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Absorption Spectrum Analysis in Arabica Polymer Exudates modified by Electrical Beam Irradiation and Fruit Acid Solvents

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ABSTRACT:

In this study an effort has been devoted to extend/improve the visible light absorption capabilities (major part of solar spectrum) by tailoring their size, morphology, surface area, doping of non-metals and most importantly defect concentrations related to oxygen (vacancies or interstitials). This process has been achieved in gum Arabica biopolymer where high Voltage impulse from an IEC standard Marx generator of ten stages imparted on biopolymer exudates of plant origin in both unmodified form and after reactive modification with chromophores of weak acid solvents of fruit black grape. The resultant of the products has been observed in absorption spectroscopy and analyzed. The analysis shows prominent characteristic red shift and selection of proper fruit acid solvent makes appearance of spectra in visible spectrum range. Intensity of the absorption spectra is greatly improved by providing electromagnetic radiation through standardized Marx generator to the specimens in the preparation stage. The prepared biopolymer treated with such irradiation has high impact in medical, biological as well in different branches of material science.

KEYWORDS: Biopolymers, Marx Generator, Sol-gel process, Chromospheres, Optical Property.

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INTRODUCTION:

The development of visible light response in conductive polymers would permit sustainable solutions to many environmental issues like photo-catalytic activities for water treatment, energy conversion and storage applications[1,2]. ‘‘Biopolymer’’ refers to polymers that are bio-based, biodegradable or both. The production and use of biopolymers increases continuously with a very high rate. Biopolymers are a renewable resource and have a wide range of uses, functioning as energy storage, transport, signaling, and structural components[3]. The chemical structure of biopolymers opens up possibilities to their reactive modification. One technique in this study is by imparting electromagnetic radiation which can create structural changes in biopolymer chains and other is cross-linking with chromospheres of weak acid solvents of fruit black grape to modify bonding properties of the biopolymers. Plant originated polymers have diverse applications in pharmaceutical industry, cosmetic and paint industry, in food products[4].

Natural polymers like gum Acacia, gum Ghatti, gum Karaya, gum Tragacanth are among few names find from the exudates of shrubs and trees. The term “gum” is used to describe a group of naturally occurring polysaccharides and/or proteins originated from different sources (i.e., animal, plant and microbial). Natural plant gums are usually safe for oral consumption and are preferred over analogous synthetic gums due to their safety (non-toxic), bio-degradable, and cost effective vis-à-vis the availability of resources makes them acceptable over their synthetic counter parts[5]. Plant gums are usually hetero polysaccharide gums composed of simple hexoses and deoxy sugar units such as arabinose, galactose, glucose, mannose, xylose, uronic acids and etc. The chemical composition and molecular structure of polysaccharide plant gums play a significant role in their biological properties. In fact, the functional properties of polysaccharide plant gums are governed by the chemical composition, molecular weight, sequence of monosaccharide, configuration of glycoside linkages, and the position of glycoside linkages in the backbone and side chains[6].

Gum Acacia is the amber like, amorphous dried exudates from the bark of Acacia Arabica or other related species of Acacia plants. It is an ion conducting, water soluble biopolymer, colorless, weakly acidic (pH ≈ 4.5) salt of a complex polysachharide[7]. It is a natural polymer of plant origin has vital role in industrial manufacturing, spanning from food, pharmaceutics, paint, textile, and printing industries. It has proved itself indispensable as stabilizer, emulsifier, bulking agent, shelf-life enhancer, encapsulating agent for bioactive components, and satiating agent. Its anti-inflammatory effects on multiple organs have elevated its status as a safe food additive. Now, gum Acacia is increasingly being implicated in nano-medicines and biosensors. Among other effective uses, controlled drug delivery and better bio-dispersion of nano-paticles are most pronounced[8]. Gum Acacia with specific chemical activity forms ionic Gel which can be used as an electrolyte for

practical implications of a cell[9]. Though several structural, morphological, electrical properties of gum Acacia have been studied extensively[7,9], this study reports the interaction of pulse radiation by using Marx generator on gum Acacia solution for growth of defect.

MATERIALS AND METHODS:

Marx Generator

Marx generator is a device, capable of producing relativistic high energetic impulse wave[10]. It is an assembly of Capacitors and Resistors arrayed in both series and parallel combination.This high voltage impulse generator system first charges a capacitor bank in parallel. When the charging capacitor breaks down, discharges in series through charging and discharging resistors within "Spark Gap" and produces High Voltage (HV) impulse waveform. The detailed process of the experimental design following the IEC standard has been reported[11]. The interaction is made by High Voltage impulse from IEC standard Marx generator of ten stages of the experimental specimens. The discharge is visualised as lightning impulse of very short duration is shown below.

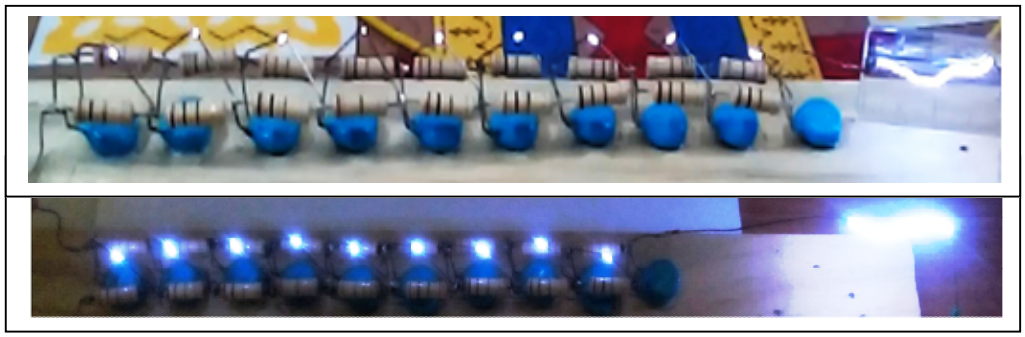

Fig. 1: Marx Circuit And Electron Beam Generation

Material Synthesis:

To prepare the experimental specimens, gum Acacia biopolymer is taken in powder form (LOBA CHEMICAL, Bombay: Average M.W. 2.5×10^5 of 98% purity grade).

The experimental specimens were prepared in the following routes.

I. Aqueous solution of gum Acacia (Specimen "a") is prepared by uniformly stirring in deionised water (Millipore System, 18.2 MΩ) at 60^0C and kept for 24 hours to reach equilibrium.

II. Complex of gum acacia dissolved in weak acid solvents of chromophores collected from fruit black grapes is prepared in a controlled process and is named as Specimen "b". Fresh black grapes (pH ≈ 2.8–3.5) are washed in ethyl alcohol and de-ionised water, dried and grinded. The grinded material is filtered in a beaker. The extract is then treated with gum Acacia powder in sol-gel process at 50^0 C to form complex. The sol–gel process allows the

low/intermediate temperature synthesis by a chemical reaction in solution and offers high chemical homogeneity.

III. Specimens “a” and “b” are transferred in separate cells of equal geometry and pulse radiation is given between two electrodes kept at same distance. One electrode is inserted within the solution at a depth of 1 cm below the surface and other electrode is placed 1 cm above the surface level. Both specimens are then treated with pulse radiation produced by Marx generator system and kept for 24 hours to reach equilibrium.

All the specimens prepared are deposited over glass substrate, air-dried and employed for experimental analysis. Absorbance spectra of the as prepared specimens are recorded by PerkinElmer Lambda 25 UV VIS Spectrometer within the wavelength range 200–1000 nm.

RESULTS AND DISCUSSIONS:

Biopolymers often have inferior properties compared to commodity polymers. Modification is a way to improve properties and achieve property combinations required for specific applications. Radiations can create impact on materials in solid and liquid states by ionisation of materials as per radiation energies and frequencies. Photon energies corresponds to visible region of the spectrum excites energetically favored electron promotion (HOMO to LUMO). Absorption of UV and visible radiation in organic molecules is restricted to certain functional groups called Chromophores. Chromospheres are the light absorbing groups of a molecule contain π electron functions and hetero-atoms having bonding electron pairs (lone pair). The X-ray diffraction pattern reveals the amorphous nature of the carbohydrate biopolymer gum acacia[12].

In polymers, atoms are connected to each other by a conjugated backbone (alternating single and double bonds) as shown in the figure 2. Every bond contains a localised “sigma” (σ) bond which forms a strong chemical bond. Every double bond contains a less strongly localised “pi” (π) bond.The p-orbitals in the series of **π**-bonds overlap each other, electrons are delocalized and move freely between the atoms. But conjugation is not enough to make the polymer conductive.

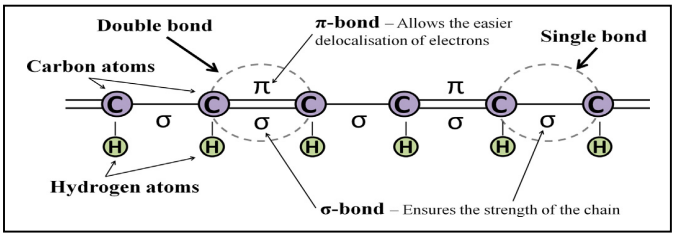

Fig. 2: Schematic diagram of conjugated polymer

Plant gum Acacia shows absorption capability in UV light due to its high band gap. The absorbance spectra of specimen “a” before and after treatment of pulse radiation are shown in Fig. 3.

For both specimens the absorbance peak observed in UV region is attributed to the overlapping of arabinogalacton components of gum acacia[13].

UV and visible radiation alters the electron distribution of molecules and promotes transition of electrons from a bonding σ or π orbital or a nonbonding n orbital to an anti-bonding σ* or π* orbital[14]. The energy of transition increases in the following order: (n→π*) < (n→σ*) < (π→π*) < (σ→σ*). The electronic excitation involves translational, rotational, and vibrational excitation. The σ→σ* transition needs energy corresponding to deep ultra violet range. Observable transitions in the UV-VIS region are due to only π→π* and n→π* transitions. Radiation induced photochemical reactions often localize their excitation on one chromophore and produce (*a*) high levels of electronic excitation, (*b*) alterations in chemical reactivity[15]. Consequently, saturated groups do not exhibit strong absorption in the ordinary ultraviolet region. The bands for gum Acacia is assigned to the n→π* electronic transition[16,17].

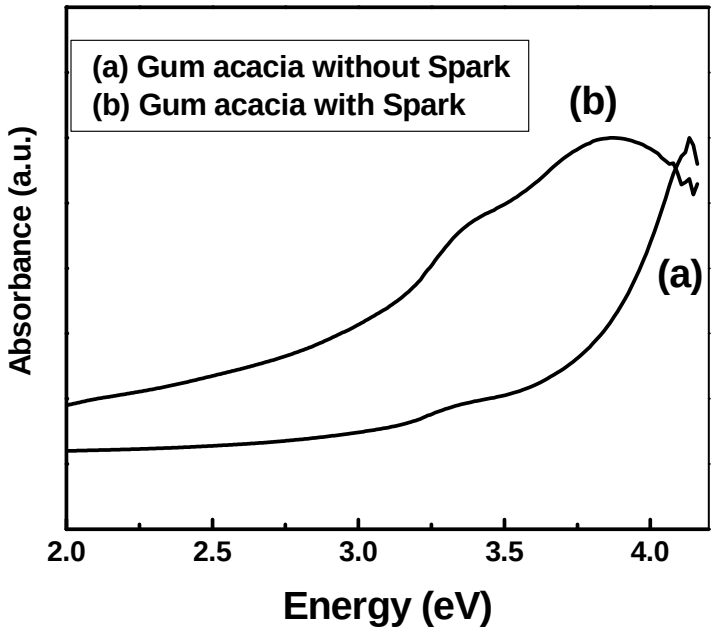

Fig. 3: The absorbance peak of gum acacia as prepared and after irradiation by e-beam

Pulse radiation induces polymerization in gum Acacia, hence it changes in molecular weight of Acacia in aqueous phase[18]. As conjugated pi systems become larger, the geometrical structure of the molecule changes so the energy gap for a π–π* transition becomes narrow and the wavelength of light absorbed correspondingly becomes larger. Along with oxygen vacancy is created which in one hand increases the visible light absorption and also restrains the recombination processes of photo

generated e– and h+ pairs by acting trap centers[19] which remains a severe problem for most commonly used TiO_2 as photocatalyst[20].

The UV-VIS absorptions of both specimens are positioned out of visible range. To make the polymer conductive it has to be doped by redox reaction. The dopant removes/adds an electron from/to the polymer chain creating a delocalized charge. But it is energetically favourable that this charge remains localized by a local distortion of the crystal lattice called polaron. This polaron can travel along the polymer chain. The conductivity depends on the methods of preparation, choice of particular solvent[9] and other factors. Hence chemical routes have been formulated to extend the visible light absorption capabilities (major part of solar spectrum) by tailoring defect concentrations related to oxygen (vacancies or interstitials) by interaction and crosslinking with weak acids.

Fig. 4 shows absorbance spectra of specimen "b" before and after treatment of pulse radiation. The characteristic absorption peak of gum Acacia modified with chromophores of black grapes is shown in the inset of Fig. 4. The absorption peak in the visible region (~2.16 eV) is greatly improved for pulse radiated sample. Whole grape contains water, sugar, organic acids and phenolic compounds. Phenolic compounds play a vital role in determining the colour of the compound. The two main substances included in this group of compounds are Anthocyanins and Tannins. Anthocyanins are pigments and they are responsible for the red and purple color of the grapes. This coloured compound possesses extensively conjugated π electrons. Conjugation of double and triple bonds with lone pairs shifts absorption maximum to longer wavelength region with peaks appearing in the visible region. Compound Tannins are large molecules which polymerize. This polymerization leads to increased molecular size[21]. Attractive polarisation forces between chromophores and the solvent (Acids) lower the energy levels of both the excited and unexcited states. This effect is greater for the excited state and so the energy difference between the states is reduced so less energy is required to promote HOMO LUMO transitions at higher wavelength radiation – resulting in a red shift (π–π*) transition[20].

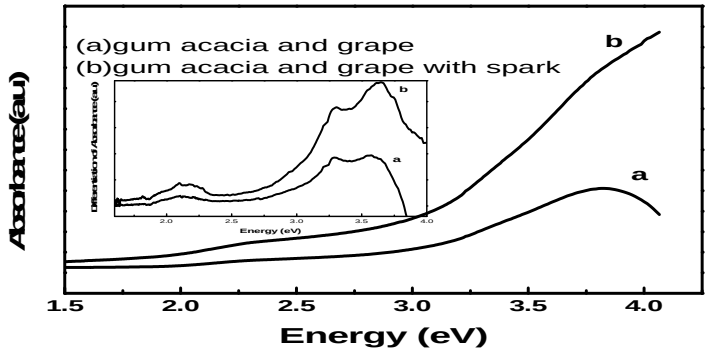

Fig. 4: UV-VIS spectrum of acacia gum, treated with black grapes of e-beam irradiated samples.

CONCLUSIONS:

All the samples have been synthesised by low cost sol-gel technique. Absorption spectra of the specimen show the transition in the uv-visible region. The pure gum Acacia shows the transition in the UV-region, where as the transition is occurred in the visible region of gum Acacia modified with chromophore of black grape and the intensity is found to be enhanced because of pulse radiation driven by Marx generator. A correlation between the structural and optical properties of the samples has been established. The prepared biopolymer treated with such irradiation has high impact in medical, biological as well in different branches of material science.

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REFERENCES:

1. Zhang Q, Uchaker E, Candelaria SL, Cao G, Nanomaterials for energy conversion and storage. Chem. Soc. Rev. 2013; 42: 3127–71.
2. Asahi R, Morikawa T, Ohwaki T, Aoki K, Taga Y, Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides. Science. 2001; 293: 269–71.
3. Finkenstadt VL, Natural polysachharides as electroactive polymers. Appl. Microbiol. Biotechnol. 2005; 67(6): 735–45.
4. Gross RA, Kalra B, Biodegradable Polymers for the Environment. Science. 2002; 297(5582): 803–07.
5. Rana V, Rai P, Tiwary AK, Singh RS, Kennedy JF, Knill CJ, Modified gums: approaches and applications in drug delivery. Carbohydr Polym. 2011; 83: 1031–47.
6. Chaubey M, Kapoor VP, Structure of a galactomannan from the seeds of Cassia angustifolia Vahl. Carbohydrate Res. 2001; 332: 439–44.
7. Mallick H, Sarkar A, An experimental investigation of electrical conductivities in biopolymers. Bull. Mater. Sci. 2000; 23: 319–24.
8. Patel S, Goyal A, Application of natural polymer gum Arabic: a review. Int. Jour. of Food Prop. 2005; 18: 986–98.
9. Mallik H, Sarkar A, Electrical characterization of ion conducting biopolymeric gel. Jour. of Non-Cryst. Sol. 2006; 352: 795–800.
10. Choyal Y, Gupta L, Preeti V et al. Development of a 300-kV Marx generator and its application to drive a relativistic electron beam. Sadhana, 2005; 30(6): 757–64.

11. Roy S, Chowdhury A, Choudhury KB, A novel electrical model to achieve the IEC standard impulse waveform (~60kV), measureable in a normal oscilloscope. Int. Jour. of Tech. Enhan. Emer. Engg, Res. 2016; 4(3): 9–12.
12. Mallik H, Gupta N, Sarkar A, Anisotropic electrical conduction in gum Arabica- a biopolymer. Mater. Sci. Eng. C. 2002; 20: 215–18.
13. Xue Y, Nie H, Zhu L, Li S, Zhang H, Immobilization of modified papa in with anhydride groups on activated cotton fabric. Appl. Biochem. Biotech. 2010; 160(1): 109-21.
14. Rabek JF, Mechanisms of photo physical processes and photochemical reactions in polymers: Theory and applications. Wiley & Sons: Chichester UK; 1987: 756 pp.
15. Fisher JP, Dean D, Engel PS, Mikos AG, Photo initiated polymerization of biomaterials. Annu. Rev. Mater. Res. 2001; 31: 171–81.
16. Papagianni GG, Stergiou DV, Armatas GS et al. Synthesis, characterization and performance of polyaniline-polyoxometalates (XM_{12}, X = P, Si and M = Mo, W) composites as electro catalysts of bromates. Sensors and Actuators B:Chemical. 2012; 173: 346–53.
17. Binitha NN, Sugunan S, Polyaniline/pillared montmorillonite clay composite nanofibers. J. Appl. Poly. Sci. 2008; 107(5): 3367–72.
18. Tsuyoshi K, Makoto N, Setsuko T, Phillips OG, Mikiro T, Radiation-induced polymerization of gum arabic (acacia senegal) in aqueous solution. Food Hydrocolloids. 2006; 20: 983–9.
19. Jipa IM, Stroescu M, Guzun AS et al. Effect of gamma irradiation on biopolymer composite films of poly(vinyl alcohol) and bacterial cellulose, Nuc. Inst. Methods in Physics Research B: Beam Int. Mater. Atoms. Elsevier 2012; 278: 82–7.
20. Ghosh S, Kouame NA, Remita S et al. Visible-light active conducting polymer nanostructures with superior photo catalytic activity. Sci. Rep. 20156; 5(18002): 1-8.
21. Xia EQ, Deng GF, Guo YF, Li HB, Biological activities of polyphones from grapes, Int. J. Mol. Sci. 2010; 11(2): 622-46.