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Development of molybdenum disulphide reinforced alginic acid composites

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Alginates from brown algae are biopolymers, recently being used in various fields such as medical implants, food packaging, *etc.* The non toxicity, biodegradability, and biocompatibility of these alginates makes them an excellent candidate that be exploited to meet different applications. Through this paper, we are incorporating monolayer of molybdenum disulphide into the matrix of alginic acid from brown algae in the presence of a plasticizer to form film composites with enhanced properties. The casted films were flexible and smooth. The impact of filler loading in crystalline nature and mechanical strength of the composites are also studied. Differential scanning calorimetry was utilized to study the effect of MoS_2 on the thermal properties of the composites. It was seen that both the mechanical and thermal properties of the prepared film were enhanced with the incorporation of an optimal filler concentration.

Keywords: Alginates, Biopolymers, Crystallinity, MoS_2, Tensile strength

Alginates are one of the most extensively studied biopolymers. They are biocompatible, biodegradable, renewable[1], and non-toxic biopolymers[19]. Alginic acid(AA) is a natural polysaccharide extracted from brown seaweeds like *Laminaria, Macrocystis, Sargassum, Ascophyllum*[2]. Alginates are the salts of AA. They are linear copolymer comprised of β-(1-4)-linked D-mannuronic acid and α-(1-4)-linked L-glucuronic acid units. AA posses unique colloidal properties like film- forming, thickening, gelation, stabilizing suspending *etc*. These colloidal properties make them a sufficient material capable of forming biodegradable or edible films[18]. The gelation property makes AA superior over other biopolymers and the same is made utilized in food and medical fields. Alginic acid finds applications also in wound healing, ion-exchange, metal ion adsorption[3], pharmaceutical industries, electronics, and tissue engineering[1]. Most of the studies were carried out on sodium or calcium treated alginates, as these have excellent film-forming properties. Different materials like silica[4], hydroxyapatite[5], graphene oxide[6], chitosan[7] *etc.* have been cooperated into the alginic acid matrix to obtain nanocomposites with enhanced properties to meet various application requirements. Molybdenum disulphide (MoS_2) is 2D Layered material which has been used as filler materials in polymer matrix because of its intercalation properties. MoS_2 can form intercalation chemistry with strong reducing agents like n-butyl lithium[8] and LiAHA[9] in solvents like water[10], NMP[11], and DMF[12], n-hexane[13]. The resulting $LiMoS_2$ on further treatments allows the flocculation of layers in the presence of guest material to form sandwiched compounds.

Through this paper, we are reporting the introduction of exfoliated MoS_2 as a reinforcement inorganic material into the Alginic acid (from brown algae) matrix. From the literature, there are no detailed studies on AA/MoS_2 composites. Further, we are using Alginic acid as such from brown algae. And therefore it is interesting to study the effect of this combination and to study the properties of the resultant. Since AA from brown algae is incapable of film formation, glycerol was added as a plasticizer. The composites were prepared with different MoS_2 loading (1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 6 wt%).

Experimental

Materials Used

Alginic acid from brown algae [(A7003); Sigma Aldrich (formula weight= 176.10 g/mol). Chloroform ($CHCl_3$) [Merck Specialities, India]. Molybdenum Disulphide [HPLC, LR; MW: 160.06], 6-Aminohexanoic acid [Sigma Aldrich, Fluka Analytical, NT; MW:131.17], Lithium Hydroxide (Monohydrate)

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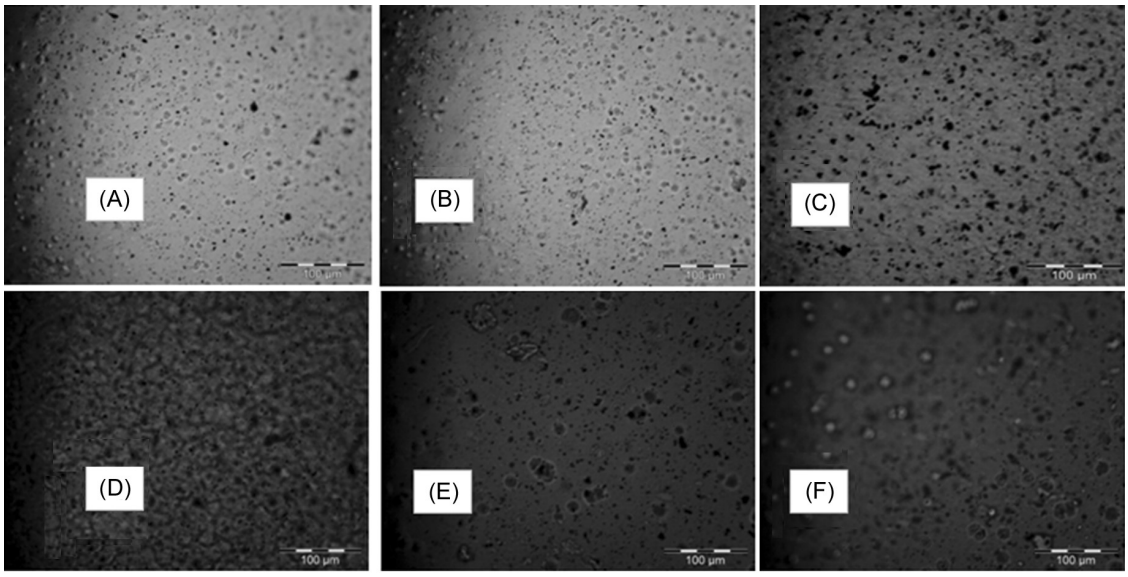

Fig. 1 — Optical micrographs of (A) AA/1 wt% MoS_2; (B) AA/2 wt% MoS_2; (C) AA/3 wt% MoS_2; (D) AA/4 wt% MoS_2; (E) AA/5 wt% MoS_2; and (F) AA/6 wt% MoS_2

[Molychem, GR; MW:41.96], N-Methyl-2-Pyrrolidone [RFCL, MW:99.13], Glycerol [Sigma Aldrich].

Preparation of composites

MoS_2 was exfoliated as per reference[9] in a mixed solvent. AA/MoS_2 composites were prepared via solution casting technique. MoS_2 was dispersed in chloroform using a magnetic stirrer and further with an ultrasonicator. This solution was then mixed with solvated AA and was stirred using a magnetic stirrer. The required amount of glycerol (0.05 wt% of MoS_2) was added to the solution and was mixed well by ultrasonication. The resultant was casted on a level surface and was left to evaporate. The cast films were then peeled off and the properties were studied.

Characterization

The crystal structure of the material was studied by X-Ray Diffraction (Philips X-Pert Pro.). The X-ray of wavelength (λ=1.54 Å) emanating from copper target filtered through nickel was used for our diffraction study. The XRD patterns were recorded with a step scan with a step size of 0.05 between 5° and 80° (2θ). The tensile properties of the composites were performed using INSTRON universal testing machine 6025 UK within 200-N load cell according to ASTMD 882. All specimens were 20 mM wide and 0.15 mM thickness. The grip separation distance is 50 mM. The test speed was 100 mM/min. The results were taken as the average of five specimens of each sample. DSC tests were carried out under nitrogen atmosphere using TA Q20, TA types of equipments, USA following ASTM D 3418 standards. The samples were heated to 200°C at a heating rate of 10°C/min, followed by an isothermal step for 5 min, and then cooled to 20°C at a rate of 10°C/min. The second heating scans were monitored between 20 and 200°C at a heating rate of 5°C/min to determine the glass transition temperature (Tg), cold crystallization temperature (Tcc), crystallization temperature (Tc) and melting temperature (Tm). The samples were then cooled at the rate of 5°C/min to characterize crystallization behavior.

Results and Discussion

Since AA from brown algae as such cannot form films as such, glycerol as a plasticizer[14] was added to form films. The prepared composites were flexible, smooth, and homogenous. The optical microscopic images of the casted films are given in (Fig. 1). It is clear from the micrographs that on increasing MoS_2 loading, the films get more and more inhomogeneous and visible cracks and agglomeration points towards, reduced bonding of the components on higher filler concentrations.

Mechanical Studies

The calculated mechanical parameters of the composites are tabulated in (Table 1). It is seen that there is an increase in both tensile strength and modulus of elasticity upto 3 wt% loading of

Table 1 — Mechanical parameters of prepared composites

Sample	Tensile Strength (MPa)	Elongation at break (%)	Modulus of elasticity(MPa)
AA	26.4	18.2	1084
AA/2 wt% MoS_2	27.1	18.67	1214
AA/3 wt% MoS_2	28.9	21.5	1357
AA/4 wt% MoS_2	26.3	20.4	1129
AA/5 wt% MoS_2	25.8	17.6.	1095

MoS_2 concentration. Further increase in filler loading diminishes the mechanical strength of the composites. This can be attributed to the agglomeration and less binding of components at higher filler concentrations. The increase in tensile strength and modulus of elasticity indicates a better dispersion rate and the reinforcement of AA by MoS_2. The variations in the mechanical properties are shown in (Fig. 2).

It was observed from the table that the tensile strength, elongation at break, and modulus of elasticity was improved with the optimized addition of filler particles. The enhanced mechanical stabilities infer that the better dispersion of MoS_2 in the AA matrix. For AA/3 wt% MoS_2, the tensile strength was improved by 9.1%. But the further increase in filler loading resulted a reduction in tensile strength. For 5 wt% of filler loading, the tensile strength was even less than that of AA. This can be attributed to the low binding of MoS_2 to the AA matrix. This is maybe because that, the filler concentration had resulted in a highly stretched structure, which in turn transfers the material to a brittle form.

Differential Scanning Calorimetry

DSC was also employed for the evaluation of the thermal nature of AA and AA/MoS_2 composites. The DSC curves for the samples are given in (Fig. 3). The DSC thermogram for AA shows a prominent endothermic peak at 162.91°C and a suppressed Tcc curve at 102°C. The Tg was observed at 83°C for AA. The MoS_2 incorporated samples also showed similar curves to AA except that of an increased value for Tm. The Tm for AA/3 wt% MoS_2 and AA/4 wt% MoS_2 was seen to be 184.2°C and 179.8°C, respectively. No traces for Tcc were observed for filler associated composites. There was a marginal increase in Tg for 3 wt% filler loading when compared with AA. It is supposed that the associated MoS_2 particles hinder the mobility of polymer chains which results in an enhanced Tg.

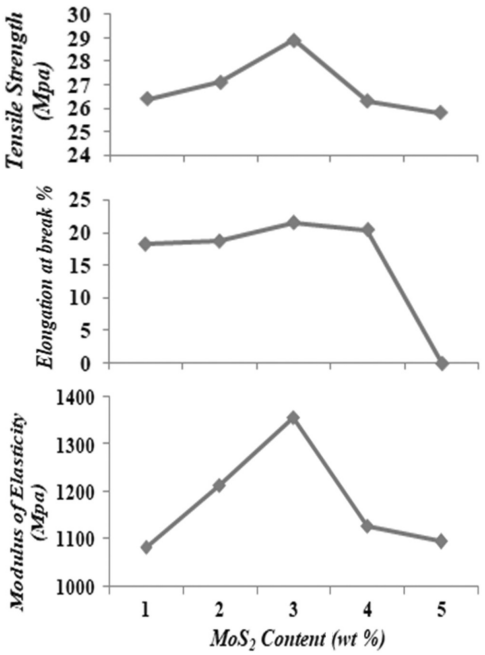

Fig. 2 — Variations of mechanical parameters with MoS_2 content for AA/MoS_2composites

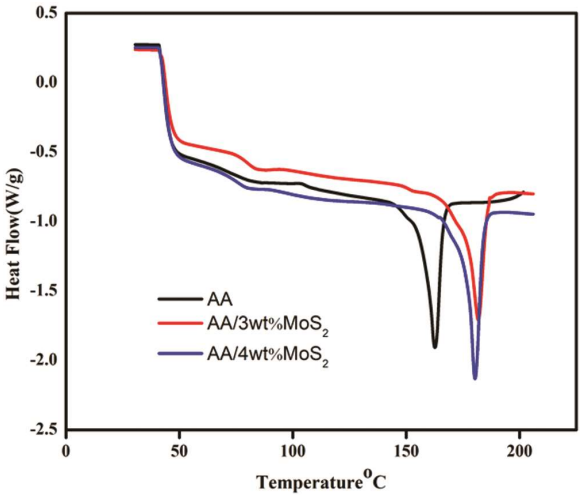

Fig. 3 — DSC curves for AA, AA/3 wt% MoS_2 and AA/4 wt% MoS_2

X- ray Analysis

The XRD spectrums of the prepared composites are shown in (Fig. 4). The well- defined peaks in the spectrum shows the crystalline nature of the composite[15]. Peaks at 2θ~ 14° and 21° corresponds to MoS_2 (JCPDS card no. 37-1492) and AA[16], respectively. The characteristic peak of AA observed at 2θ = ~ 20.5° was assigned to (002) planes as reported by[17]. Both the AA/MoS_2 composites showed an intense (002) peaks. The interfacial interaction between the AA and the MoS_2 has resulted in the dominance of characteristic peak of (002) at 2θ= 19.4° and 20.3° for

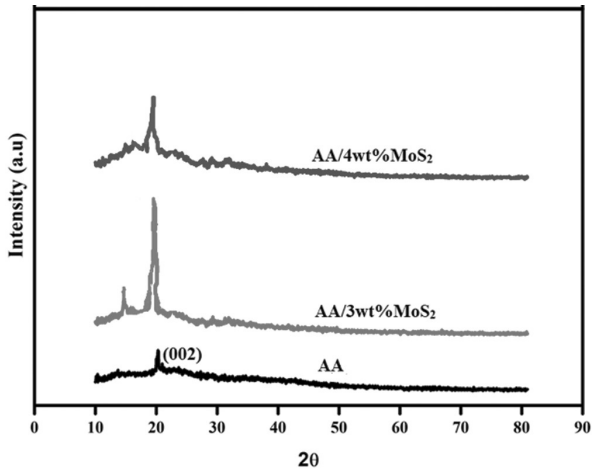

Fig. 4 — XRD spectrum of (A) Virgin AA; (B) AA/3 wt% MoS_2; and (C) AA/4 wt% MoS_2

3 wt% filler loading and 4 wt% filler loading, respectively. The difference in the intensities of the peaks for each composition reflects the sequential structure of complex formed between AA and MoS_2 in the presence of glycerol, with AA/3 wt% MoS_2 with greater ordered morphology. The intensity of the peaks reduced with the addition of optimal MoS_2 concentration beyond 3 wt%. Further, an additional peak observed at 2θ~14° corresponds to Li-MoS_2[9]. The shift towards lower angle for AA/3 wt% MoS_2 confirms better intercalation of MoS_2 to the AA matrix, as the d-spacing calculated using Scherrer formula increases by 5%.

Conclusion

MoS_2 reinforced AA composite films were successfully casted with glycerol as a plasticizer. The prepared flexible films were homogenous up to an optimum filler concentration of 3 wt%. Further increase in filler loading resulted in the agglomeration and hence the casted out films were inhomogeneous. The crystalline nature of the composites was confirmed from XRD results. The X-ray spectrum also confirmed the presence of MoS_2 in the sample through the prominent characteristic peaks being exhibited by the samples. Enhancement in mechanical strength was seen for MoS_2 added AA, when compared with virgin AA. An increase in tensile strength by 9.5% and modulus of elasticity by 25% was seen for AA/3 wt% MoS_2. This can also be attributed to the better dispersion and reinforcement of AA with the addition of MoS_2. The glass transition temperature was enhanced with the incorporation of filler particles as they are supposed to hinder the mobility of polymer chains. This AA/MoS_2 composite can promise a future in the field of biomaterials and further investigations on the properties are under process.

Conflict of interest

All authors declare no conflict of interest.

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