

## **Interpenetrating polymer networks based on polyamine modified castor oil , chitosan and poly methylmethacrylate: Synthesis, chemical, physical and mechanical properties**

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### **Abstract**

A series of interpenetrating polymer networks (IPNs) of castor oil based polyamine/Polymethylmethacrylate (Polyamine/Polymethylmethacrylate: 80/20, 60/40, 50/50, 40/60 and 20/80) were synthesized by condensation reaction of castor oil with chitosan and methylmethacrylate, employing benzoyl peroxide and ethylene glycol dimethylacrylate as initiator and cross linkers respectively. The physical, chemical, optical and some of the physical and mechanical properties of Polyamine/Polymethylmethacrylate were studied.

*Keywords* : castor oil; chitosan; interpenetrating; mechanical; physical ; strain.

(IPNs)

Polyamine/Polymethylmethacrylate: 80/20, 60/40, 50/50, )

( 40/60 , 20/80

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### **Introduction**

Interpenetrating polymer networks (IPNs) constitute a group of polymer composite materials possessing unique properties which are related to their method of synthesis<sup>[1]</sup>.

Interpenetrating polymer networks (IPNs) is defined as a combination of two polymer networks where at least one polymer is synthesised or crosslinked in

the presence of the other. As physical blends and copolymerization the IPN is another way to combine two different polymers. There are no covalent bonds between the two polymers, so a generic A monomer reacts only with other A ones, and on the other hand B monomer reacts only with B ones. The resulting material swells but does not dissolve in a given solvent<sup>[2]</sup>.

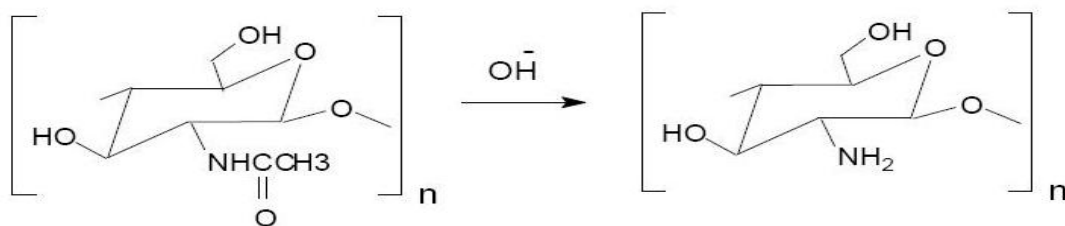
IPNs could be classified as sequential or simultaneous, depending on the way that the polymerisation is carried out. They could be also defined as a *latex IPNs*, when the polymers are synthesised by emulsion polymerisation; a *gradient IPN*, when each surface of the film is predominately of one type of polymer and there is a gradient inside the film; a *thermoplastic IPN*, when there is physical crosslink rather than chemical crosslink in the polymers, and a *semi-IPN* (SIPN) when just one of the polymers is a network [3].

Chitosan a natural linear polyamine with a high ratio of glucosamine to acetylglucosamine units, is a weak base and

carries a positive charge. Its solubility is pH-dependent, and it reacts readily with negatively charged surfaces [4].

Chitosan is obtained from the deacetylation of chitin. Chitin is one of the most abundantly available polymers after cellulose. Chitosan is a copolymer of glucosamine and N-acetyl -glucosamine and it has an amine functional group which is strongly reactive [5].

In terms of its chemical structure (Scheme 1), chitin and chitosan have similar chemical structure. Chitin exhibits structural similarity to cellulose and differs from it with the replacement of C-2 hydroxyl residues by acetamide groups [6].



**Scheme 1: Chemical structures of chitin and chitosan**

Chitin can be transformed into chitosan that has free amino groups by removing acetyl groups ( $\text{CH}_3\text{-CO}$ ) from chitin molecules. Chitosan (deacetylated chitin) is insoluble in water, alkali and organic solvents, but soluble in most diluted acids with pH less than 6. When chitosan is dissolved in an acid solution, it becomes a cationic polymer due to the protonation of free amino groups on the C-2 position of pyranose ring [7].

Its cationic properties in acidic solutions give it the ability to interact readily with negatively charged molecules such as fats, cholesterol, metal ions, and proteins [8].

## Experimental

### Materials and Sample Preparation

Castor oil and chitosan was obtained from the local market, ethylene glycol dimethylacrylate and benzoyl

peroxide from Aldrich, USA. Methylmethacrylate monomer from MR. Dental supplies LTD, UK was freed from stabilizer prior to use.

### Preparation of chitosan

The raw material, exoskeleton of fresh prawn for preparation of chitosan was obtained from local market. The shells and head of fresh prawn were thoroughly and repeatedly washed in water and sun drained. The raw material was completely immersed (steel container) in 3 % sodium hydroxide and boiled for 30 minutes for deprotenization. After cooling the alkali solution is drained off and washed repeatedly and finally with ionized water to obtain neutral pH. The contents were transferred to a plastic container and 5 % hydrochloric acid added and allowed to act for 30 minutes. The acid was decanted and repeatedly washed with water and then

with ionized water. The excess water from the chitin obtained is removed by squeezing in a sterile lint cloth and air-dried. Chitin was immersed in 40 % sodium hydroxide and heated up to 90 °C for 90 minutes. The sodium hydroxide is quickly drained off, the content washed repeatedly with water, finally with ionized water and the chitosan obtained was air dried after removing the excess water as above. The prepared chitin and chitosan was sterilized with ethylene oxide and packed in pre autoclaved polyethylene containers<sup>[9]</sup>.

### Prepolymer preparations

The prepolymer was prepared by reacting the chitosan (2.11 g) and castor oil (3.14 g) were taken in 50 ml beaker, thoroughly mixed with a glass rod and then heated about 4 hours at 170 °C in a vacuum oven until bubbling ceased followed by ( 2 ) hours post-curing. Stirring was carried out for 15– 20 min to complete the reaction such that terminated polyamine prepolymer was obtained as a thick yellow syrup.

### Synthesis of Poly amine– Polymethylmethacrylate interpenetrating polymer networks

The required quantities of amine prepolymer methylmethacrylate, ethylene glycol dimethylacrylate (0.5% based methylmethacrylate used), and benzoyl peroxide (0.5%) were placed in a round bottom flask fitted with a mechanical stirrer. The mixture was stirred at room temperature for (10–15) min. to form a uniform mixture. Compositions having higher amounts of prepolymer were highly viscous and the air entrapped during mixture was removed by applying vacuum. On the other hand, compositions rich in methylmethacrylate were heated at 70°C (to initiate the polymerization of methylmethacrylate) for different intervals of time until an optimum viscosity was obtained.

## Polymer Characterization

### Infrared spectra

Infrared spectra of the synthesized IPNs in KBr pellets were obtained from Shimadzu FTIR-8400S spectrophotometer. Whereas in case of PA, being a liquid, a thin film was cast over the NaCl block and its FTIR was recorded in laboratory of sciences college .

### Physical properties

The IPNs were characterized according to the ASTM standard specification. Density was determined by the displacement method according to ASTM-D-792-86[10] , ASTM D-676-58 J for shore-A hardness<sup>[11]</sup>.

### Optical properties

The optical properties were measured using a Suga Test, Hazemeter (Japan) using dust and grease free film of IPNs as per ASTM D-1003<sup>[12]</sup>.

### Mechanical properties:

The tensile strength and elongation at break were measured at room temperature using Instron Houns-Field universal testing machine model 4204 as per ASTM D-638 method<sup>[13]</sup>. Hardness measurements were made on Shore A hardness test apparatus using ASTM-2240 method<sup>[14]</sup>.

### Resistance to chemical reagents:

Acid, alkali and solvent resistance were estimated according to ASTM-D-543-67 method. Samples were hung in the reagent for seven days and tested for change in weight and for their film appearance<sup>[15]</sup>.

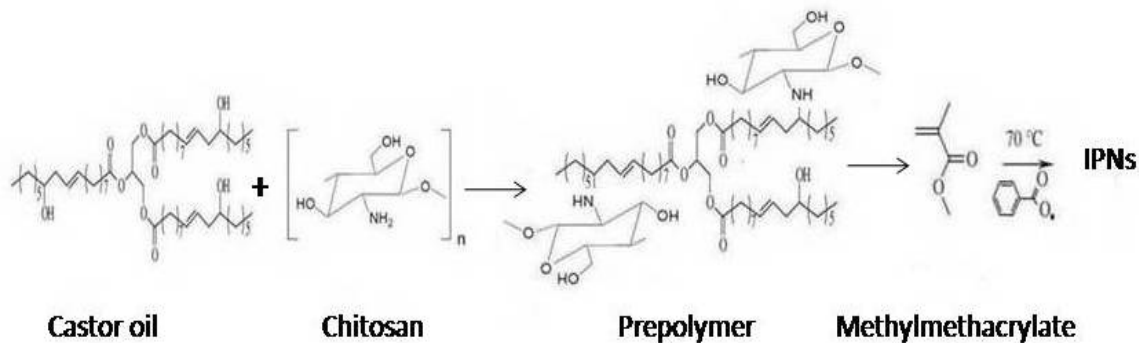
## Results and Discussion

### Infrared spectroscopy (IR)

The IPNs synthesis consists of sequential polymerization reactions as shown in the Scheme 2. In the first reaction, a step-growth polymerization between the castor oil hydroxyl groups and amine groups occurs resulting in chitosan . If the mixture was heated for a shorter period, then gelling took place, and the viscosity was so low that it led to the formation of molds in the sheet. The

polyamine obtained in a network form is swelled in methylmethacrylate and a free-

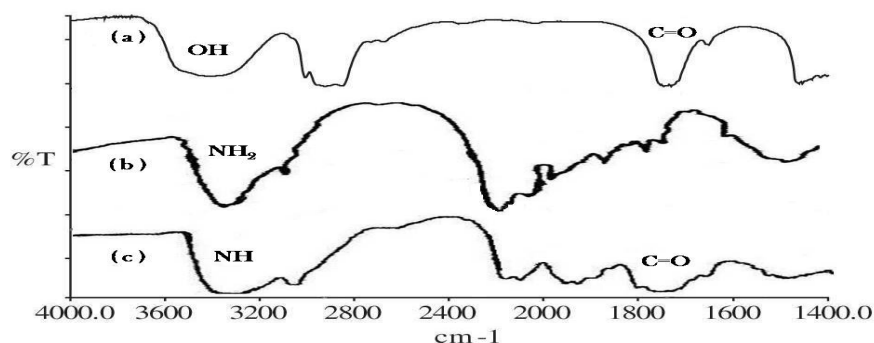
radical polymerization of it is carried out initiated by benzoyl peroxide.



**Scheme 2 : Chemical reaction between castor oil , chitosan and methylmethacrylate**

The chemical structure of castor oil polyamine network was analyzed by infrared spectroscopy. Figure 1 shows the infrared spectrums of castor oil , chitosan and the polyamine prepolymer. The reaction between castor oil -OH groups and chitosan -NH<sub>2</sub> groups run out after 30 min, regarding to the disappearance of the broad band in the spectrum around 3418 cm<sup>-1</sup>, due to -OH axial stretching vibration, and the appearance of a narrow

absorption in 3344 cm<sup>-1</sup>, related to the -NH axial stretching vibration. On the other hand the carbonyl absorption at 1737 cm<sup>-1</sup> changes the profile from the castor oil monomer to the polyamine been wider in that one obtained after 30 min. and the broad band in the region 3200 -3300 cm<sup>-1</sup> due to -NH in the spectrum of chitosan have become quite smaller around 3200 cm<sup>-1</sup> in the spectrum of polyamine . These indicate the formation of amine bonds .



**Figure 1 : FTIR spectra of a) castor oil; b) chitosan ; c) polyamine prepolymer .**

### Physical properties

All IPNs were synthesized as tough films from golden yellow to yellow color. The IPNs are almost insoluble and their densities are heavier than water. The densities of IPNs range from 40 to 67 g/cc. Density of IPNs increases with increase in Polymethylmethacrylate (because

polymethylmethacrylate density is > 1) composition. The densities of all IPNs are given in table 1 along with the composition of individual IPNs.

Surface hardness of the IPNs (table 1) reflects the resistance to local deformation which is a complex property related to modulus strength, elasticity and plasticity.

Surface hardness values lie in the range 6.1–19.5. Shore A surface hardness increases with increase in polymethylmethacrylate percentage which is due to hard nature of polymethylmethacrylate

### Optical properties

Results of diffuse light, total light transmittance and haze measurements are given in table 1. These indicate that the percentage of transmittance of light was very good in all IPNs films and in the range 49.2–82.8%. The difference is attributed to the variation in PA content of IPNs. The increase in polymethylmethacrylate content of IPNs decreases the transmittance and increases percent haze. Comparison of optical properties of 100% poly amine, as well as 100% polymethylmethacrylate component polymers indicate that polymethylmethacrylate is a transparent film than polyamine (castor oil + chitosan), has transmittance around 43% depending on the levels of  $\text{NH}_2/\text{OH}$  ratios. Thus IPNs containing a low poly amine content are good transparent films with minimum haze percentage.

### Mechanical properties

From the stress–strain curve, tensile strength, percent elongation at break, tear strength and initial modulus were tabulated in table 2. Tensile strength,

tear strength and modulus increased with increasing methylmethacrylate component, whereas, percent elongation decreased. It is probably because polymethylmethacrylate is harder and brittle in nature. Interpenetration of poly amine as a separate phase in polymethylmethacrylate brings about the enhanced modification in mechanical properties such as, tensile strength, tensile modulus and tear strength.

### Chemical resistance

The percentage weight loss of IPNs were determined in  $\text{H}_2\text{SO}_4$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{NaOH}$  etc. the results are furnished in table 3. All the IPNs show excellent acid and alkali resistance .

IPNs are swelled in solvents like methyl ethyl ketone (MEK),  $\text{CCl}_4$  and toluene.

### Conclusion

Interpenetrating polymer networks prepared from polymethylmethacrylate and the castor oil+ chitosan (polyamine) showed excellent chemical resistance, hardness, elongation, tensile strength properties and higher compatibility. Hence, it can be concluded that using the IPN concept, it is possible to design the most desirable material for a specific end use requirement.

**Table 1. Physical and optical properties of Poly amine / Polymethylmethacrylate IPNs.**

Sample code	Density (g/cc)	Shore A hardness	Total percentage of Transmittance	Percentage of haze
IPN1	40.0	6.1	49.2	90.0
IPN2	42.1	10.9	58.0	82.2
IPN3	52.8	16.8	75.5	80.1
IPN4	61.6	18.0	79.0	79.7
IPN5	67.0	19.5	82.8	78.0

**Table 2. Effect of Poly amine / Polymethylmethacrylate composition on the mechanical properties of IPN.**

Sample code	Tensile strength (MPa)	% Elongation	Tear strength (N/mm <sup>2</sup> )	Tensile modulus (MPa)
IPN1	2.00	109.6	1.45	27.0
IPN2	3.50	89.6	2.71	35.8
IPN3	7.11	84.0	2.96	43.0
IPN4	13.25	39.9	5.69	69.1
IPN5	30.95	15.3	8.98	91.2

**Table 3: Chemical resistance test (% weight loss on treatment with different chemical reagents).**

Chemical reagents	IPN1	IPN2	IPN3	IPN4	IPN5
25% CH <sub>3</sub> COOH	2.82	2.24	2.00	1.86	1.63
25% H <sub>2</sub> SO <sub>4</sub>	1.20	1.20	1.21	1.15	1.13
25% HCl	0.60	0.58	0.53	0.49	0.45
5% HNO <sub>3</sub>	0.56	0.51	0.50	0.44	0.41
10% NaOH	0.51	0.55	0.59	0.62	0.64
CCl <sub>4</sub>	18.52	17.23	15.42	13.00	12.04
Toluene	9.31	9.10	8.43	7.88	7.43
MEK	10.33	9.52	9.00	8.45	8.12

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