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# PREPARATION OF CASEIN-G-POLY (ETHYL METHACRYLATE) NANOPARTICLES

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## ABSTRACT

Poly (ethyl methacrylate)(PEMA)/Casein nanoparticles with a well defined core shell structure having diameter 3.4 nm was prepared through direct graft copolymerization using small amount of benzoyl peroxide in water as catalyst at 80°C. The presence of casein micelles promoted the emulsion polymerization of the monomer and the particles stability. The graft copolymer and homo polymer were separated using chloroform as the solvent. The separated copolymer emulsion was immediately spread over a glass plate and was dried in air to form a bionanopolymer sheet. The polymer sheet sample was characterized using FTIR, TG-DTA and X-Ray diffraction studies. The scanning electron microscopic image of the nanoparticles showed that PEMA cores were coated with casein shells with well-defined core shell morphology. The conversion and grafting efficiency were also calculated.

**Key words**: Casein, Copolymerization, Micelles, Homopolymer.

## INTRODUCTION

Now a days, most of the research and development processes are accelerated on the basis of biodegradable polymer by using natural resources such as proteins and natural oils[1]. Casein, a milk protein has been a principal binder in leather finishing for a long time because of its good strength, dyeability, resistance to oil, grease and solvents. It is brittle and its water absorption is very high because of the presence of hydrogen bonds of carbonyl and amino groups[2].

Casein has inherent hydrophilicity which impairs water resistance, so to overcome this, several researchers utilize graft copolymerization technique.

Some of the examples are synthesis of casein-g-poly(methyl acrylate)[3], poly(methyl acrylate)-II[4], poly(n-butyl methacrylate)[5], graft copolymerization of acrylamide onto casein[6],

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poly(vinyl acetate)-II[7], poly(butyl acrylate)[8] etc. Grafting casein onto polyacrylonitile fiber[9], graft co-polymerization of butyl acrylate[10], wool[11] as well as styrene[12] onto casein are examples for surface modification.

Recently, some researchers reinforce starch nanocrystals to prepare soy protein plastics[13] while some researchers synthesize nanoparticles with core-shell structure[14-17]. In the case of casein, only one researcher[18] synthesized poly (methyl methacrylate)/casein nanoparticles with a well-defined core shell structure. In the present study, poly (ethyl methacrylate)/casein nano particles with a well-defined core shell structure was prepared.

## EXPERIMENTAL

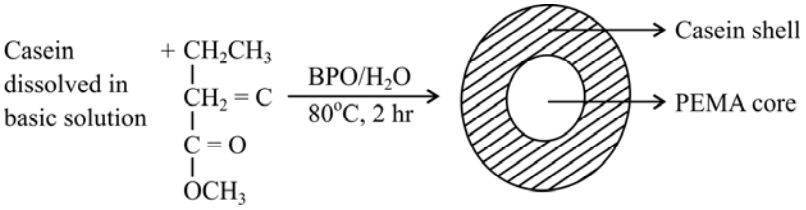
### Materials

### Preparation of casein from skimmed milk[19]

A solution for precipitation was prepared by dissolving 7 mL of glacial acetic acid in 50 mL of water. Skimmed milk (600 mL) was taken in a 1 liter beaker and warmed up to 110◦F. The above prepared acetic acid solution was added drop wise till a mass of casein was separated. The separated casein was filtered and washed with water followed by ethanol to remove organic as well as inorganic impurities. Other chemicals used were EMA (Sigma Aldrich), benzoyl peroxide (Emparta, Merck), sodium carbonate (nice chemicals). Fresh deionized and distilled water was used as the dispersion medium.

### Preparation of casein/PEMA nanoparticles

Purified casein (1 g) and sodium carbonate (0.4 g) were dissolved in water at 50°C. This mixture was then mixed with ethyl methacrylate (4 g) in a water-jacketed three necked flask equipped with a thermometer, condenser and a stirrer. After 30 min, benzoyl peroxide (0.08 g) was added and heated for about 2 hrs. The product obtained was dissolved in chloroform and the PEMA homopolymer and casein-G nanoparticles were separated using the separating funnel. The jelly layer contains the bionanoparticles. The reaction for the formation of casein-G-PEMA was shown in the **Scheme 1**.



**Scheme 1: Chemical equation for the formation of casein-G-PEMA**

## Measurement and characterization of the nano particles

### FT-IR

Infrared spectra were recorded on a Nicolet 750 Ft-IR spectrophotometer with KBr disks.

### X-ray Diffraction structures

The XRD measurement was taken on a XPERT-PRO diffractometer system at room temperature with scanning range from 10° to 80°.

### Thermo gravimetric analysis

The TG-DTA measurement was carried out in a nitrogen atmosphere on a TG/DTA with DSC calculation, SIINT 6300, Japan.

### Scanning electron microscopy

The SEM micrographs were taken by using the instrument JEOL/EO JSM-6610 with 5 and 10 micrometer size ranges.

### Grafting percentage

Grafting percentage and grafting efficiency were calculated using the formula as follows:

$$\text{Grafting (\%)} = \frac{\text{Weight of PEMA branches}}{\text{Weight of casein changed}} \times 100 \qquad \ldots(1)$$

$$\text{Grafting efficiency (\%)} = \frac{\text{Weight of PEMA branches}}{\text{Weight of EMA polymerized}} \times 100 \qquad \ldots(2)$$

### Water absorptivity

The water absorptivity of the sample was analyzed by immersing in a known volume of water and the sample was weighed at an interval of 15 days.

Water absorption (%) has been calculated using the formula.

$$\text{Water absorption (\%)} = \frac{A - B}{B} \times 100 \qquad \ldots(3)$$

Where A – Weight of sample after immersion in water, and

B – Weight of the original sample

# RESULTS AND DISCUSSION

## FT-IR spectral analysis

FT-IR spectrum of pure casein is shown in Fig. 1. FT-IR spectrum of grafted polymer is shown in Fig. 2. The additional carbonyl peak at 1720 $cm^{-1}$ proved the grafting of casein and poly (ethyl methacrylate).

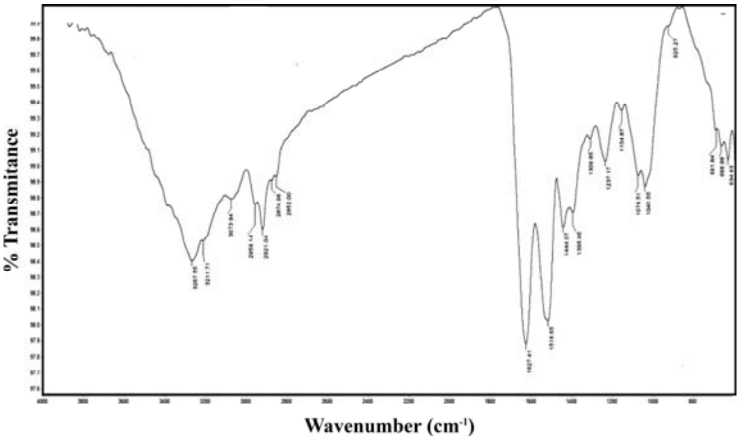


**Fig. 1: FT-IR spectrum of casein**

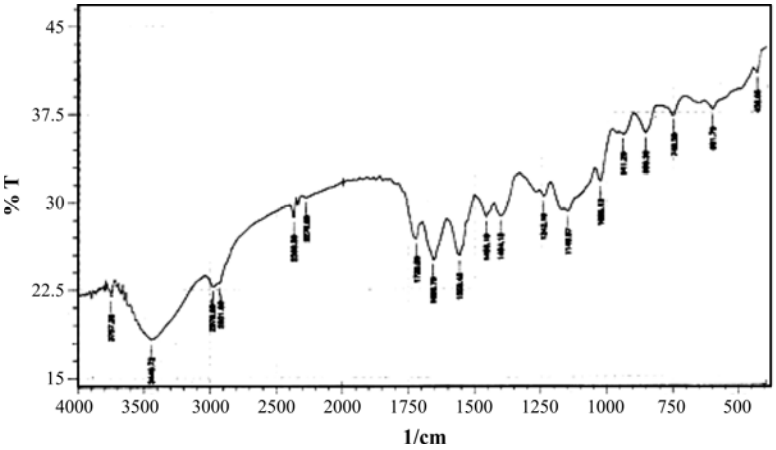


**Fig. 2: FT-IR spectrum of casein-G-PEMA**

## X-Ray diffraction studies

The broad peaks of XRD showed the presence of nanoparticles. The size of the nanoparticles was determined using Scherer's equation[20].

$$I = \frac{K\lambda}{\beta \cos\theta} \quad \ldots(4)$$

Where, I – means size, K – dimensionless shape factor ~0.9, λ – X-ray wave length, β – FWHM, and θ – Bragg angle.

The size was calculated as 3.4 nm

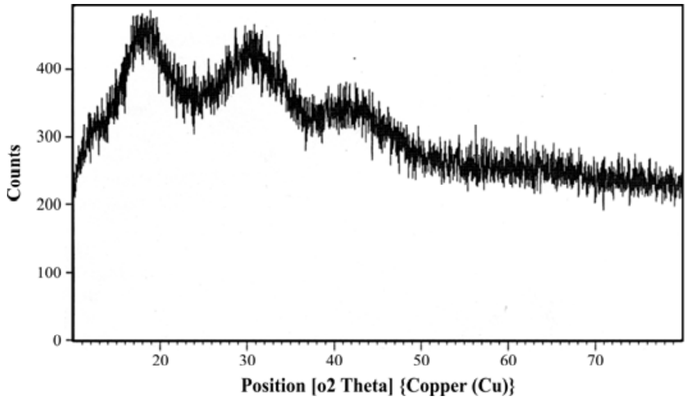


**Fig. 3: XRD pattern**

## TG-DTA

TGA scan of casein-G-PEMA nanopolymer sheet is represented in Fig. 4. The degradation temperature between 100-200°C was due to the moisture absorption. The decomposition temperature above 275°C showed the removal of grafting between casein and PEMA. The decomposition temperature above 490°C, showed the decomposition of both casein and PEMA.

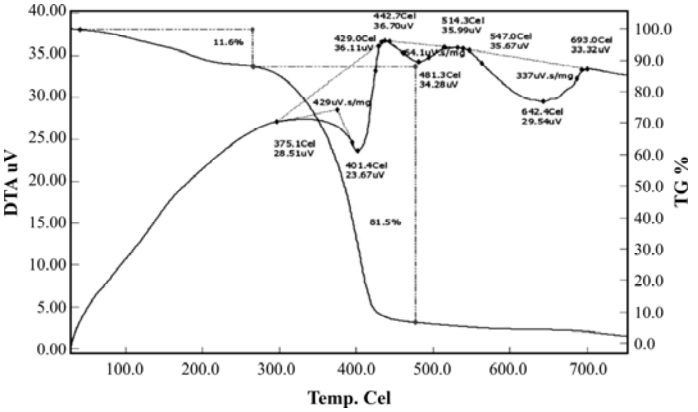


**Fig. 4: TG-DTA curve of casein-g-PEMA**

The DTA curves showed two exothermic and two endothermic peaks which showed that chemical and physical changes both occurred in the nanoparticle during heating.

## SEM

The SEM micrograph of the nanoparticles is presented in Fig. 5. The core-shell structure of casein-G-PEMA was confirmed from the SEM image.

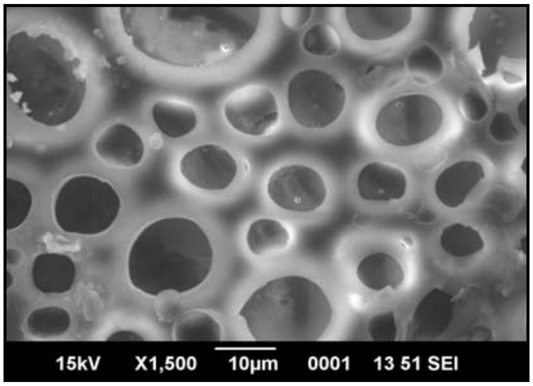


**Fig. 5: SEM image of casein-G-PEMA**

## Water absorptivity

It is clear from Fig. 6 that water absorptivity increased for the first 30 days as shown by the weight change and but after 45 days and after 90 days, there is no absorptivity of water and the weight remains the same. This is due to the hydrophilicity of casein. So this nanoparticle may be used as drug delivery carriers.

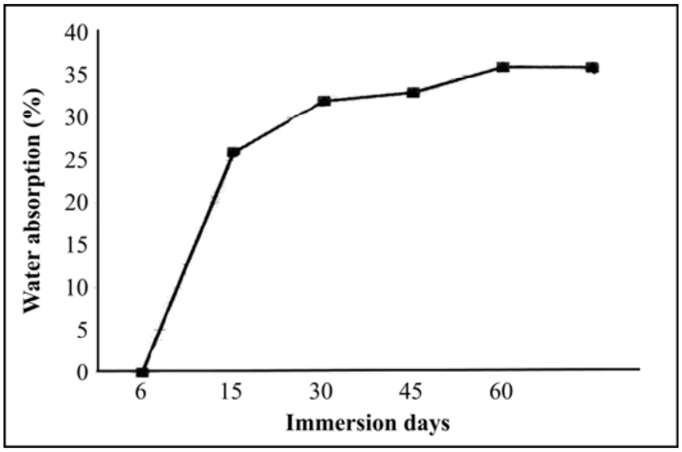


**Fig. 6: Water absorptivity of casein-G-PEMA bionanoplastic**.

## Grafting percentage

The grafting percentage of casein-G-PEMA bionanoplastic was 12.9% and grafting efficiency (%) was 32.25%.

## CONCLUSION

From the SEM results, it is clear that casein-G-PEMA biopolymer was having nanoparticles with a well-defined core-shell structure with casein as a core shell surrounding PEMA. The FTIR results confirmed the grafting of casein and PEMA. XRD studies also confirmed the presence of nanoparticles. Thus, casein-G-PEMA was confirmed to be a bionanoplastic with a well-defined core-shell structure.

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