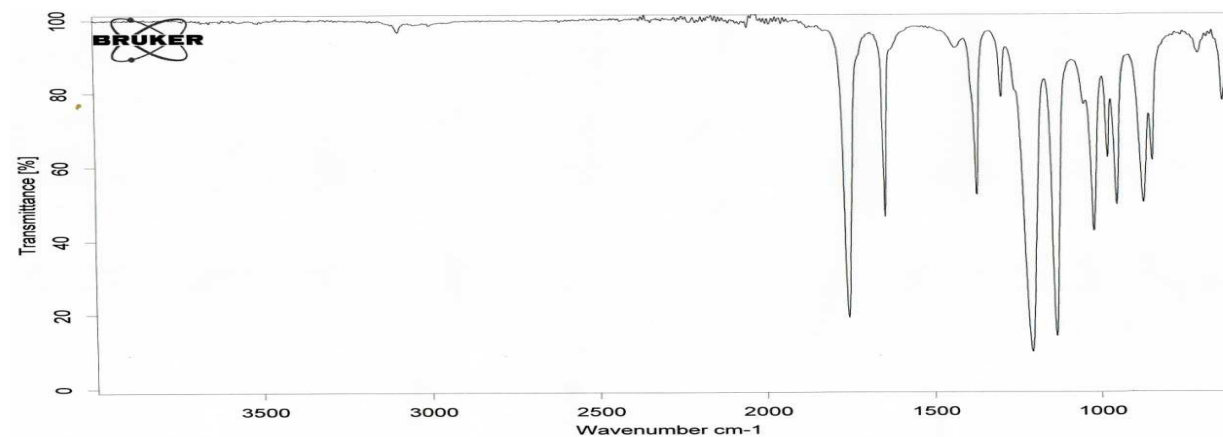


Figure 2: FTIR spectrum of vinyl acetate monomer

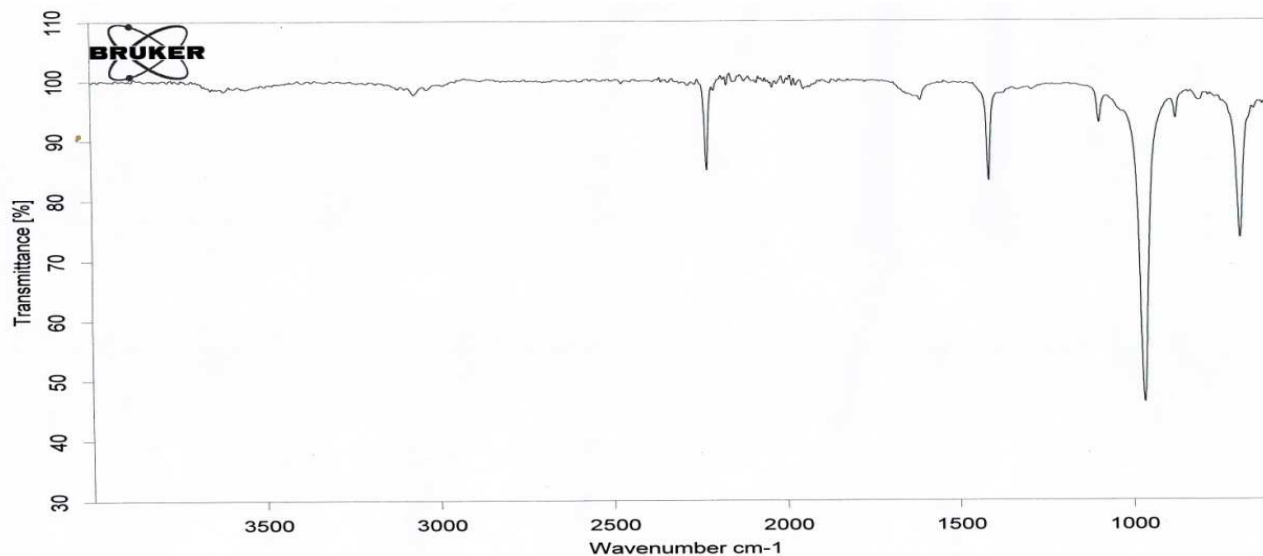


Figure 3: FTIR spectrum of acrylonitrile

IR studies of gelatin grafted copolymer

The FTIR spectrum of Sample W-1 is presented in the Fig. 4. The IR results confirmed the grafting process of monomers on the backbone of gelatin. The spectrum shows bands at 1680 cm^{-1} and 1250 cm^{-1} due to the symmetric and asymmetric stretching of carboxylate anion. The short band at 1440 cm^{-1} was observed due to the asymmetric stretching of the carboxylate anion.

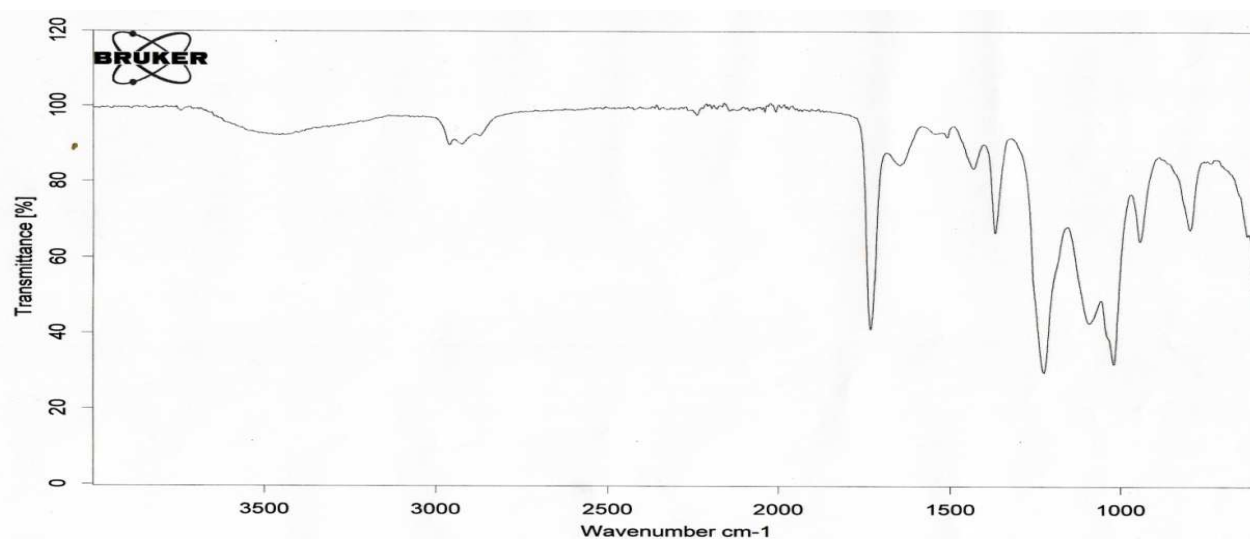


Fig. 4: FTIR spectrum of W-1 r

Thermal degradation studies by TGA-DSC analysis. TGA-DSC is a recommended technique for thermal degradation studies [25], [26]. It analyzes the loss in weight of polymer with a constant increase in temperature.

TGA-DSC analysis of gelatin copolymer

The degradation behavior of W-1 is given in Fig. 5. It was observed that weight was continuously decreasing with the increase in temperature except at melting stage. The TGA line represents the decomposition of the Gelatin-g-poly (vinyl acetate-co-acrylonitril) polymer. 5% polymer was decomposed at 250°C . 50% polymer was decomposed at 350°C . This decrease was observed to be steep up to 425°C . Again a steady steep has been observed from 425°C to 500°C . 87% polymer was exhausted at 500°C . The DSC line showed three humps. It demonstrated that sample has 10% impurity which is due to moisture and some unreacted monomers in the sample. The heat flow of the

polymer showed three humps. The complete melting of the polymer was observed at 330°C. After that, it recrystallized and showed a slight melting at 400°C.

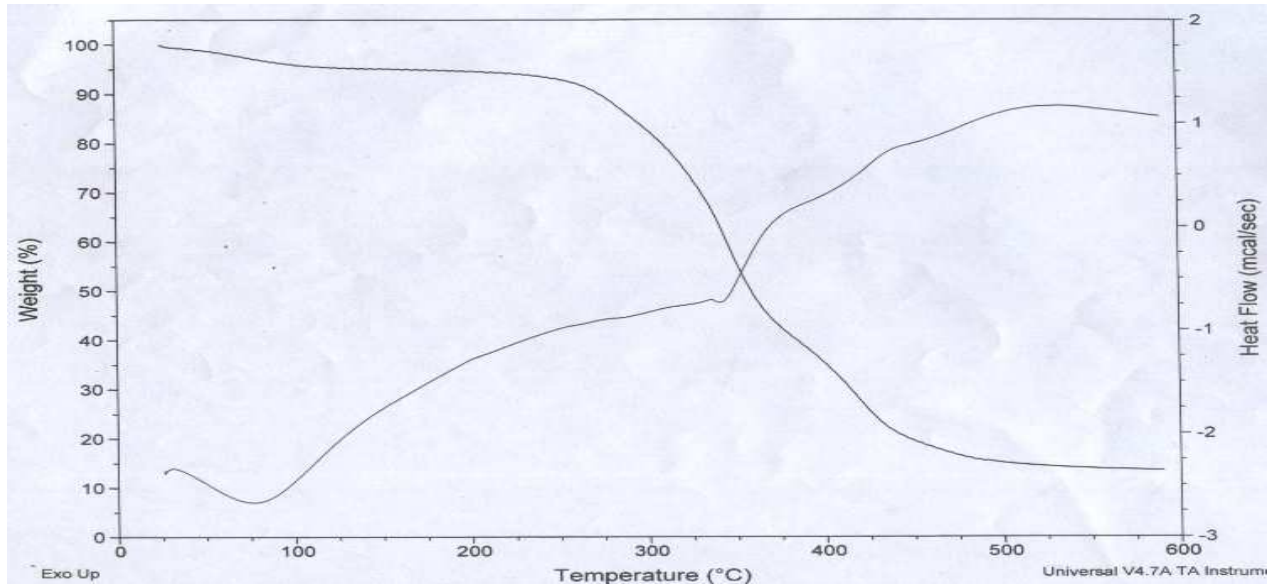


Figure 5: TGA-DSC curves of W-1

TGA-DSC analysis of nanocomposite biopolymer

Fig. 6 elaborate the thermal degradation results of W-2. Its 5% weight was exhausted at the 275°C which was more than sample W-1. The 50% weight was exhausted at 360°C and 85% exhausted at the 500°C. DSC line of W-2 also showed three humps. The NBP melted at 350°C and then recrystallized. Its second melting point was observed at 450°C which due to the presence of nanoparticles.

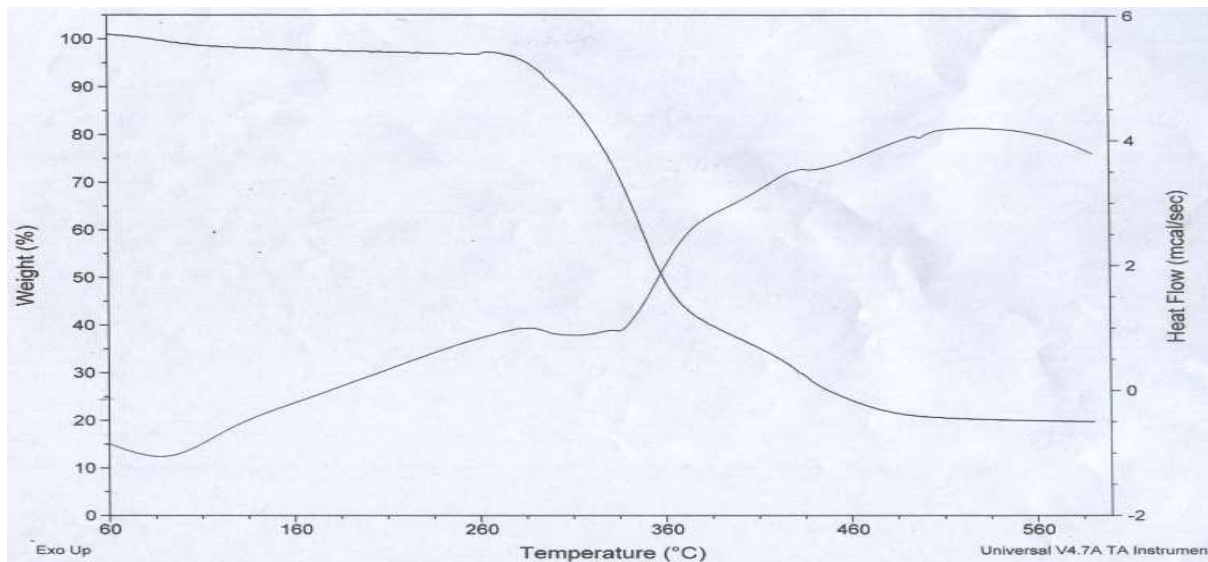


Figure 6: TGA-DSC curves of Sample W-2

Biodegradation studies. Soil Burial method was used for the biodegradation study of synthetic polymer samples. Many microorganisms (bacteria, fungi) were present in the soil which plays a core role in the decomposition of polymers or materials which decompose the polymers through the action of their enzymes [17].

The biodegradation results (Table 1) depicted that percentage weight loss of nanocomposite biopolymer was very low than simple grafted polymer. The sample W-1 absorbed moisture in the initial days and its weight increased but

W-2 was found to be moisture resistant and its mass did not increase. These results also proved that nanoparticles provided resistance against microbial action and decreased its degradation rate. This resulted in much lower percentage weight loss in W-2 as compare to W-1 (Fig. 7).

Table 1: Weight loss of W-1 and W-2 in soil

Sample ID	Initial weight of Sample (grams)	Weight loss after 10 days (%)	Weight loss after 20 days (%)	Weight loss after 30 days (%)	Weight loss after 40 days (%)	Weight loss after 40 days (%)	Weight loss after 50 days (%)
W-1	0.98	-9.37	-3.128	5.10	14.58	19.69	29.09
W-2	1.02	0.99	2.96	4.92	6.8	8.5	11.05

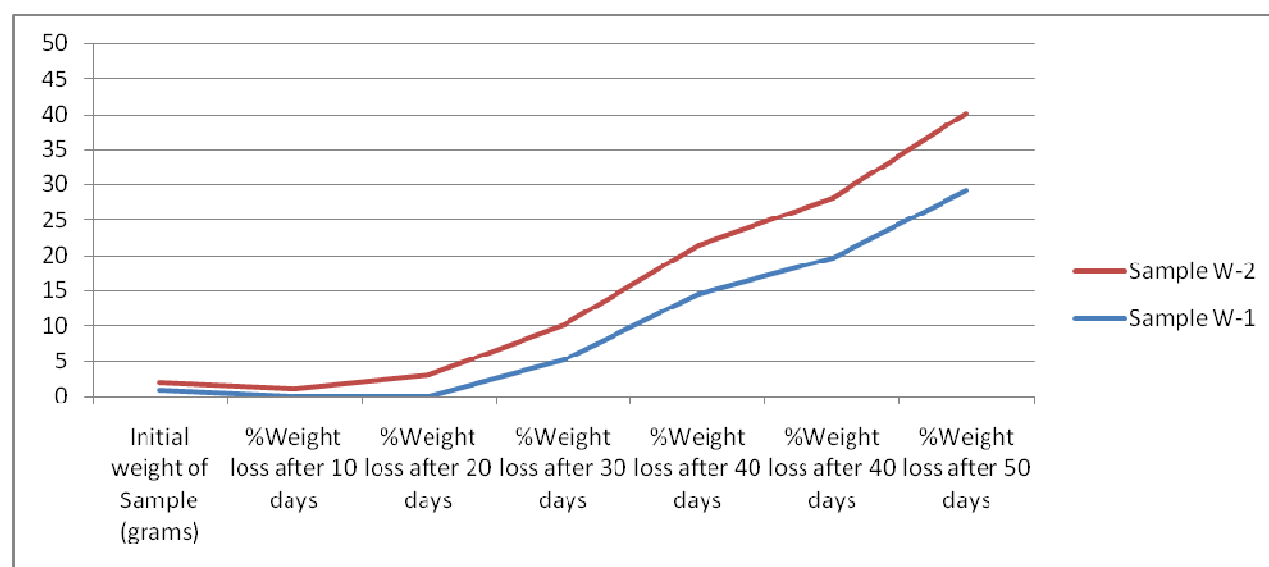


Figure 7: Comparison of weight loss of W-1 and W-2

Conclusion

Gelatin based grafted copolymer was synthesized with vinyl acetate and acrylonitrile monomers. This grafting process was carried out through the free radical polymerization mechanism with the use of an initiator (potassium per sulfate). The copolymers were analyzed by the use of FTIR, TGA-DSC techniques. FTIR peaks at 1250, 1680 and 1440 cm^{-1} confirmed the grafting of monomers on the gelatin backbone. TGA and DSC results demonstrated the thermal degradation and melting points of the copolymer and nanocomposite biopolymer. The TGA analysis was proved that degradation rate of nanocomposite biopolymer was lower than simple grafted polymer. DSC proved that nanocomposite biopolymer melting point was higher than unblended copolymer. Soil burial method was used for the estimation of biodegradation of these polymers. The biodegradation study of the prepared samples depicted that the percentage weight loss of nanocomposite biopolymer was very low than copolymer. Nanocomposite biopolymer was found to be moisture resistant and having low biodegradation rate. It was observed that the grafting was a useful process to induce microbial resistance in natural polymers. It was concluded that the nanocomposite biopolymers impart resistance against the fungi and bacteria, therefore these nanocomposite polymers can be successfully employed for the manufacturing food packaging material and disposable medical articles.

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