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PREPARATION OF SOYPROTEIN BASED NANOPARTICLE

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Abstract

Soy protein based Nanoparticles were prepared via direct graft copolymerisation of soyprotein isolate (SPI) with ethyl methacrylate at a temperature of 120◦c using benzoyl peroxide as a catalyst. The technique used here was emulsion polymerisation technique. The products obtained ie., the graft copolymer and the homopolymer Poly(ethyl methacrylate)(PEMA) were separated from the product mixture by dissolving the mixture using chloroform in a separating funnel. The separated graft copolymer in the emulsion form was then spreaded over a glass plate to make a nano plastic sheet and the sheet was allowed to dry for 24 hrs at room temperature to remove chloroform from it. FTIR study confirmed the grafting of SPI and PEMA. XRD studies confirmed the presence of nanoparticles. TG-DTA, Hydrolytic stability, chemical resistivity and water absorption of the sample were studied. Grafting efficiency and grafting percentage of the sample were calculated.

Keywords: Nanoparticles, Copolymerisation, homopolymer, emulsion.

INRODUCTION

Bio macromolecules from various renewable biomass resources such as polysaccharides and proteins have been considered as alternatives for petroleum-based polymers. Soy protein, generally regarded as one of the most potential to be used as plastics in many applications, which will reduce environmental waste and add value to agricultural products .But it was hydrophilic in nature [1]. So, many researchers done their research works based on soy protein grafted polymers.

Many researchers prepared SPI films for making packaging materials by grafting SPI with fatty acids to increase the water barrier characters. Some examples were SPI films modified by glycerol and oleic acid. [2], Extrusion of soy protein with gelatin and sugars at low moisture content [3] and SPI/Cellulose derivative blends [4]. Heat resistant sustainable adhesives based on soy protein isolate [5] were prepared by Jane L O Dell, Christopher G Hunt etal. Textile fibres were prepared from soy protein and zein blend [6] .To improve the properties of certain fibers some researchers were modified the surface of the fibers by using soyprotein.Zhao Jia and Yangong Yang modified PAN [7] and PAC fibers using soy protein [8].

Green plastics and Bio composites were also prepared by researchers. Preethi Lodha and Anil N Netravali [9] synthesised green plastics from stearic acid modified SPI and Bio composites from SPI and ramie fiber[10]. Chabba and Netravali [11] prepared green composites from flax yarn and gluteraldehyde/PVC modified SPC. Greencomposites and nanocomposites were also synthesised from soybean oil. [12] Bionanocomposite films were prepared by reinforcing nanoparticles such as montmorillonite in protein matrix. [13]. recently some researchers synthesized casein grafted nanoparticles [14] having excellent properties. The objective of the present study was to prepare and characterize nanoparticles using SPI and PEMA.

MATERIALS AND METHODS

Materials Required

SPI (ebay.in), Ethylene diamine tetraacetic acid disodium salt dihydrate (Nice chemicals), distilled and deionised water, Ethyl methacrylate (Sigma Aldrich), Benzoyl peroxide (Emparta, Merck), Sodium bicarbonate (Nice chemicals).

Method of Preparation of Soy grafted Poly (ethyl methacrylate)

SPI was first purified by adding 1% EDTA disodium salt dihydrate with it and stirred it at 50◦c for 48 hrs. This method was used to remove any metal ions present in SPI.

The purified SPI was then dissolved in the mixture of water (100ml) and Na2CO3 (0.1g) at 50◦c. Then ethyl methacrylate was added to it. The Ethyl methacrylate and SPI ratio must be 4:1.The mixture was then taken in a water-jacketed three necked flask equipped with thermometer, condenser and nitrogen inlet. The flask was then kept on a rota mantle which had both stirring and heating. First the mixture was heated at 120◦c for 30 minutes. After 30 min Benzoyl peroxide (~o.o8g) was added to it and again heated at the same temperature for 4hrs.The product obtained was taken in a separating funnel along with chloroform and the homopolymer PEMA and SPI-g-PEMA Nanoparticls were separated.

The emulsion form of SPI-g-PEMA was then spreaded over a glass plate and it was allowed to dry for one day and it was made into a sheet of nanoparticles.

CHARACTERIZATION OF SPI-g-PEMA NANOPARTICLES

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FTIR Measurements

A piece of SPI-g-PEMA Nanoparticles sheet was pulverized and compressed in KBr to form pellets. The Nicolet 750 FT-IR spectrometer was used to analyse the grafting of the above sample.

X-Ray diffraction studies

The X-ray diffraction patterns of the sample were measured using XPERT-PRO Diffractometer system at room temperature with a scanning range from 10◦to 80◦.

Thermogravimetric Analysis

Thermogravimetric properties of SPI-g-PEMA Nanoparticle sheet was measured using TG/DTA Instrument SIINT 6300, Japan with DSc calculations. The specimen was scanned in nitrogen atmosphere from 100to700◦c at a temperature range of 10°C/min.

Water Absorption Measurement

Soy based nanoparticle was dried in an oven at 50◦c for 24 hrs and cooled in a dessicator before weighing. This sample was then submerged in distilled water with 15 days interval time, water on the surface of the sample was removed and the sample weight was measured

Water absorption % = $\frac{A-B}{B}$ *100

Where A → weight of the sample after immersion in water

B → weight of Original sample

Grafting Percentage

The grafting % a nd grafting efficiency were calculated using the formula as follows.

Grafting % =weight of PEMA branches x100

Weight of SPI charged

Grafting Efficiency = weight of PEMA branches x100

Weight of EMA charged

Hydrolytic stability test

In this test, the soy based nanoplastic sheet was immersed in 5ml of water, ethanol, salt solution (1N NaCl) and the weight change was noted in15 days interval upto 60 days.

Chemical resistance test

For this, the soy based nanoplastic sheet was immersed in Acid [HCl,1N], Base[NaOH,1N] andH2O2[oxidant].at room temperature and weighed at 15 days interval for 60 days.

Stability in Organic solvents:

Organic solvents like chloroform, DMA, DMF, Hexane were taken and the soy based nanoparticle was immersed in it. The change in weight was noted at room temperature at 15 days interval for 60 days.

RESULTS AND DISCUSSION

FTIR

Fig 1 represents the ftir spectrum of SPI and Fig 2 represents the ftir spectrum of SPI-g- PEMA.The additional peak at 1743 cm^{-1} confirmed the grafting of SPI and PEMA.From the spectra,it was known that the methoxy group from the PEMA combined with one of the hydrogen present in the -NH_2 group forming a new amide linkage.

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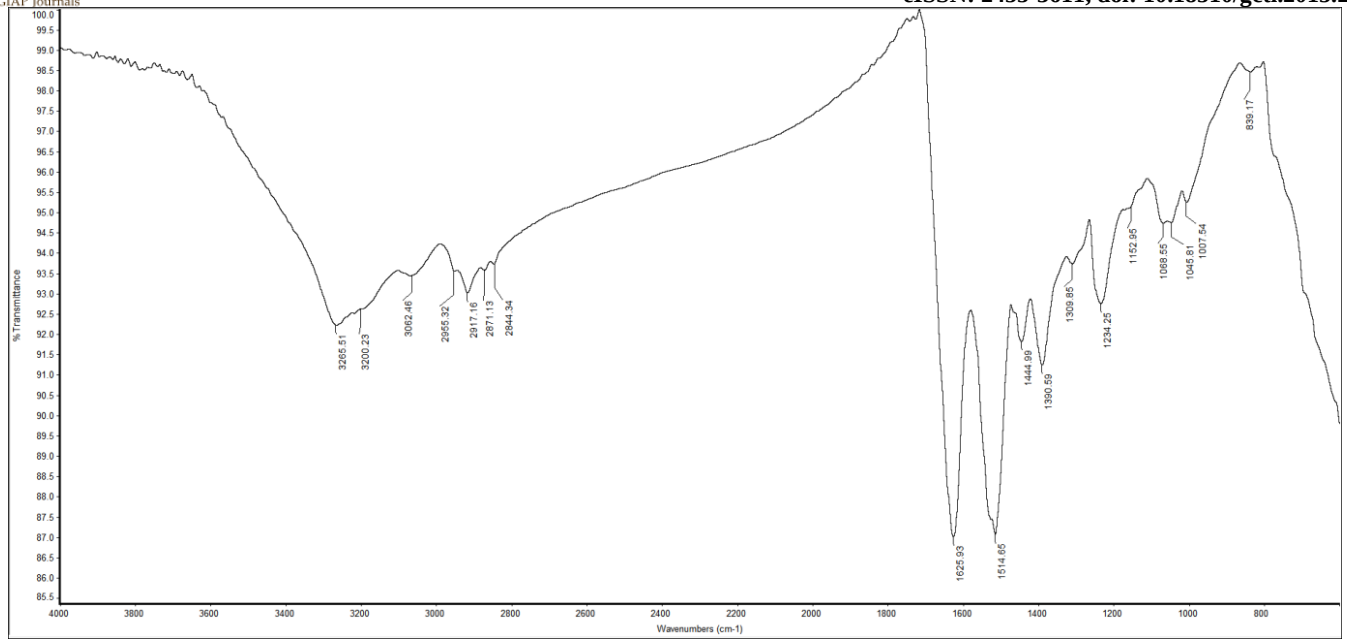

Figure 1: FTIR spectrum of pure SPI

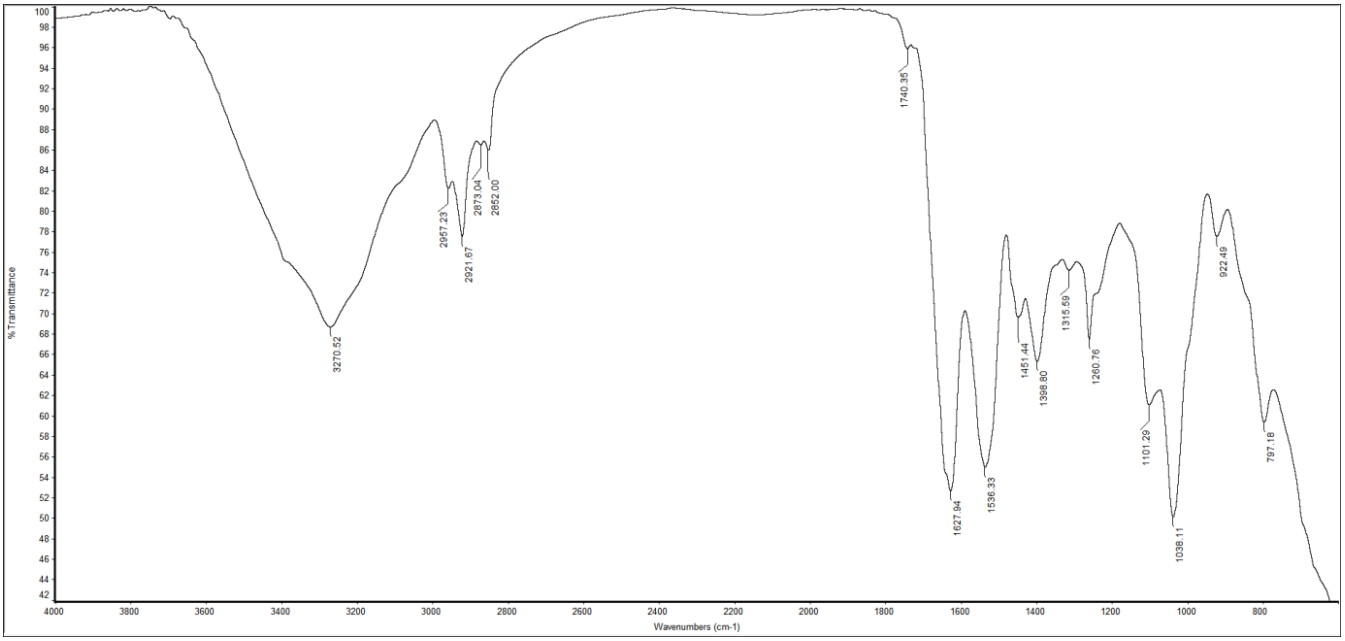

Figure 2: FTIR Spectrum of soy-g-pema.

XRD Studies

The CXRD graph (fig 3) showed a broad peak at a position of 2φ range of 12.26 in which the d-spacing was 7.2A◦.The broad peak in the XRD measurement confirmed the presence of SPI-g-PEMA nanoparticles. From the scherrer's equation, the size of the nanoparticles can be calculated.

$$T = \frac{K\lambda}{\beta \cos\theta} \quad \text{..... (15)}$$

Where, I – means size, K – dimensionless shape factor ~0.9,

λ – X-ray wave length, β – FWHM, θ – Bragg angle.

The size was calculated as 5.3 nm.

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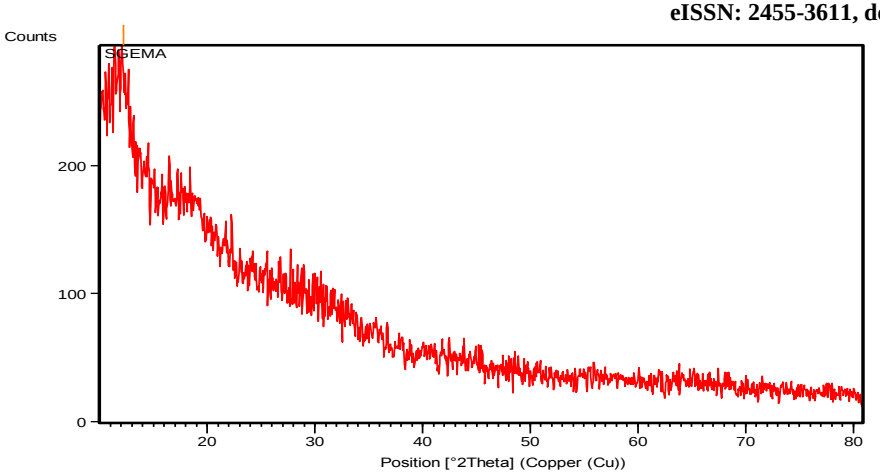

Figure 3: XRD graph

Thermogravimetric Analysis

TGA: The TG-DTA thermogram was illustrated in the (fig. 4)

The first degradation temperature starts above 80° C with a weight loss % of ~11.6. The second decomposition temperature starts above ~420^{0}C with a weight loss % of ~90.

DTA

The first broad endothermic peak at about 300^{0}C showed that first decomposition starts at this temperature and then this nano particle regain its original shape at ~400^{0}C. The second broad endothermic peak at about 450^{0}C showed that the remaining part of nano particle starts its complete decomposition at this point.

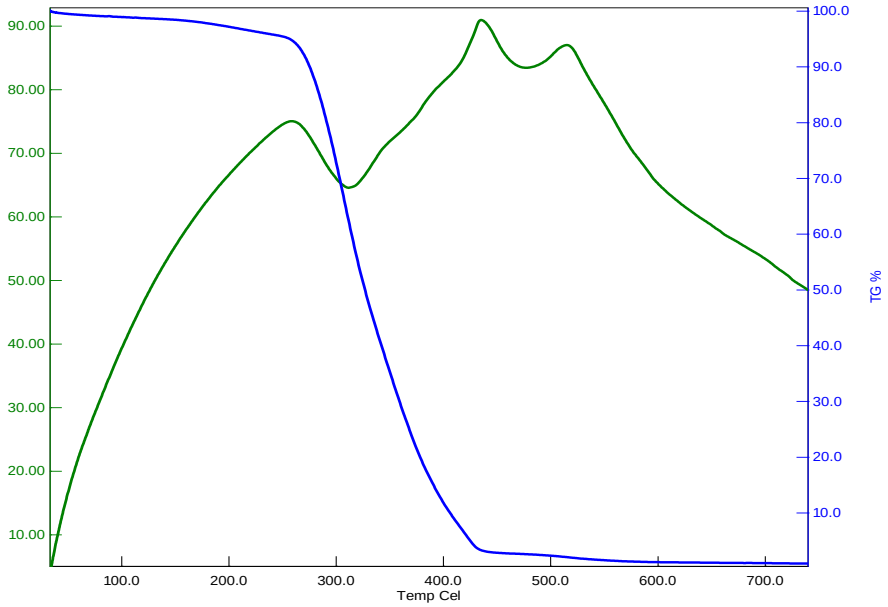

Figure 4: Thermogram of soy-g-PEMA

Water absorption measurement

Since SPI was hydrophilic in nature. It was expected that the SPI-g-PEMA nano particle sheet would absorb some amount of water but there would be no water absorption in the SPI-g-PEMA nano particle sheet which showed the improvement of water repulsion property in the nano particle sheet.

Grafting % and Efficiency

The grafting % of SPI-g-PEMA bionanoplastic was 13.2%. The grafting efficiency % of the sample was ~40% which was greater than casein-g-PEMA.

Hydrolytic stability test

The result for this test was shown in table. 1

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Table 1: Hydrolytic stability test

Solvent	Inference
Water	Insoluble
Ethanol	Insoluble
1N NaCl	Insoluble

This showed high stability nature of nano plastic. So that it could be used as packing material.

Chemical Resistant test

The result were shown in table.2

Table 2: Chemical Resistant test

Solvent	Inference
HCl	Insoluble
NaOH	Insoluble
H_2O_2	Insoluble

From the result chemical resistance was identified. This showed the excellent grafting between SPI and PEMA.

Stability in Organic solvent

The nano plastics would dissolve in chloroform within 1 hr but it was insoluble in other solvent. This also proved the strong grafting between SPI and PEMA.

CONCLUSION

FT-IR study confirmed the grafting between SPI and PEMA. XRD confirmed that SPI-g-PEMA was a bio nano plastic. TG-DTA showed its thermal stability up to a temperature of 450^0 C. various other results also showed that this nano plastic would have high hydrolytic stability, chemical resistance and also stable in even organic solvent except chloroform. From this it was found that chloroform is the only solvent to dissolve this nano plastic. From the water absorption measurement it was assumed that there would be reduction in moisture absorption in this nano particle. There would be increase in grafting % and efficiency in this nano particle than casein-g-PEMA.

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