Mechanical and Chemical effect of Chitosan on BisGMA/PEOZ Blend Based Composites

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Abstract: ***This paper describes the mechanical and chemical effect of chitosan as reinforcing filler (0,10,20,30,40,50 wt%) on Bisphenol-A glycidyldimethacrylate (BisGMA)-Polyethyleneoxazoline (PEOZ)blend based composites. For this, BisGMA was synthesized followed by the preparation of various BisGMA/PEOZ blends using varying proportions of PEOZ (0, 30, 50, 60, 70 wt %). Mechanical properties of blends like tensile stress, Young's Modulus, elongation at break and impact strength were studied. The results suggested that the blend having 50 wt% of PEOZ and BisGMA is the optimum composition due to maximum improvement in all the mechanical properties. Thus, the composites were fabricated using the 50 wt% blend composition alongwith different weight percentage of chitosan and their properties were studied. The tensile strength, Young's Modulus, impact strength and hardness of composites were found to be increasing with increase in chitosan loading, reached an optimum at 40 wt% and thereafter decreased with further increase in chitosan content, whereas elongation at break decreased with chitosan content. Chemical resistance and ageing studies of composite systems were also investigated to ascertain their structural applications in aerospace and automobile industries.***

Keywords: BisGMA/PEOZ blend, Chitosan, Mechanical properties, Chemical resistance, Ageing studies

1. Introduction

The use of polymer blends and composites provides a very versatile strategy for designing new materials that fulfill the "green" requirements like lower costs without sacrificing properties, ability to tailor properties without creation of completely new polymer, high performance blend from synergistically interacting polymers and recycling of industrial and municipal scrap. Today, BisGMA is utilized as high performance matrix resin for composites due to its outstanding mechanical properties, thermal stability and moisture resistance[1]. But due to its high viscosity it has been blended with PEOZ, a thermoplastic polymer for its better structural, handling properties and improved performance [2]. Chitosan often described as "fiber from the sea" is a nontoxic, semicrystalline [3], biodegradable[4,5] and biocompatible[6,7] linear polysaccharide of randomly distributed N-acetyl glucosamine and glucosamine units. Chitosan offers remarkable biological properties, which have paved the way for its application in numerous fields[8,9] including polymer science.

Nowadays, the incorporation of polymer blends as the matrix resin in the fabrication of polymer composites is currently being investigated due to its diversified structural applications[10, 11, 12]. But information on the utilization of chitosan in polymeric composites is limited in the literature. Due to the biodegradability and the various material properties of chitosan, we have tried to explore it as a reinforcing filler in the composites. In this work, the optimum 50:50 BisGMA-PEOZ blend composition ($BGPO_{50}$) which is already reported[2] has been used as the matrix resin due to its enhanced mechanical properties. Here, chitosan, after being synthesized from chitin has been used as reinforcing filler in the composites which eliminates the use of any other fiber. Besides the fabrication of composites, the mechanical properties like tensile strength, Young's Modulus, elongation at break, impact strength and hardness have been studied here. Chemical resistance and ageing studies have also been conducted to test the durability of the fabricated composites. This work addresses the effectiveness of varying composition of chitosan as reinforcing filler on the mechanical properties, ageing studies and chemical resistance of BisGMA-PEOZ blend based composites.

2. Experimental

2.1. Raw Materials

BisGMA prepolymer was synthesized from methacrylic acid and diglycidyl ether of bisphenol-A-type epoxy resin (DGEBA) by using a reported method in our laboratory[1]. Similarly, BisGMA-PEOZ blend ($BGPO_{50}$) was prepared using Benzoyl peroxide (BPO) and t-Benzoyl peroxide (t-BPO) as initiator which is already reported[2]. Dicumyl peroxide (DCP) was purchased from Sigma-Aldrich. All other chemicals were available in our laboratory.

2.2. Methods

2.2.1. Deacetylation of Chitin to Chitosan

Raw prawn shell and crawfish shell were washed and dried followed by grinding and sieving. Then demineralization and deproteination was carried out with HCl and NaOH respectively. The product was decolourised with acetone, washed and dried after which chitin was obtained. It was again deacetylated with acetone, washed and dried to finally yield chitosan which was used directly used as filler.

2.2.2. Fabrication of BisGMA/PEOZ blend based Chitosan Composites

Firstly, various matrix formulations were prepared by adding chitosan in different weight proportions i.e. 0, 10, 20, 30, 40, 50 wt% to BisGMA-PEOZ blend ($BGPO_{50}$). At the beginning of fabrication, gelcoat with 2% (w/w) DCP was uniformly brushed in to the finished side of male and female parts of the mould. After one hour when curing of gelcoat was completed, the formulated matrices were poured into the mould one at a time for the fabrication of different composites. Then the mould was subjected to hot-press. The temperature was 110 °C for 1 h and pressure was 5 tons. The composite specimens are named as BGPOCC for BisGMA-PEOZ/Chitosan Composite where $BGPOCC_0$ refers to the pure 50:50 BisGMA-PEOZ blend system ($BGPO_{50}$) without any chitosan in it. Hence, the pure blend will be referred as $BGPCC_0$ hereafter. Details of the composite specification are given in Table 1.

Table 1: Materials Code

Sl.No.	*Materials Code*	*BisGMA(in grams)*	*PEOZ (in grams)*	*Chitosan* w.r.t BisGMA
1	$BGPOCC_0$	50	50	0
2	$BGPOCC_{10}$	50	50	10
3	$BGPOCC_{20}$	50	50	20
4	$BGPOCC_{30}$	50	50	30
5	$BGPOCC_{40}$	50	50	40
6	$BGPOCC_{50}$	50	50	50

3. Characterization

3.1 Fourier Transform Infrared Spectroscopy

FTIR spectra were collected using Thermo-Nicolate Model 400 instrument equipped with a controlled temperature cell (Model HT-32 heated demountable cell used with an Omega 9000-A temperature controller).

3.2 Mechanical testing

Mechanical properties like Tensile strength, Young's Modulus and Elongation at Break were evaluated using an INSTRON universal testing machine (Model 3369) according to ASTM D790-03 standard. Impact strength (IZOD) was measured in an impact tester as per D256-05. Hardness was measured under ASTM-D2240 standard using durometer (hardness Shore A). Standardized hardness-measuring equipment using a sharp needle was applied directly onto the surface of specimens to measure hardness. Data were averaged over five different positions. Data reported in this work are calculated as averages of the measurement carried out for five specimens.

3.3 Ageing studies

The ageing of composites on exposure to water was evaluated by keeping the samples immersed in water. Five specimens (25 mm x 25 mm) of each sample were kept immersed in distilled water at 30 ^{0}C for 31 days. The samples were taken out, dried at room temperature and their weights were taken. Data reported is the calculated average value of the samples taken.

3.4. Chemical resistance test

The chemical resistance properties of the BisGMA-PVP/chitosan composites in CCl_4, water, NaOH and HNO_3 were studied according to ASTM: D543-06. In each case, five pre-weighed samples were dipped in the respective chemical reagents for 24 h. They were then removed and immediately washed in distilled water and dried by pressing them on both sides with a tissue paper at room temperature. The samples were then weighed and the percentage weight loss/gain was determined using the following equation.

Weight loss/gain (%) = Final weight - Original weight/
Original weight (1)

4. Results and Discussion

4.1. Deacetylation of Chitin to Chitosan

In order to fully characterize the starting materials, a spectrum of pure chitosan was recorded as shown in Figure 1. The stretching vibrations of OH groups at 3447 cm^{-1} are overlapped to the stretching vibration of N-H and C–H bond in $–CH_2$ (2920 cm^{-1}) and $–CH_3$ (2874 cm^{-1})groups, respectively. Bending vibrations of methylene and methyl groups are visible at 1383 cm^{-1} and 1423 cm^{-1}. Absorption in the range of 1680–1480 cm−1 was related to the vibrations of carbonyl bonds (C=O) of the amide group CONHR (secondary amide at 1655 cm^{-1}) and to the vibrations of protonated amine group (NH_2 at 1599 cm^{-1}). Absorption in the range from 1160 cm^{-1} -1000 cm^{-1} has been attributed to vibrations of CO group. The band at 1156 cm^{-1} is related to asymmetric vibrations of CO in the oxygen bridge resulting from deacetylation of chitin. The bands near 1080–1025 cm^{-1} are attributed to CO of the ring COH, COC and CH_2OH. The small peak at ~894 cm^{-1} corresponds to wagging of the saccharide structure of chitosan.

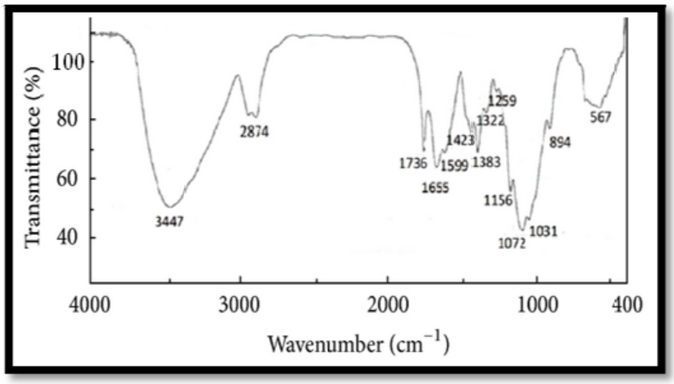

Figure 1: FTIR spectrum of Chitosan

4.2. Mechanical properties of BisGMA-PEOZ blend/Chitosan Composites

$BGPOCC_0$ shows improved mechanical properties than pure BisGMA. due to specific interactions like H-bonding and dipole-dipole interactions between molecules of the constituent polymers[2].

4.2.1. Tensile strength and Young's Modulus

Reinforcement of $BGPOCC_0$ with chitosan resulted in improved tensile property of composites because chitosan withstands maximum part of the load enabling efficient stress transfer. Thus, the values increase upto 40 wt% of chitosan content but decrease thereafter shown in Figure 2.

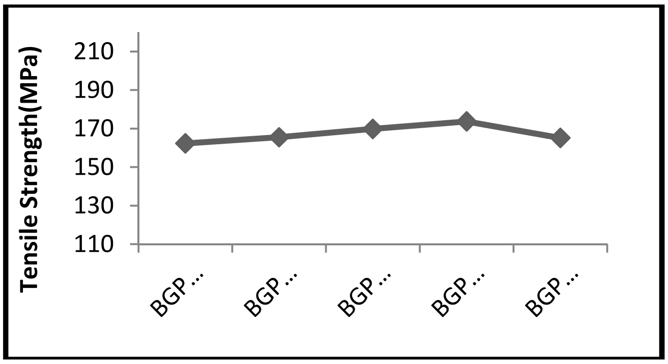

Figure 2: Tensile strength of composites

This decrease can be explained by the fact that as filler loading increases, the tendency of excess filler particles to agglomerate also increases. This leads to incompatibility between the components of the composites that give rise to low interphase adhesion between the matrix and the dispersed phase, particularly the adhesion of chitosan to BGPOCC$_0$.Similar observations have been reported by Bigg[13] and Fuad *et al*[14] for other filled systems.

The values of Young’s Modulus showed a similar increasing trend with chitosan content (Figure 3). This observation highlights the fact that incorporation of fillers into polymer matrix improves the stiffness of the composites. The better dispersion of filler with increasing composition and filler-matrix interaction may be the two main reasons or factors responsible for the observed trend.

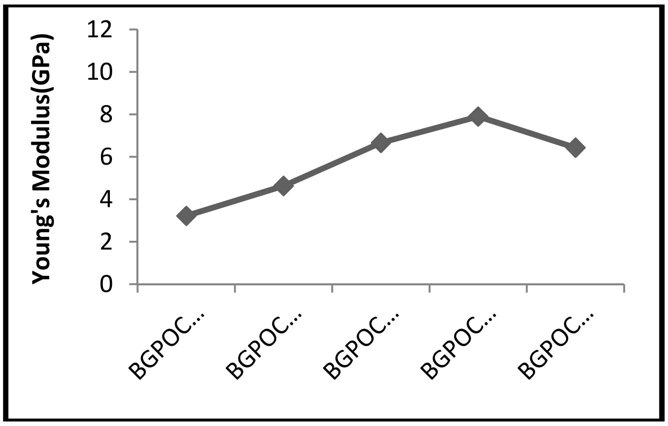

Figure 3: Young's Modulus of composites

4.2.2. Elongation at Break

Figure 4 shows that the elongation at break for BisGMA-PEOZ blend/chitosan composites decreases with increase in chitosan content. Fillers are structural elements embedded in the polymer matrix and at the concentrations used (10-40 wt%), the contents might not be high enough to significantly restrain the BisGMA-PEOZ blend. Consequently, highly localized strains might have occurred at the concentrations investigated, causing debonding between filler and matrix, and thus, essentially giving rise to a matrix that is non ductile. Such a reduction in elongation at break with increase in filler content has been reported by Ismail *et.al*[15] . But the gradual increase in the values after 40 wt% is due to the reduction in the strain of the composites.

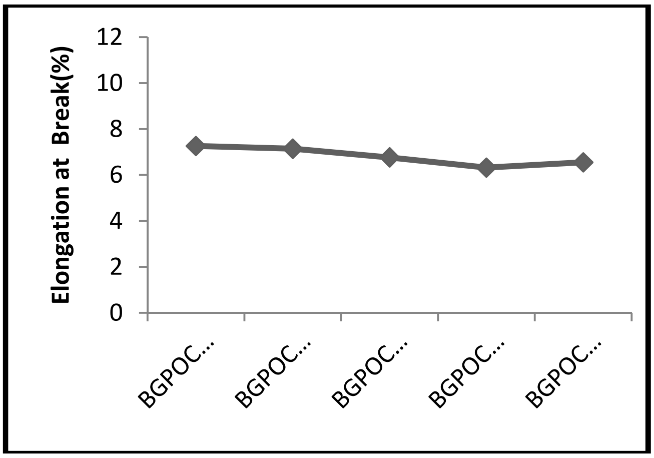

Figure 4: Elongation at break of composites

4.2.3. Impact strength

The impact strength of the composites was observed to increase with increase in chitosan content (Figure 5). This indicates that chitosan as reinforcing filler was quite effective in distributing the applied stress over a large volume at the base of the notch, which helped to prevent the propagation of cracks by carrying large part of the load in the area under the crack.But interestingly, the values of impact strength decreased after the 40 wt% chitosan content. This is because the agglomerating filler particles cause phase separation of the matrix and the dispersed phase which results in the formation of voids on the composite surface. As a result, the interfacial stress fails to propagate throughout the surface area thereby forming cracks easily and reducing the impact strength.

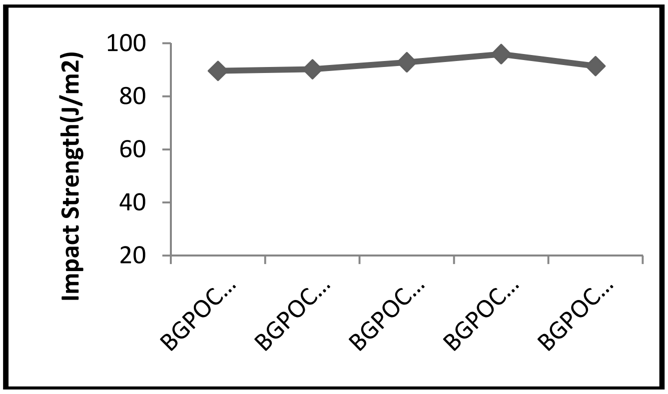

Figure 5: Impact strength of composites

4.2.4. Hardness

The hardness was found be to increased with increase in the amount of chitosan incorporated in the composites (Figure 6). This is due to the increase in strengthening effect of the reinforcing filler with increasing composition. This also indicates increase in abrasion and impact strength of the composites. But with gradual increase in filler content, the values decreased. This is because beyond the 40 wt% filler composition, development of voids takes place on the composite surface which deteriorates its surface quality to a great extent. This gives rise to low toughness and decreased hardness.

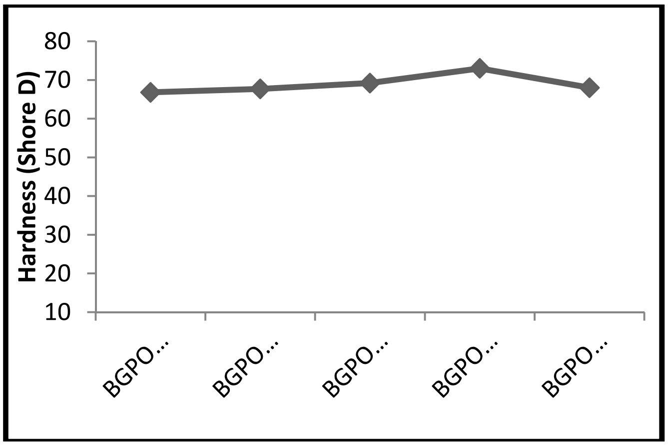

Figure 6: Hardness of composites

4.2.5.Ageing studies-in water

It is a well known fact that chitosan is hydrophilic in nature with high moisture retention capacity. Thus, the composites samples were subjected to ageing to ascertain their utility during applications. The change in weight of composites after exposing to water is shown in Figure 7. Since untreated chitosan was used in the composites, these were expected to exhibit considerable weight gain. But interestingly, it was observed that the fabricated composites showed less weight change as compared to $BGPOCC_0$. Moreover, the change in weight reduced with the increase in chitosan content and reached a minimum at 40 wt%. This may be due to the hydrophobic nature of BisGMA-PEOZ blend and efficient chitosan adhesion with the matrix caused by hydrogen bonding between the two. But with increased chitosan loading ($BGPOCC_{50}$), the water uptake increases. This is because with filler aggregation and phase separation, voids are formed on composite surface. Water filled voids at the interface results in interfacial de-bonding. This causes cracks on the surface of composites[16]. Once water penetrates inside composites materials, chitosan starts swelling and matrix tend to change reorientation resulting in poor mechanical properties.

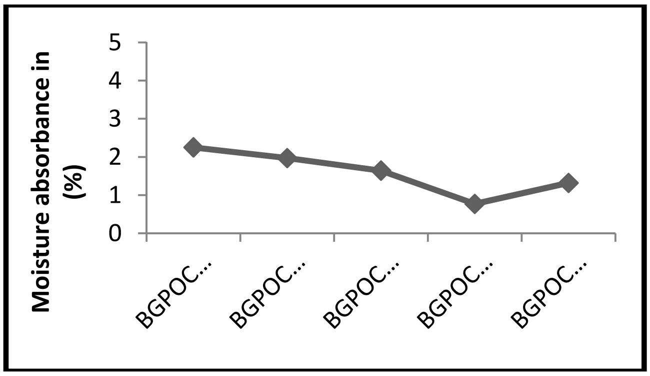

Figure 7: Ageing of composites

4.2.6.Chemical Resistance

There has been major interest in the surface characteristics of composites since it is the surface of these materials that first comes into contact with the biological surroundings. The ability of the composite samples to resist chemical environment such as acid, alkali, solvent and water were tested and is given in Table 2.

Table 2: Chemical resistance of composites

Samples	*HNO_3 (%)*	*H_2O (%)*	*NaOH (%)*	*CCl_4 (%)*
$BGPOCC_0$	0.821	1.015	0.783	0.756
$BGPOCC_{10}$	0.752	0.683	0.645	0.624
$BGPOCC_{20}$	0.643	0.677	0.633	0.610
$BGPOCC_{30}$	0.521	0.581	0.564	0.574
$BGPOCC_{40}$	0.510	0.576	0.548	0.509
$BGPOCC_{50}$	0.586	0.585	0.559	0.517

This clearly indicates that all composites show minimum weight loss. The composites showed a lesser solvent uptake or increased chemical resistance compared to $BGPOCC_0$. The incorporation of chitosan as reinforcing filler increased the interfacial bonding between filler and matrix resulting in reduced void content. This increased interfacial interaction increases with filler content which makes the polymeric segments around the filler immobile. These factors offer higher resistance to the movement of solvent molecules into the composites system[17]. Restricted equilibrium technique has been used as a tool by many researchers to analyze the filler–matrix bonding in the composites system[18,19]. It is reported that increased interfacial interaction results in lower solvent uptake by composites systems. Therefore the solvent uptake by composites systems decrease with increased filler content and attain minimum value at 40 wt% chitosan content. But the voids formed in $BGPOCC_{50}$ accelerate the solvent diffusion into the matrix system thereby making the composite unsuitable for any structural applications.

5. Conclusion

The results of present study showed that composites with low cost and improved mechanical strength could be developed successfully by incorporating chitosan as reinforcing filler in BisGMA-PEOZ blend system. Tensile strength, Young's Modulus, elongation at break, impact strength and hardness of composites were much higher than that of pure blend. The values of tensile strength, Young's Modulus, impact strength and hardness increased upto 40 wt% chitosan content whereas elongation at break decreased with increasing content of chitosan. There was also improvement in the chemical resistance and ageing studies of composites with increased chitosan loading. But the composite with higher concentration of chitosan displayed poor mechanical properties, ageing studies and chemical resistance. From the above studies, it can be concluded that among all the fabricated composites, the $BGPOCC_{40}$ showed maximum improvement in all the above mentioned properties. Thus, it could be the optimum composite specification suitable for applications in aerospace, automobile and the light weight materials industry.

6. Acknowledgement

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7. Future Scope

The thermal and electrical properties of the above fabricated composites can be studied to increase the scope of their applications in thermal and electrical industries.

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