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INTERFACIAL PROPERTIES OF PHOSPHATE GLASS FIBRES/PLA COMPOSITES: EFFECT OF THE END FUNCTIONALITIES OF OLIGOMERIC PLA COUPLING AGENTS

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ABSTRACT

Polylactic acid (PLA) oligomers as coupling agents have shown higher interfacial shear strength in phosphate based glass fibres/ PLA composites. To influence bonding on the glass fibre surface, short chain PLA oligomers with different end groups were used as coupling agents. The low molecular weight PLA with a sodium salt terminal group, a carboxylic acid end group and also with one, two and five hydroxyl groups were produced and applied on the fibre surface through a condensation reaction. Mechanical properties of the sized fibres/PLA composites were found to be increased. XPS and TG analyses showed the presence of the coupling agents on the fibres surface. SEM analysis further confirms the presence of the agents.

Keywords: Polymer-matrix composites (A), Glass fibres (A), Coupling agents (A), Mechanical properties (B), Polylactic acid.

1. Introduction

Bioabsorbable phosphate glass fibres/polymer composites are being investigated as alternatives to commonly used metal alloy-based bone fracture fixation devices [1].

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According to Knowles [2], these 'Third Generation' implants remain in the body for the short term necessary for mechanical stabilisation of tissue. In addition the degradation products of the bioabsorbable implants perform an active function in the tissue regeneration process. A bioabsorbable fracture plate could potentially transfer load to the healing bone gradually over time.

Among bioabsorbable polymers, polyhydroxy acids and especially poly(lactic acid) (PLA) are well known for a number of biomedical applications; sutures, pins, screws, drug delivery systems and scaffolds for use in tissue engineering applications [3, 4]. Hydrolytic degradation, or complete mass loss of PLA takes approximately 12 to 16 months [5]. PLA degrades to form lactic acid which is normally present in the body [6]. The reported elastic modulus of PLA ranged from 0.6 to 4 GPa which is higher compared to the familiar bioabsorbable polyhydroxy acids such as polycaprolactone, polydioxanone [7]. However, the elastic modulus of cortical bone ranges from 6 to 20 GPa [7], which is much higher than that of the polymers. Therefore, reinforcement of the polymer has been considered to attain sufficient mechanical properties for fracture fixation [3].

Phosphate based glasses (PBG) have great potential to be used as reinforcement in bioabsorbable composites for bone implants. PBG show a complete and congruent degradation in aqueous media with zero order release of incorporated oxides [8]. The chemical composition of PBG can be designed to closely match that of the inorganic phase of bone [9]. Moreover, the composition of PBG can be easily tailored giving variation in mechanical, thermal and biological properties to suit the end application.

The major limitation of PBG fibre reinforced polymer composites encountered thus far is rapid strength loss after exposure to an aqueous physiological environment [10].

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Recent research on glass fibres has involved surface treatments and coupling agents to try and enhance the hydrolytic stability of the fibre-polymer interface [11, 12]. Apart from silane, modified oligomers/macromers of the matrix materials have currently been investigated to improve the interfacial bonding between fibre and matrix. Phosphate glass fibres (PGF) coated with a mixture of modified methacrylate macromer and 2-hydroxyethyl methacrylate (HEMA), in the same macromer matrix gave the composite a bending strength of around 115 MPa [13]. However, the fibres used were 125 µm in diameter, which would have made them weaker and less flexible due to their large size, and therefore not appropriate as reinforcing fibres. Polyacrylic acid (PAA) and glycidyl acrylate modified PAA coupling agents have been applied to E-glass fibres and electron spectroscopy for chemical analysis (ESCA) studies showed broad and shifted C_{1s} peak at 288.5 eV (O-C=O) suggesting adhesion of polymers to the fibre surface [14].

The recent researches mentioned above suggest that some polymeric materials can make chemical bonds with some glass fibres. In this study, the matrix material was PLA and this is why the present study was conducted in order to investigate the effects of different PLA oligomer coupling agents on PGF/PLA composites.

2. Experimental

2.1. Phosphate glass and fibre production

PGF were produced by melt-draw spinning of phosphate glass (composition $40P_2O_5$-24MgO-16CaO-$16Na_2O$-$4Fe_2O_3$ in mol%) using a dedicated in-house fibre manufacturing facility and then annealed at 474ºC [15]. The fibres were kept in a desiccator prior to use. These annealed and untreated fibres were used as control for the

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study. The mechanical properties of PGF produced fluctuate slightly from batch to batch due to their variation in diameter and severity of surface flaws. Due to this slight variation, the properties of control and sized fibres were compared using fibres produced from within the same batch. Two batches of the control fibres produced were named as control-1 and control-2.

2.2. PLA oligomers synthesis

Acid ended PLA (PLA-acid) and its sodium salt (PLA-Na)

The PLA-acid and PLA-Na both were synthesised by ring opening polymerisation of D, L lactide (Sigma Aldrich, U.K.) and the resulting products were used without further purification. The PLA-acid and PLA-Na were synthesised using a dried lactide and lactic acid ratio of 5g: 0.105g and a dried lactide and lactic acid sodium salt ratio of 5 g: 0.112 g respectively. The mixtures were then heated to 130°C and stirred for 48 hours and heated to 140°C and stirred for 24 hours under a nitrogen atmosphere for PLA-acid and PLA-Na respectively. After this time period the mixtures were decanted whilst hot onto aluminium foil and allowed to cool to room temperature. The molecular weight and the polydispersity of the PLA-acid and PLA-Na were obtained 1921 (Mn) and 1.77 (PDI) and 4410 (Mn) and 2.33 (PDI) respectively.

Hydroxyl groups ended PLA

The PLA oligomers with different number of hydroxyl terminals were produced by depolymerisation of Natureworks PLA (PLA- grade 3051D, Natureworks LLC, U.S.A) catalysed by stannous octoate (Sigma Aldrich, U.K.) using different alcohols as initiators. Ethylene glycol, glycerol and sorbitol (Sigma Aldrich, U.K.) ended short chain PLA oligomers were synthesised by degrading dried Natureworks PLA (10 g)

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using ethylene glycol (0.72g), glycerol (1.068g) and sorbitol (2.108g) and named as EG-PLA, G-PLA and S-PLA respectively. Tin catalyst was used 0.05g for each of the mixtures. The weighed amount of PLA, catalyst and initiator of each batch were added to a 100 mL round bottomed flask equipped with a magnetic stirrer. The mixtures were heated to 180-185°C for 2 hours until melt and then the reactions were continued at 170°C for 14 hours under a nitrogen atmosphere and with constant stirring. After this time period the mixtures were again heated to 180 °C and stirred for 2 hours. The mixtures were then decanted like PLA-acid and PLA-Na. A further short chain sorbitol ended PLA (S-PLA-1) of lower molecular weight compared to S-PLA was also synthesised in order to investigate the effect of molecular weight on the mechanical properties of sized fibres. The S-PLA-1 was produced in the same way as mentioned above for S-PLA, with the only exception is that the reaction was continued at 170 °C for 24 hours. The resulting oligomers were then dissolved in dichloromethane (Sigma Aldrich, U.K.) and precipitated in methanol (Sigma Aldrich, U.K.) to purify them. The precipitates were then dried under vacuum. The molecular weight and the polydispersity of the EG-PLA, G-PLA, S-PLA and S-PLA-1 obtained were 8210 (Mn) and 1.98 (PDI), 1217 (Mn) and 2.71 (PDI), 2881 (Mn) and 3.2 (PDI) and 115 (Mn) and 3.25 (PDI) respectively.

2.3. Gel permeation chromatography (GPC)

The number average molecular weight (Mn) and polydispersity index (PDI) of the oligomers were determined using GPC. GPC was performed utilising a refractive index (RI) detector with HPLC grade tetrahydrofuran (Fisher Scientific, U.K.) as the eluent. Analysis was performed at 40°C with a flow rate of 1 mL/min through two PLgel Mixed-C columns with a calibration range of 2000 – 5000 Da calibrated with

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poly(styrene) narrow standards. All GPC equipment and standards were supplied by Polymer Laboratories (Varian Inc). GPC data was analysed using the Cirrus GPC Offline software package.

2.4. Coupling/sizing agent application processes

The fibres were sized with the above PLA oligomers (6 oligomers), 3-aminopropyl triethoxy silane (silane) and 2-carboxyethyl phosphonic acid (phosphonic acid) (Sigma Aldrich, U.K.). Silane is a common sizing agent used for various glass fibres and this is why silane has been investigated as one of the sizing agents in this study. Phosphonic acid contains a phosphonic group which has similarities in chemical structure to the PGF and it has been investigated whether this similarity in structure can facilitate the bonding between this acid and the PGF. The interfacial properties of silane and phosphonic acid sized fibres were compared with those of the PLA oligomers sized fibres. Using a dip-coating process, the agents were applied to the control fibres with a fibre:solution ratio of 1.5g:100ml and a sizing agent:solvent ratio of 0.0043moles:100ml [15]. This was followed by heat curing and finally rinsing with the sizing solvents to remove any residual artefacts. The solvents used in the sizing processes were (a) ethanol (Sigma Aldrich, U.K.) /deionised water (90:10 v/v ratio) for silane and phosphonic acid, (b) chloroform (Sigma Aldrich, U.K.) for PLA-Na and PLA-acid, and (c) dichloromethane for EG-PLA, G-PLA, S-PLA and S-PLA-1. Fig. 1 shows the chemical structures of all the sizing agents applied.

2.5. Single fibre tensile test (SFTT)

The tensile properties of the fibres produced were obtained by single filament testing using a Series S Hounsfield machine, following the international standard BS ISO

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11566 [16]. 20-30 samples were prepared at a gauge length of 25mm for each treatment type. The crosshead speed of the machine was 1mm/min and the load cell capacity was 5N. PGF are essentially brittle and Weibull distribution is an accepted statistical tool used to characterise the failure mode of brittle fibres. In this study, Weibull parameters were obtained from the tensile strength data calculated using Minitab® 15 (version 3.2.1).

2.6. Interfacial shear strength (IFSS) studies

The IFSS was measured from single fibre composites (SFC) by using the single fibre fragmentation method. SFC specimens were produced by placing an axially aligned single fibre between two rectangular pieces of PLA film [15] of 80 x 20 x 0.4 mm^3 and hot pressing at 210ºC with a 2.5 kg weight for 1 minute. The resulting specimens were cooled to room temperature and finally cut into dog-bone shapes. These were axially loaded in a tensile testing machine (Hounsfield series S testing, U.K.) with a load cell of 1kN and crosshead speed of 1mm/min. All IFSS values were obtained from an average of 5-10 repeat specimens. After having conducted the tensile tests, the specimens were placed under an optical microscope (Nikon Optiphot, Japan) and the numbers of fibre fragments present in the 25mm gauge length were tallied, in order to calculate the IFSS.

These IFSS values obtained were calculated using the Kelly-Tyson equation below [17];

$\tau_i = d.\sigma_f / 2L_c$ (Equation 1)

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where τ_i is the IFSS, d is the fibre diameter, σ_f is the single fibre tensile strength at the critical fragment length L_c.

$\sigma_f = \sigma_o(L_c/L_0)^{-1/m}$ (Equation 2)

$L_c = 4/3(L_f)$ (Equation 3)

$L_f = L_0/N$ (Equation 4)

where σ_o and m are the Weibull scale and shape parameter respectively, for the fibre strength at gauge length L_0, L_f is the average fragment length and N is the number of fibre fragments obtained from the SFC tests [18].

2.7. Thermogravimetric (TG) analysis

TG analysis was performed to quantify the amount of sizing agents present on the fibre surfaces. The analyses were conducted from room temperature to 450ºC using a SDQ600 Thermogravimetric analyzer from TA instruments (U.S.A.) with a heating ramp rate of 20ºC /min under an air flow of 100ml/min.

2.8. X-ray photoelectron spectroscopy (XPS) analysis

XPS analysis investigated the effectiveness of compatiblising / sizing agent application to the fibre surfaces. A Kratos AXIS ULTRA with a mono-chromated Al kα X-ray source (1486.6eV) was operated at 15mA emission current and 10kV anode potential. For the XPS measurement, a small batch of fibres was mounted on a hollow steel bar using a high vacuum adhesive tape at two ends. Drift of the electron binding energy of the peaks due to a surface charging effect was calibrated by utilising the C 1s peak of the contamination (285eV).

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2.9. Scanning electron microscopy (SEM)

Samples of each of the fibres were sputter coated with carbon and micrographs were taken using a JEOL 6400 SEM at an accelerating voltage of 20 kV using SE (Secondary electron) modes.

2.10. Statistical analysis

A t-test was conducted to identify whether there were statistically significant differences between the means of the two sets of data [19]. The statistical analysis of the uncorrected and corrected IFSS values was performed using a paired t-test. The statistical analysis of the tensile strength and the IFSS values of the fibres and the SFC respectively was conducted using a two sample unpaired t-test. To interpret the t-test results, a two tailed P-value (P) was considered with a 95% confidence interval and the value of significance level 0.05. The difference was accepted as significant when P obtained was less than 0.05.

3. Results and discussions

3.1. Effect of carboxylic acid and sodium ended PLA oligomer coupling agents

The IFSS values obtained for the PLA-acid, PLA-Na, silane and phosphonic acid sized and the control-1 fibres are presented in Fig. 2. All the values were calculated using a 2-parameter Weibull model for the control-1 fibres. The Weibull scale and shape parameters of the control-1 fibres obtained were 340.0 and 6.3 respectively (Fig. 3a). The IFSS obtained for the control-1 fibres was 8.9 ± 2.9 MPa. The highest IFSS value of 13.3 ± 2.3 MPa was obtained for PLA-Na sized specimens. PLA-acid treated fibres showed IFSS very close to that of PLA-Na sized fibres (12 ± 2.3 MPa). The IFSS

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of silane and phosphonic acid sized fibres obtained were 8.4 ± 2.1 and 8.7 ± 2.2 MPa respectively.

It is observed from Fig. 2 that the IFSS values of PLA-acid and PLA-Na sized fibres were higher than that of the control-1. The low molecular weight PLA-acid and PLA-Na coupling agents showed relatively high IFSS values (i.e. improved bonding), which was suggested to be due to similarities in the chemical structures of the agents and matrix. The PLA-Na showed better bonding between the fibre surface and matrix as compared to the PLA-acid. The processing used and the relatively high level of hydrolytic instability of PLA-acid may result in it decomposing during preparation of the test specimens. However, the IFSS values of the silane and phosphonic acid treated fibres obtained were similar to that of the control-1. A similar result was also obtained by Cozien-Cazuc et al. for both unsized and silane sized $P_{40}Na_{20}Ca_{16}Mg_{24}$ PBG fibres within a PCL matrix [20].

The strength profile in relation to the SFTT of the PLA-Na sized fibres was investigated in order to verify if their Weibull parameters were different to that of control-1. The Weibull scale and shape parameters obtained for PLA-Na sized fibres were 419.5 and 5.8 respectively (Fig. 3b), which were different from those of control-1 (Fig. 3a). The IFSS value of PLA-Na sized fibres was therefore corrected using the Weibull parameters of the PLA-Na sized fibres in order to obtain more accurate results. After correction, the IFSS value obtained was 17.2 MPa. It was observed that the change in IFSS with and without correction of the Weibull parameters was statistically significant ($P < 0.0001$) for the PLA-Na sized fibres.

3.2. Effect of different hydroxyl groups ended PLA oligomer coupling agents

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Fig. 4 shows the tensile strength and modulus of the different functionalized PLA oligomers sized and control-2 fibres. The tensile strengths of control-2 and EG-PLA, G-PLA and S-PLA sized fibres obtained were 321.1 ± 93.3, 355.9 ± 82.9, 327.4 ± 81.0 and 339.6 ± 108.6 MPa respectively. The tensile modulus values of control-2 and EG-PLA, G-PLA and S-PLA sized fibres obtained were 74.0 ± 7.3, 81.0 ± 5.6, 75.1 ± 6.2, 77.0 ± 5.8 GPa respectively. However, the difference between the tensile strength and modulus of all the sized fibres was found to be statistically insignificant in comparison to control-2.

Fig. 5 shows the IFSS values of control-2 and EG-PLA, G-PLA and S-PLA sized fibres within a PLA matrix, along with the Mn of the oligomers. The effects of the end-group choice of these low molecular weight oligomer coupling agents were investigated from their IFSS values. These IFSS values were calculated using the individual Weibull parameters of control-2 and each of the sized fibres. The IFSS of control-2 and EG-PLA, G-PLA and S-PLA sized fibres obtained were 14.3 ± 6.1, 8.9 ± 2.6, 16.5 ± 3.3 and 23.2 ± 10.3 MPa respectively. The IFSS of EG-PLA and S-PLA (P values are 0.019 and 0.017 respectively) were significantly different from that of control-2. The highest IFSS value was obtained from S-PLA sized fibres followed by G-PLA and EG-PLA. The polymer chain end of S-PLA contains 5 hydroxyl groups which is higher than that for G-PLA (2 hydroxyl groups) and EG-PLA (1 hydroxyl group). The interfacial reactions were expected to be either between the hydroxyl groups on the PGF surface and the coupling agents by esterification or hydrogen bonding as shown in Fig. 6, and/or formation of salt complexes with the metal cations present in the glass. Regarding the interfacial reactions, the number of hydroxyl groups in the oligomers is assumed to influence the IFSS values.

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Comparing Fig. 4 and 5, it is observed that the tensile properties of the PLA oligomers sized fibres increased with the increase of Mn of the oligomers, though the differences in their tensile properties are statistically insignificant. However, no trend was observed in the level of interfacial adhesion with a difference in their Mn. The increase in chain length of the agents is suggested to contribute to an increase in coverage of the flawed surface of the fibres. However, the functional end groups of these oligomer chains play a vital role in their ability to effectively bond to the PGF surface. The differences in the end groups of the oligomers perhaps negate any effect Mn may have on the IFSS values of the sized fibres.

3.3. Effect of different Mn of the PLA oligomers

To understand the effect of Mn of a particular oligomer on the mechanical and interfacial properties of the sized fibres, two oligomers having the same functional end group with variation in chain length were investigated. Another sorbitol ended PLA; S-PLA-1 (Mn~115 Da) was introduced to make this comparison. In Fig. 7, the mechanical properties and the IFSS value of these sized fibres were compared with that of the S-PLA (Mn ~ 2881 Da). The tensile strength and modulus of S-PLA-1 sized fibres obtained were 279.4 ± 73.9 MPa and 73.8 ± 8.0 GPa respectively, which were lower than that of S-PLA sized fibres. However, taking statistical variation into account, no difference was observed in tensile properties of S-PLA and S-PLA-1 sized fibres. The IFSS value of 9 ± 3.5 MPa was obtained for S-PLA-1 sized fibres. The IFSS values obtained for S-PLA and S-PLA-1 sized fibres were significantly different ($P = 0.0002$).

With the functional end group for S-PLA and S-PLA-1 being the same, the affinity toward the PGF surface was expected to be similar for both these oligomers.

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The matrix-philic tails of the oligomers being different in length may have shown variation in the level of affinity with the PLA matrix. S-PLA-1 having very low Mn, the chain length of the agent was not sufficient to afford significant number of interactions and/or entanglement with the matrix for achieving good interfacial adhesion. Therefore, the longer chain length (i.e. higher Mn) was seen to confer a higher shear strength value of around 23 MPa for the sized fibres.

3.4. TG analysis

TG analysis of the S-PLA sized and control-2 fibres was conducted to ascertain the mass of sizing agent that was present on the fibres by pyrolysing it from the surface. Three replicates of each type of fibres were conducted to make an average of their result. The percentage weight losses recorded were 2.4 ± 0.5 and 0.23 ± 0.02 for S-PLA sized and control-2 fibres respectively. The TG result for S-PLA sized fibres suggested that the amount of sizing agent attached to the fibres was quite low, being approximately 0.1% of the sizing agent present in the sizing solution. Currently the actual coating level achieved is thought to be due to the low concentration (0.043M) of the sizing solution used in the study. Therefore, experimentation is now underway to optimise the concentration of the sizing solutions used in this process. In the study reported here, the sizing solutions used were all fixed at the above concentration in order to obtain and evaluate comparable data.

3.5. XPS analysis

High resolution XPS analysis was performed on S-PLA sized and control-2 fibres to examine the existence of sizing agents on the fibres.

The high resolution scan of the 1s core of O (oxygen) for control-2 and S-PLA sized fibres are shown in Fig. 8 labelled a and b respectively. In narrow scan 8a, the

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oxygen peak was deconvoluted into two peaks, which were seen at 531.5 and 533.3eV binding energy for non-bridging (NBO) and bridging (BO) phosphate oxygen respectively [21]. The high resolution scan of the O1s core of the S-PLA sized fibres (scan 8 b) showed three deconvoluted peaks at 531.4, 532.3 and 533.9 eV binding energy. In this case, it is not possible to differentiate between the BO and NBO of the phosphate glass and the C-O-C and C=O bonds within the sizing agents [22], as both have absorption peaks over similar ranges of binding energy. The third peak at 532.3 eV has been attributed to the presence of C-O-H of the S-PLA.

3.6. SEM analysis

The SEM micrographs (Fig. 9a, b) show the fibre surface of the control-2 and S-PLA sized fibres. The control-2 fibre (Fig. 9a) shows a pristine surface suggesting no sizing agent on it. With regards to Fig. 9b some agent persists on the surface. These images also support the bonding of the sizing agents on the fibres surface well with the observation made above from their TG and XPS analyses.

4. Conclusion

The PLA oligomer coupling agents being similar in chemical structure to the matrix showed a better quality of interfacial bonding between PGF and the PLA matrix. The functional end groups with a greater number of hydroxyl groups showed better compatibility (or attachment) toward PGF. With regards to the number of hydroxyl groups present in the oligomers, sorbitol ended PLA showed the highest IFSS. It was also observed that the molecular weight of an oligomer had a substantial effect on the interfacial properties of the sized PGF fibres. An optimum size of PLA chain with a

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suitable functional end group is suggested to be a hugely beneficial coupling agent for the PGF/PLA composites investigated.

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Figure legends

Figure 1 Chemical structures of the coupling agents.

Figure 2 IFSS values of control-1 and silane, phosphonic acid, PLA-acid and PLA-Na sized fibres.

Figure 3 Weibull analysis of (a) control-1 and (b) PLA-Na sized fibres were completed from the tensile strength data calculated using Minitab® 15 (version 3.2.1).

Figure 4 Tensile properties of control-2 and EG-PLA, G-PLA and S-PLA sized fibres.

Figure 5 IFSS values of control-2 and EG-PLA, G-PLA and S-PLA sized fibres and the molecular weight of the oligomers.

Figure 6 Possible chemical reaction mechanisms between PGF and S-PLA, (a) esterification and (b) hydrogen bonding.

Figure 7 Effect of molecular weight of S-PLA and S-PLA-1 on the tensile and interfacial properties of sized fibres.

Figure 8 High resolution XPS spectra of O 1s core of (a) control-2 and (b) S-PLA sized fibres.

Figure 9 SEM micrographs of (a) control-2 and (b) S-PLA sized fibres.

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Figure-1

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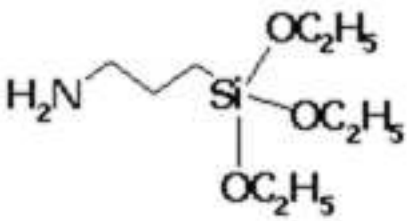
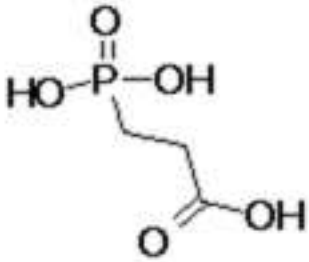
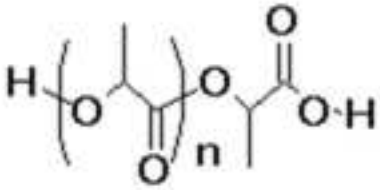


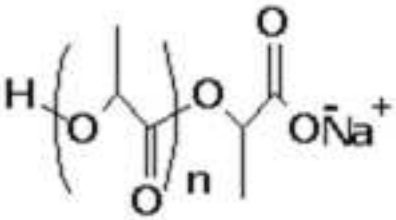
Silane



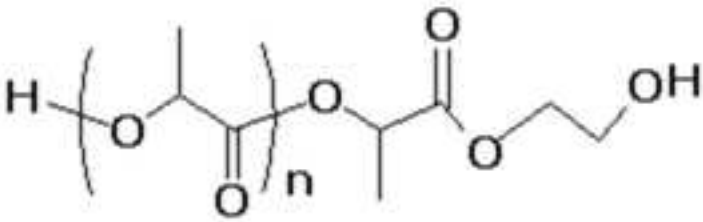
Phosphonic acid



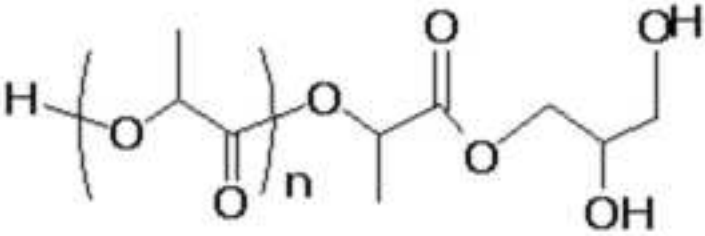
PLA-acid



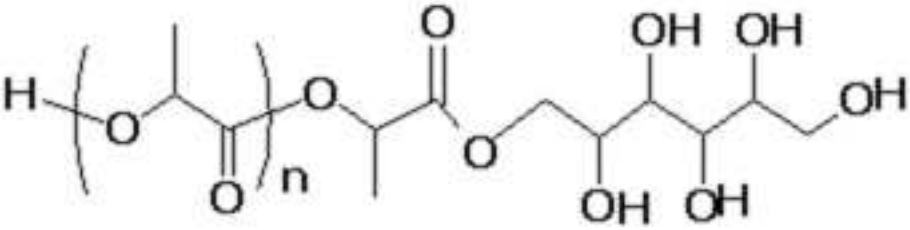
PLA-Na



EG-PLA



G-PLA



S-PLA

Figure-2

ACCEPTED MANUSCRIPT

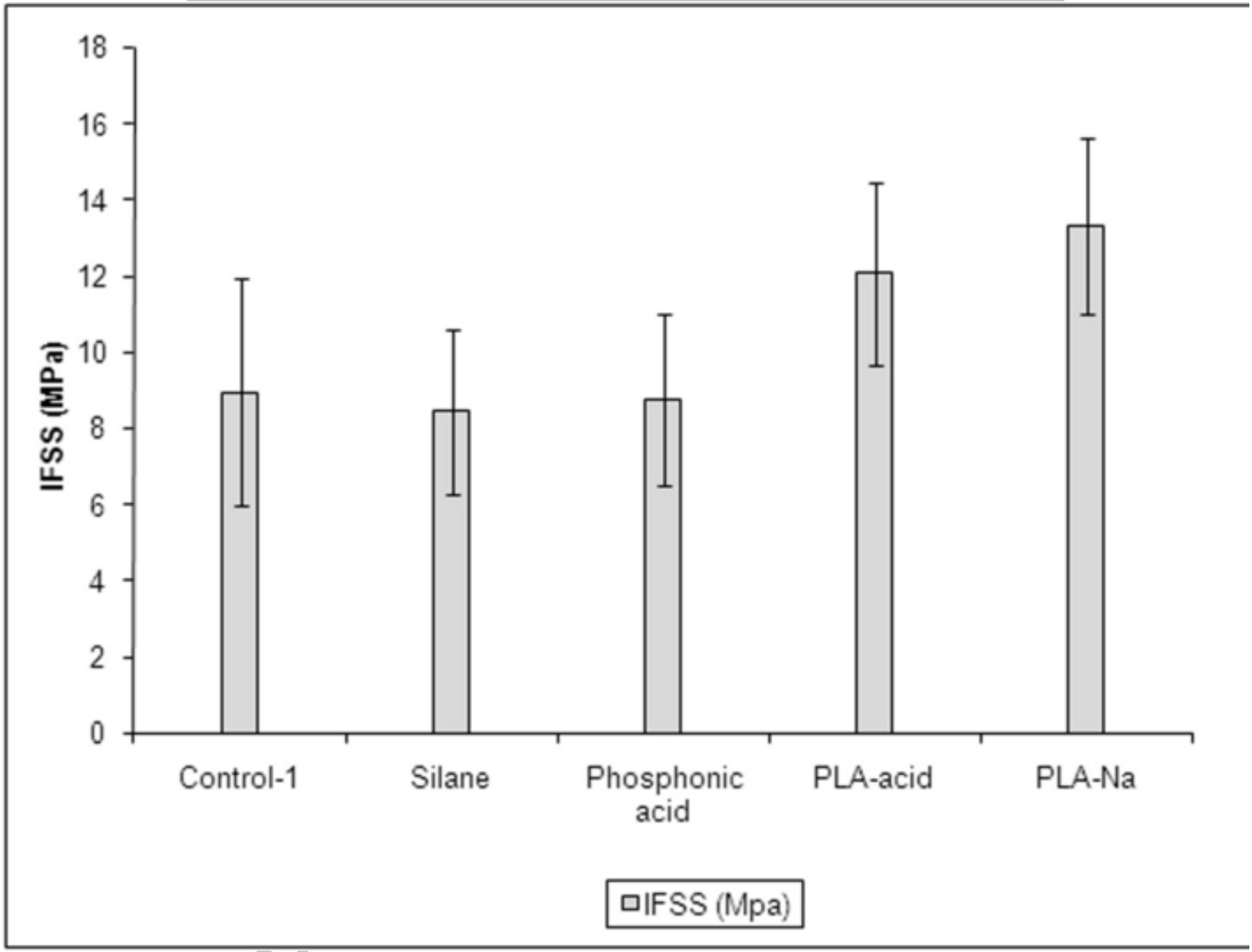
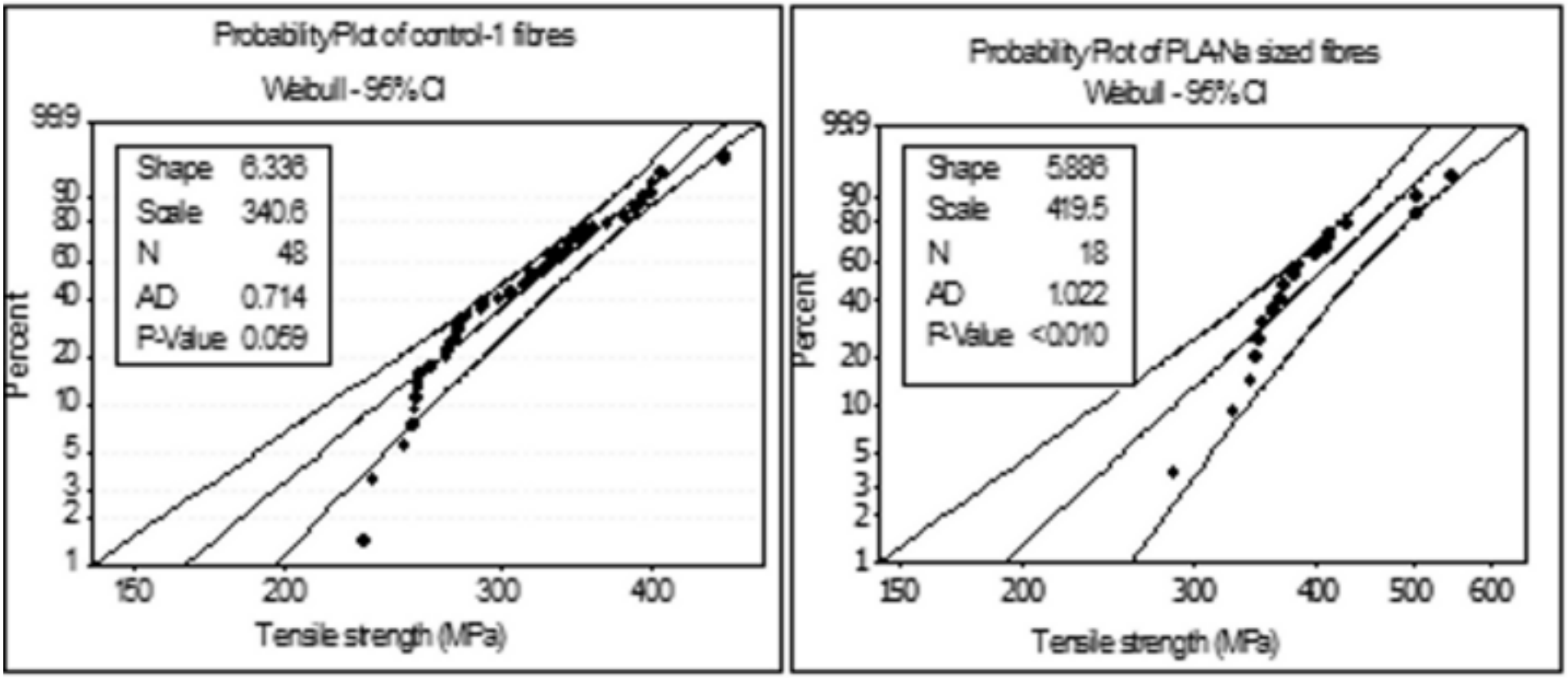


Figure-3

ACCEPTED MANUSCRIPT



(a) (b)

ACCEP

Figure-4

ACCEPTED MANUSCRIPT

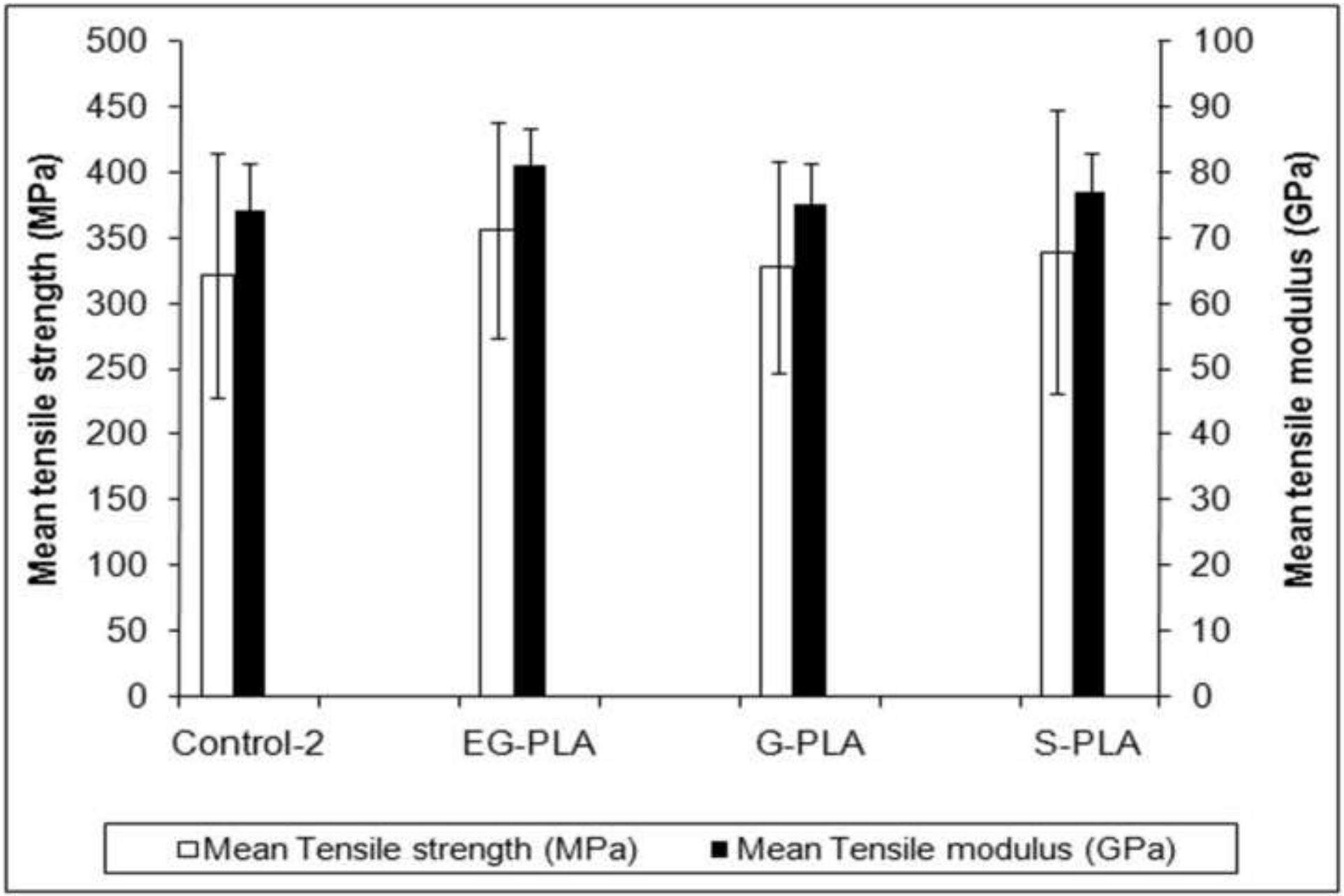


Figure-5

ACCEPTED MANUSCRIPT

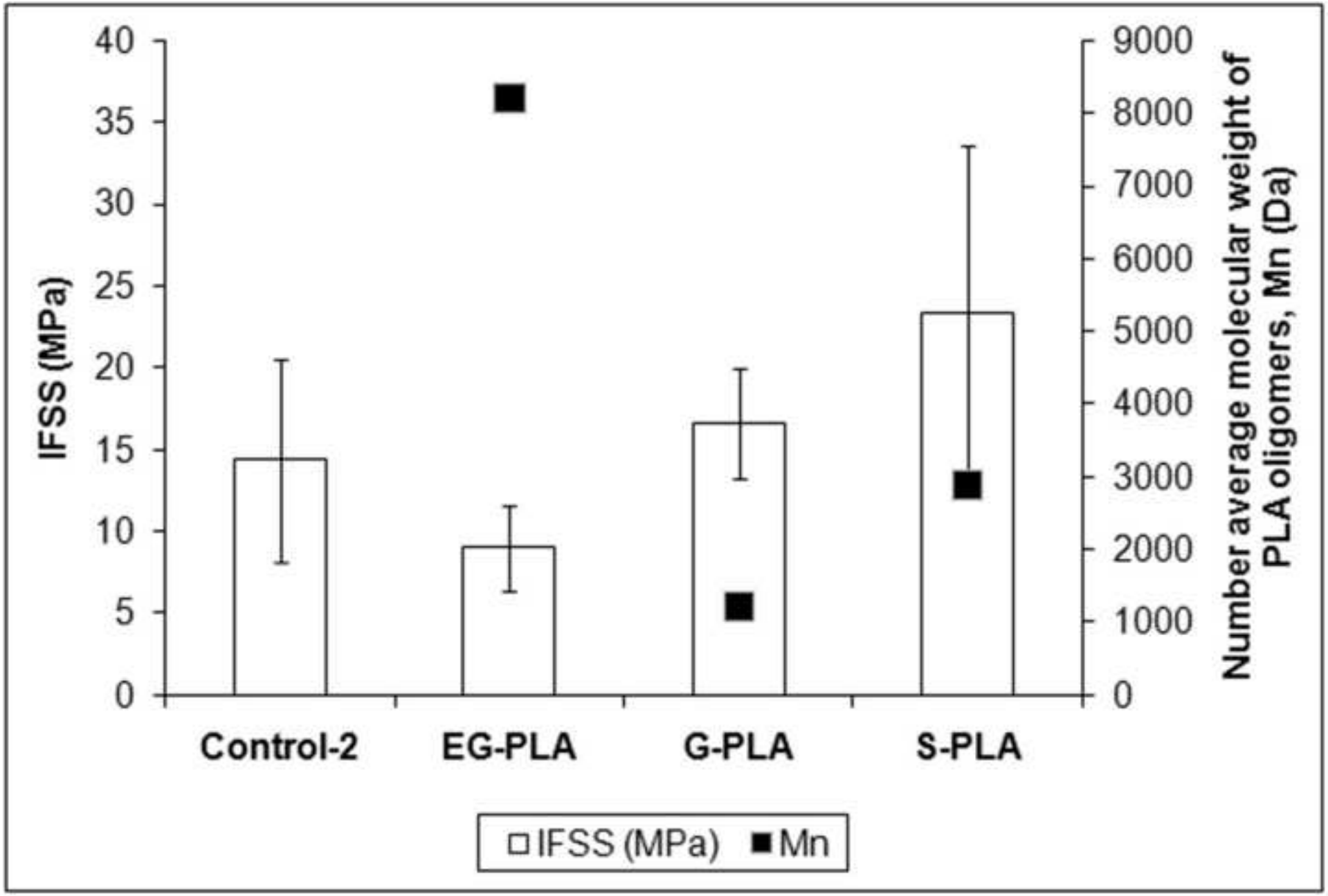
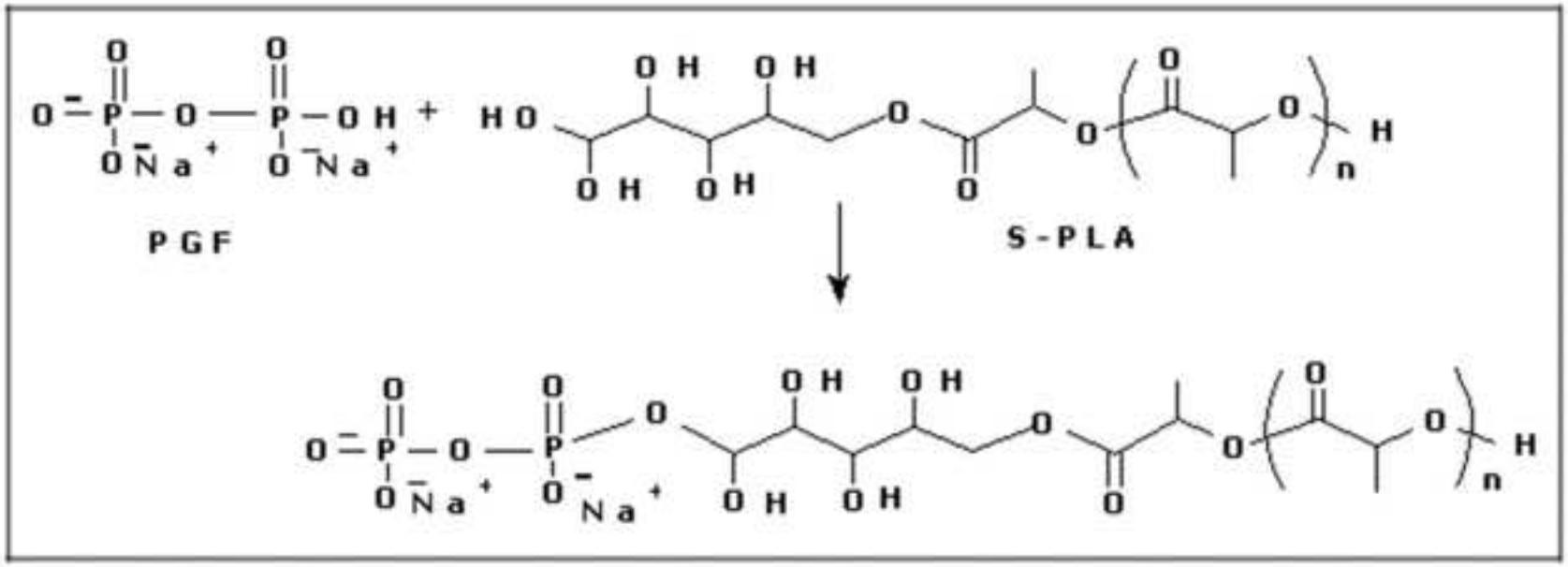
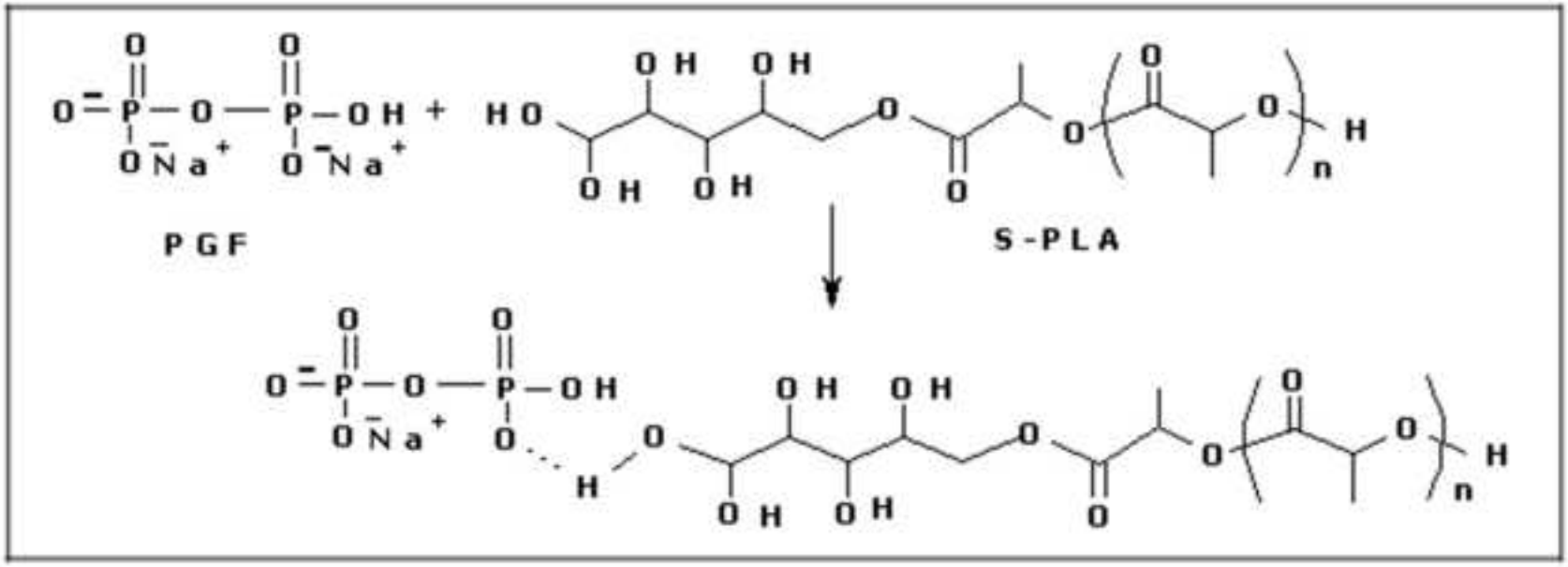


Figure-6

ACCEPTED MANUSCRIPT



(a)



(b)

Figure-7

ACCEPTED MANUSCRIPT

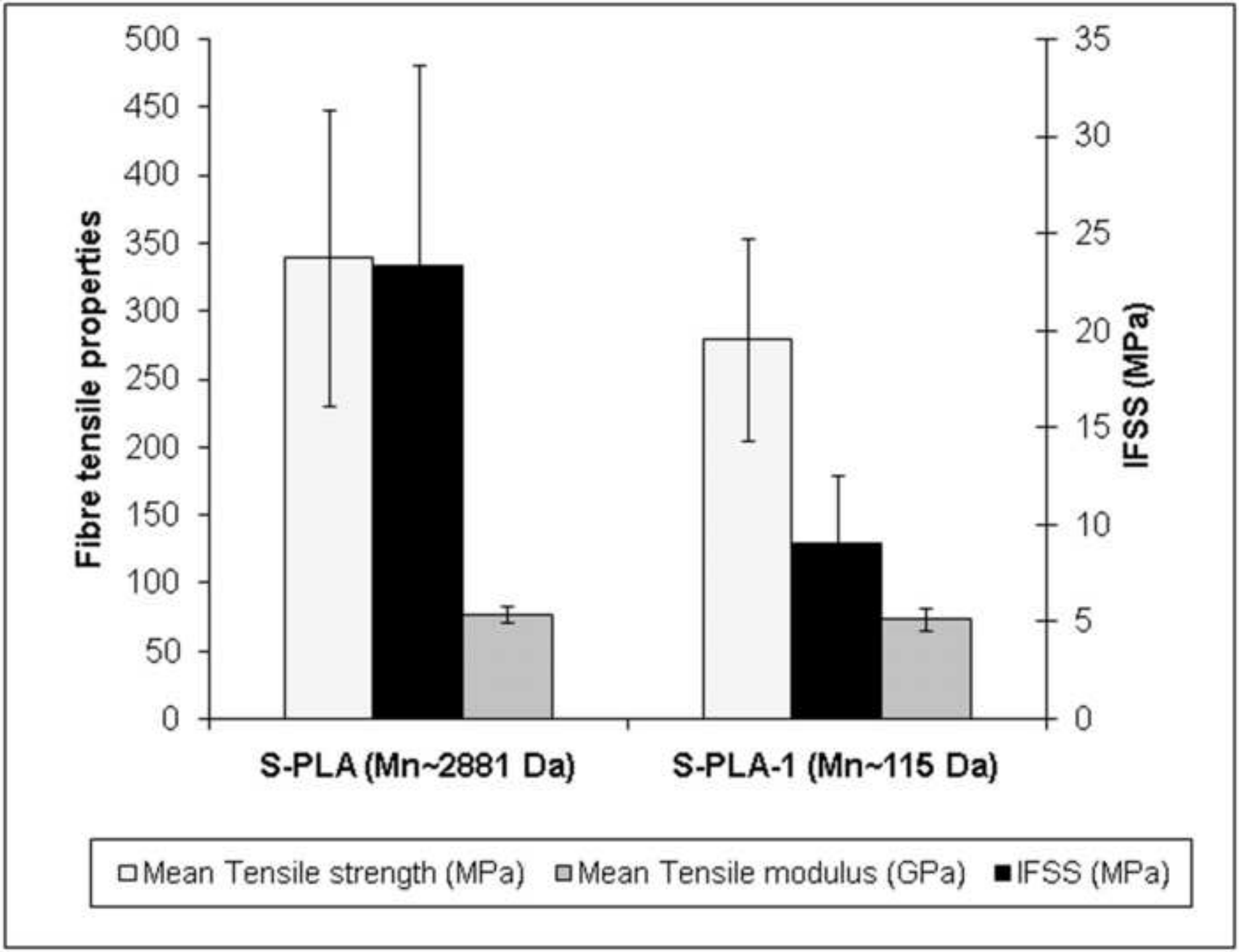


Figure-8

ACCEPTED MANUSCRIPT

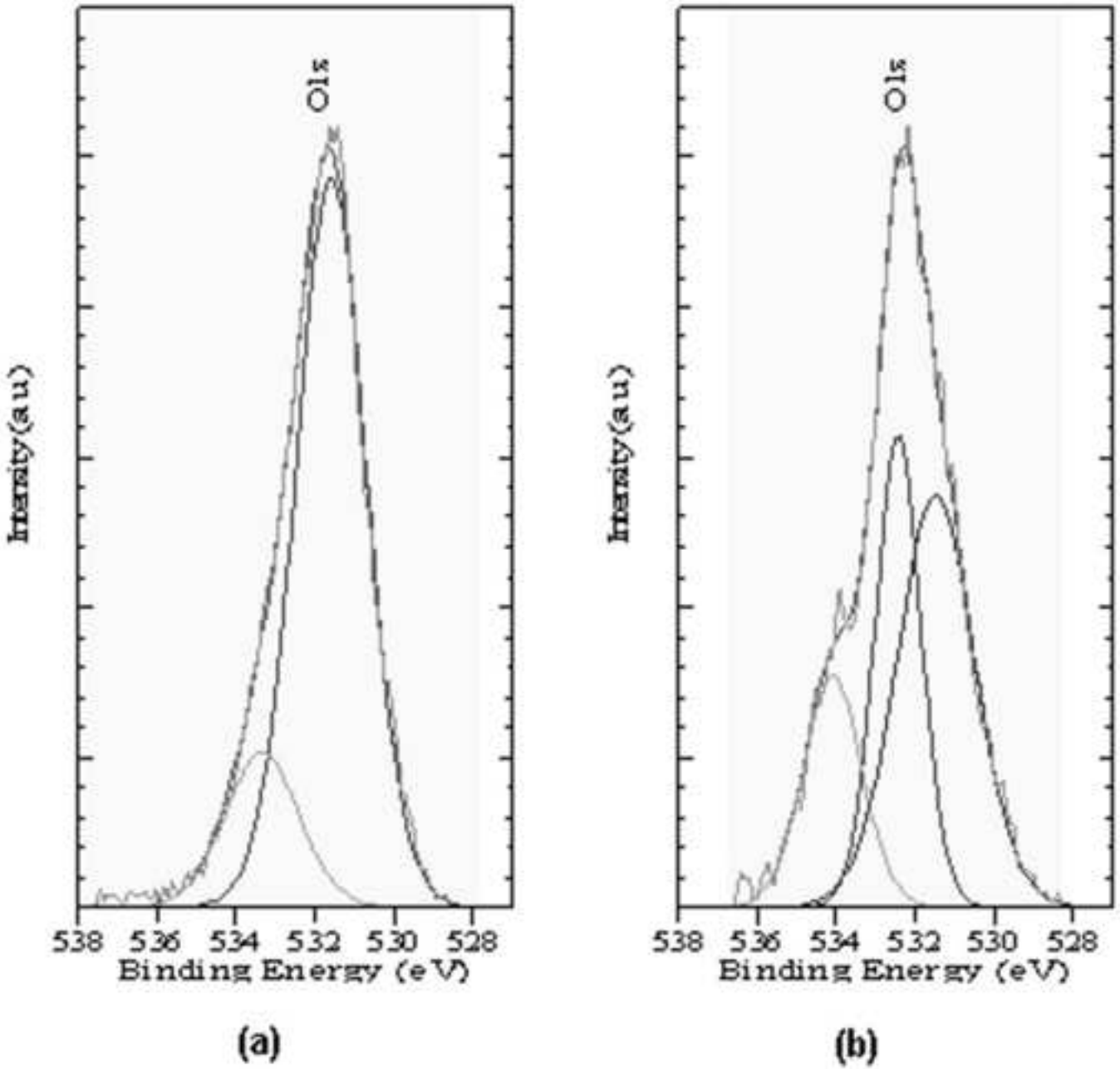
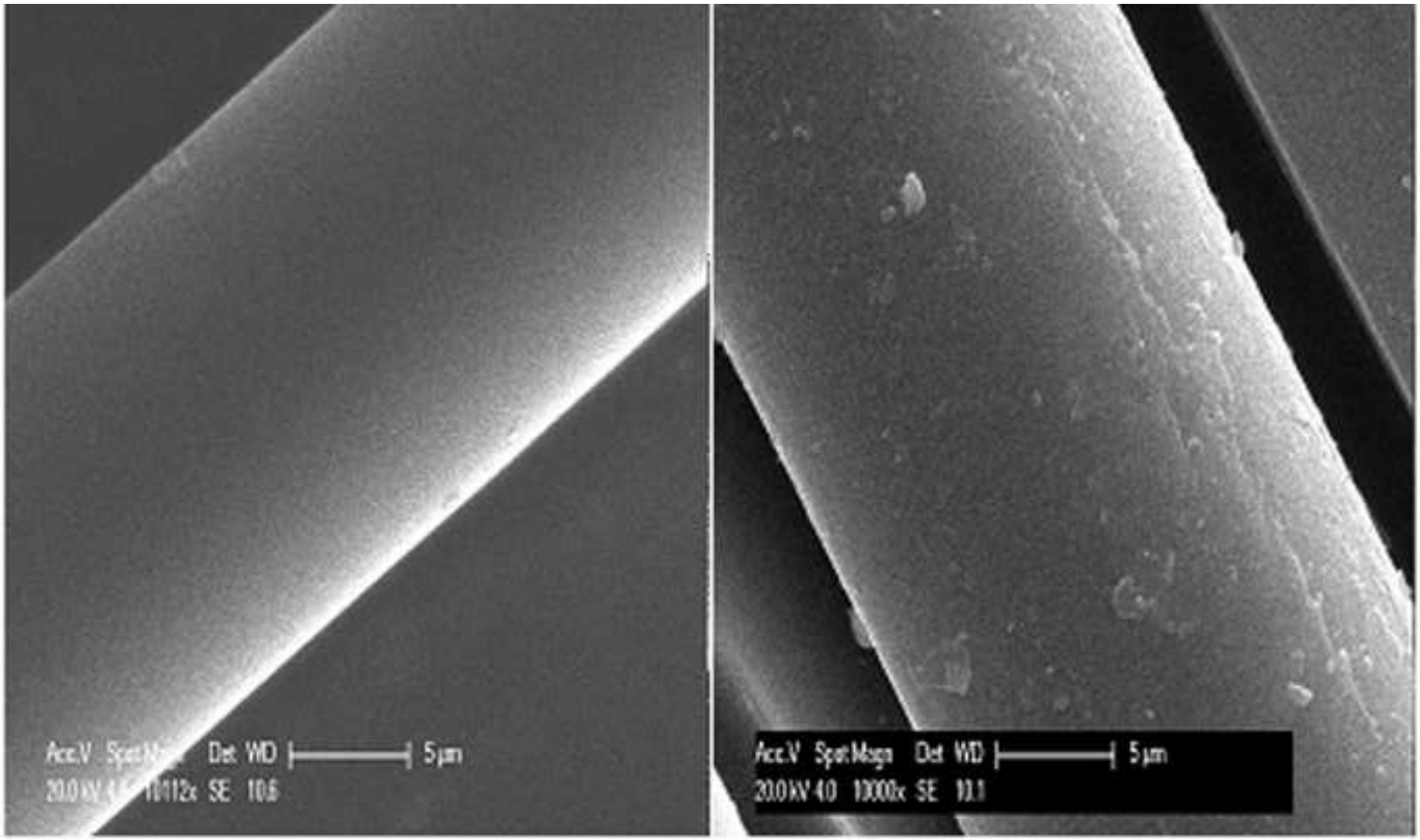


Figure-9

ACCEPTED MANUSCRIPT



(a) (b)