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Physicosurface Properties of Afzelia and Prosopis Hemicellulosic Gums: Potential Surface Active Agents

E. O. Olorunsola[1*], P. G. Bhatia[2], B. A. Tytler[3] and M. U. Adikwu[4]
[1]*Department of Pharmaceutics and Pharmaceutical Technology, University of Uyo, Uyo, Nigeria*
[2]*Department of Pharmaceutics and Pharmaceutical Microbiology, Usmanu Danfodiyo University, Sokoto, Nigeria*
[3]*Department of Pharmaceutics and Pharmaceutical Microbiology, Ahmadu Bello University, Zaria, Nigeria*
[4]*University of Abuja, Abuja, Nigeria.*

Abstract*: This study was aimed at investigating the physicosurface properties of afzelia gum (AFG) and prosopis gum (PRG). The two hemicelluloses were studied alongside sodium carboxymethylcellulose (SCMC). The physical and surface properties of the polymers were determined. There was no significant difference in the flow of the two hemicelluloses. Solubility in 2 % w/v sodium hydroxide was significantly higher than solubility in water ($P < 0.001$) for each of the three polymers. A 2 % w/v dispersion of PRG gave a significantly higher viscosity compared to the same concentration of AFG. While the two hemicelluloses have same critical micelle concentration of 0.25 % w/v which is significantly higher than that of SCMC, PRG has greater effect on reduction of surface tension. Prosopis gum and afzelia gum are hemicelluloses of the xyloglucan type. Prosopis gum possesses better surface activity compared to afzelia gum and might enable better drug delivery.*
Keywords*: surface property; HLB value; surface active agent; afzelia gum; prosopis gum.*

I. Introduction

While the chemical properties of an excipient are more indicative of its compatibility with different drugs, its physical and surface properties are mainly indicative of its effectiveness in serving specific functions in pharmaceutical formulations [1,2]. The physicosurface properties of major importance include: flow, adhesion, water sorption, solubility, surface tension, critical micelle concentration and hydrophile-lipophile balance [1,3,4].

Adsorption of surface active agents at various interfaces results in changes in the nature of such interfaces making them of considerable importance in Pharmaceutical Sciences [5]. This property confers to them usefulness as emulsifying agents, suspending agents, wetting agents, solubilizing agents and absorption enhancers [3,6]. Surfactants can also facilitate adhesion of one surface on the other. If either or both surfaces are of biological nature, the term "bioadhesion" is used [3]. For drug delivery purposes, bioadhesion refers to the attachment of drug carrier system to a biological surface which often results to increase in drug absorption [7].

Hydrocolloids have many industrial applications. They are used in paper industry, textile industry, food and drinks industry, pharmaceutical industry, et cetera [8,9]. These applications are based on their physical and surface properties [1]. This fact formed the basis of investigation of rheological and surface properties of Acacia tortuosa gum (a galactan gum) carried out by Munoz et al. [1]. The work showed that the critical micelle concentration of the polymer is 0.5 % w/v and that the polymer could reduce the surface tension of water from 72.5 to 42.6 mN/m.

Afzelia gum was found to be less acidic than hydroxypropylmethylcellulose [10]. It has poor water-solubilty; but can be solubilized by aqueous alkali and had been characterized as a xyloglucan hemicellulose [11]. Prosopis gum, though a seed gum has not been characterized as being a xyloglucan. The two gums have been used as bioadhesive polymers for the delivery of many drugs [12 – 14] showing that they may possess surface activity.

Hemicelluloses are slightly more complex than ordinary gums [10] and could exhibit different physical and surface properties. This study was aimed at determining the physicosurface properties of the two natural cellulose-based gums (AFG and PRG) as they may possess surface activity and could enhance drug delivery. These properties will be studied alongside those of sodium carboxymethylcellulose which is a sodium salt of a cellulose derivative.

II. Materials And Methods

Materials

Afzelia seeds collected from Afzelia africana tree and Prosopis seeds collected from Prosopis africana trees were purchased at Abuja, Nigeria. They were authenticated by the taxonomist in the Department of Biological Sciences, University of Abuja, Abuja, Nigeria; and issued with voucher numbers UNIABUJA I51 and UNIABUJA I53 respectively. Sodium carboxymethylcellulose, ethanol and sodium metabisulphite (BDH Chemicals, Poole, England), acetone (Merck, Germany) and diethyl ether (Sigma–Aldrich, Germany) were used as obtained.

Extraction and purification of afzelia and prosopis gums

The method described by Builders et al. [10] was used for the extraction and purification of afzelia gum while the extraction and purification of prosopis gum were carried out using the method described by Adikwu et al. [12].

Differential scanning calorimetry (DSC)

A weighed quantity of gum (3.0 mg) was placed in the 40µL A1- crucible of the DSC machine (NETZSCH Co., Germany). The sample was subjected to heating at the rate of 20 ^{o}C/min under nitrogen environment and the scanning was done over a temperature range of 0 – 500 ^{O}C.

Determination of angle of repose

A 20 g quantity of gum was poured inside a funnel of orifice diameter 0.75 cm clamped at height 10 cm above the table surface. The gum was allowed to flow freely and the height 'h' and the base diameter 'D' of the heap were measured. The angle of repose θ was calculated using the equation:

$\theta = \text{Tan}^{-1}(2h/D)$……...(1)

Determination of solubility

The solubility of the gum in water and in 1 % w/v sodium hydroxide solution was determined using the method described by Olorunsola et al. [2]. A 2 g sample was dispersed in 20 ml solvent and left overnight. The dispersion was filtered and 5 ml of the filtrate was heated to dryness over a water bath. The residue obtained was weighed and the solubility was calculated as % w/v.

Determination of apparent viscosity of the gum mucilage

The viscosity of a 2 % w/v of gum dispersion was measured using a DV1 prime viscometer (Brookfield Engineering, U.S.A.) at room temperature and 10 rpm. A 70 ml volume of the gum dispersion was placed in the cup of the viscometer and the reading was taken.

Evaluation of surface activity

Gum dispersions (100 ml) of different concentrations (0.10, 0.25, 0.50, 0.75 and 1.00 % w/v) were prepared, stirred and left for 24 h for hydration and dissolution. A Searls tensiometer (Philip Harris P23660/9, England) was used to determine the surface tension of the different dispersions. The circular plate was submerged below the surface of the dispersion and then gradually raised upward. The equipment was zeroed when the plate was just at the surface of the dispersion. The plate was subsequently raised until it just detached from the surface of the liquid. The reading was taken from the scale and converted to kg (10 mm being equal to 10^{-3} kg). The surface tension of each dispersion was calculated using the modified form of the equation of Fell [15]:

$$\gamma = \frac{F}{2\pi R} \cdot \emptyset \quad \text{..... (2)}$$

γ is the surface tension, F is the detachment force, R is radius of the circular plate and $\emptyset$ is the correction factor of the instrument. F was calculated as the product of the mass 'm' causing detachment and the acceleration due to gravity 'g'. A graph of surface tension was plotted against gum concentration for the range 0.0 to 1.0 % w/v. The critical micelle concentration was determined as the point when increase in concentration did not lead to further decrease in surface tension.

Evaluation of hydrophile-lipophile balance

A 50 ml volume of 2 % w/v gum concentration was titrated with a 5 % w/v of phenol until clouding became visible. The volume of phenol solution used (known as phenol index, PI) was noted and the HLB value was calculated using equation 3 as given by Kruglioaokor [4].

HLB = 0.89 (PI) + 1.11…… (3).

Statistical analysis

Data obtained were expressed as mean value ± standard error of the mean. They were subjected to analysis of variance (ANOVA) using GraphPad Instat-3 software to determine the significance of differences and p - values less than 0.05 were taken to be significant.

III. Results

Differential scanning thermogram

An endotherm which peaked at 77 ^{O}C was observed between 20 and 150 ^{O}C in the thermogram of AFG. No other clear transition was observed until 300 ^{O}C when an exotherm which peaked at 325 ^{O}C and extended to 345 ^{O}C was observed (Figure 1). The thermogram of PRG showed two endotherms. The first one peaked at 62 ^{O}C while the second peaked at about 300 ^{O}C. An endotherm ranging from 20 to 150 ^{O}C with a peak at 70 ^{O}C was observed in the thermogram of SCMC. This was followed by a diffuse exotherm which peaked at 295 ^{O}C.

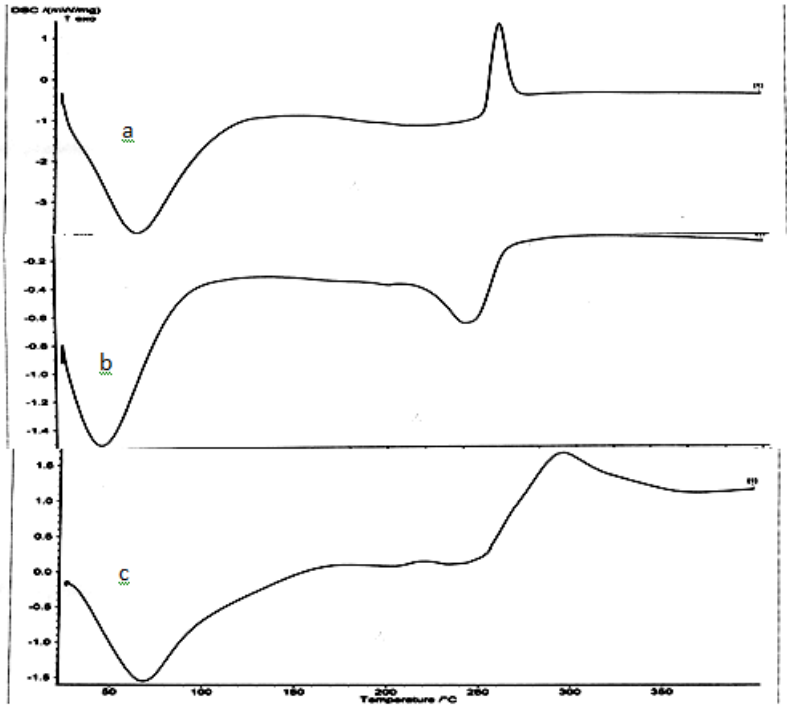

Figure 1. DSC thermograms of (a) afzelia gum (b) prosopis gum (c) sodium carboxymethylcellulose.

Some physical properties

Some physical properties of the polymers are shown in Table 1. There was no significant difference in the angle of repose of AFG and that of PRG. SCMC had a significantly higher angle of repose ($p < 0.05$). The solubility of each of the gums increased significantly ($P < 0.001$) in the presence of 1 % w/v aqueous solution of sodium hydroxide compared to their solubility in water. There was a significant difference in the viscosity of 2 % w/v dispersions of the three gums with SCMC having significantly higher value ($P < 0.001$) compared to the two hemicelluloses.

Table 1. Some physical properties of the gums

Parameter	AFG	PRG	SCMC
Angle of repose (^{O})	42.60 ± 0.29	41.37 ± 0.99	50.56 ± 0.25
Solubility in water (% w/v)	0.68±0.03	0.12±0.01	1.26±0.74
Solubility in 1% NaOH (% w/v)	7.60±0.00	7.00±2.13	6.80±2.27
Viscosity (mPa-s)	158±3.75	340±13.23	5100±22.72

AFG= afzelia gum PRG= prosopis gum SCMC= sodium carboxymethylcellulose

Surface tension and critical micelle concentration

The graph of surface tension versus gum concentration is illustrated in Figure 2. The critical micelle concentration of the gums and the lowest surface tension attained are shown in Table 2. The two hemicelluloses (AFG and PRG) had the same critical micelle concentration. The extent to which the gums could reduce the surface tension irrespective of the concentration was in the order SCMC > PRG > AFG.

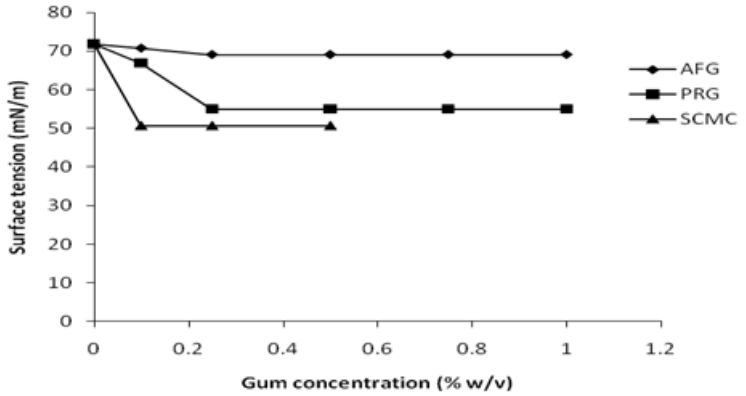

Figure 2. Plot of surface tension (mN/m) versus gum concentration (% w/v)

Table 2. Surface properties of the gums

Parameter	AFG	PRG	SCMC
Critical micelle concentration (% w/v)	0.25	0.25	0.10
Lowest surface tension attained (mN/m)	69.1±1.20	55.0±0.00	50.7±0.00
Phenol index (ml)	9.70±0.33	11.40±0.49	14.53±0.05
HLB value	9.74±0.36	11.26±0.53	14.04±0.06

AFG= afzelia gum PRG= prosopis gum SCMC= sodium carboxymethylcellulose

HLB values

There was a significant difference ($p < 0.01$) in the phenol index of the different gums (Table 2). There was also a significant difference ($p < 0.01$) in the HLB values of the gum. The values for both parameters followed the same trend of SCMC > PRG > AFG.

IV. Discussion

Differential scanning calorimetry (DSC)

The endotherm in the thermogram of AFG can be ascribed to enthalpy relaxation of the polymer [16]. The exotherm can be ascribed to crystallization of the polymer. From the peak of the exotherm, it can be inferred that the polymer has crystallization temperature (T_c) of 325 ^{O}C which is not significantly different from 317.7 ^{O}C reported by Builders et al. [10]. According to these researchers [10], the polymer has two melting temperatures (273 and 335 ^{O}C) which appeared just before and just after the exotherm respectively. It was inferred by them that AFG exists in two forms. Therefore, as one form was melting, the other form was crystallizing and vice versa; and the endotherms of melting might have been superimposed by the exotherm of crystallization. The 90.90 J/g observed as the latent heat of crystallization might thus be taken as the difference between the actual latent heat of crystallization and the latent heat of melting of the polymer.

The first endotherm in the thermogram of PRG can be ascribed to the enthalpy relaxation of the polymer [16]. There was no exothermic transition in the thermogram. The second endotherm can be ascribed to the melting of the polymer and the peak (300 ^{O}C) represents the melting temperature (T_m) of the polymer [17]. The latent heat of melting was 106.07 J/g. Hence, 106 J of heat is required to melt 1 g of the polymer. Prosopis gum exhibited similar thermal behaviour as hydroxypropylmethylcellulose [10].

The enthalpy relaxation of SCMC was illustrated by the endotherm [16]. Enthalpy relaxation is an endothermic process as it involves heat flow to the system. It is associated with increase in temperature. It is therefore, a second order reaction. The diffuse exotherm which peaked at 295 ^{O}C can be ascribed to polymer degradation [18].

There was no change in the physical state of the polymers during enthalpy relaxation. However, when the right temperature was reached, the particles attained an orderly arrangement forming crystals in the process called crystallization. Crystallization involves heat loss. Hence, it is an exothermic transition. Since, it takes place at a constant temperature; it is a first order reaction [10]. As heating continued beyond crystallization, a temperature was reached when the crystals moved out of the orderly arrangement. This is called melting. As heat gain is associated with the process of melting, it is an endothermic transition. Just as in crystallization, melting takes place at constant temperature. It is thus a first order transition [17].

It can be concluded that when polymers are heated, they are converted from the amorphous to pseudo-amorphous form in the process of enthalpy relaxation. Further heating results to a change from pseudo-amorphous conformation into crystalline form and subsequently melting. While glass transition and enthalpy relaxation are characteristic of the amorphous domain of polymers [19], melting transition is characteristic of their crystalline domain [20]. In some instances, polymers experience exothermic transition of degradation (as observed with SCMC) instead of endothermic transition of melting [18].

Cohesive property

The angle of repose of AFG and PRG which fell between 40 and 50 ^{0} suggests poor flow while that of SCMC (> 50 ^{0}) suggests very poor flow [21]. Determination of angle of repose is an indirect method of quantifying powder flowability as it is related to inter-particulate cohesion [22]. The lower angle of repose of AFG and PRG suggests better flowability and lower inter-particulate cohesion compared to SCMC. Adhesion and cohesion may be considered as two phases of the same phenomenon; cohesion occurs between similar surfaces while adhesion occurs between two unlike surfaces. Forces of cohesion acting between particles in a powder bed include: van der Waals forces, surface tensional forces and electrostatic forces. These cohesive forces are responsible for inhibition of powder flow [23].

Solubility and viscosity

The solubility of each of the three gums was significantly enhanced ($p < 0.001$) in the presence of dilute aqueous sodium hydroxide. Afzelia gum had been described as a xyloglucan having a cellulose backbone. This was suggested by solubility enhancement in dilute solution of sodium hydroxide [10]. Prosopis gum can thus be equally described as a xyloglucan hemicellulose.

Polymers to be used as suspending and/or emulsifying agents are expected to produce suspensions and/or emulsions with acceptable viscosity [1]. The significant difference in the viscosity of 2 % w/v dispersions of the polymers shows that higher amount of AFG and PRG will be needed to achieve the same viscosity attained by a given concentration of SCMC. Conversely, dispersions produced by a given concentration of AFG or PRG will be more pourable than those prepared by the same concentration of SCMC. The viscosity of afzelia gum is not significantly different from 143.4 cP reported by Ibezim et al. [14].

Surface tension and critical micelle concentration

The three gums were able to reduce the surface tension of water at different magnitudes and the effect increased with increase in the concentration of the gum. A phenomenon termed "critical micelle concentration" was observed with each of the gums. This is the point at which further increase in gum concentration did not lead to further decrease in the surface tension of water as reflected in Figure 2 [24]. At concentrations above 0.5 % w/v, the dispersion of SCMC became sticky exhibiting high adhesive strength. Hence, the plot was terminated at this concentration for the dispersion of this polymer.

When surface active agents are present below their critical micelle concentrations, they concentrate at the water surface with the hydrophobic region orientated away from the aqueous phase causing an expansion of the surface layer. This leads to reduction in the surface tension of the liquid [25]. When they are present above the critical micelle concentration, aggregates of colloidal dimensions called micelles are formed. The hydrophobic chains of the surfactant form the core of the micelles and are shielded from the aqueous environment by the hydrophilic chains [25]. Formation of micelles is responsible for solubilization of water-insoluble substances [26]. This is the principle behind the use of surface active agents as solubilizing agents.

Sodium carboxymethylcellulose is the most effective surfactant in the group as it caused the greatest reduction in the surface tension of water. The surface activity of PRG is better than that of AFG. Sodium carboxymethylcellulose is also the most efficient surfactant in the group as it possesses the lowest critical micelle concentration. There is no significant difference in the efficiency of AFG and PRG as surface active agent as they possess the same critical micelle concentration. The lowest CMC (0.1 % w/v) observed with sodium carboxymethylcellulose may be attributed to the presence of $-CH_2COO^-Na^+$ in the molecule. Presence of ions generally decreases the critical micelle concentration of surfactant and increases micellar size [25]. This is sequel to the increase in the force of repulsion between the similar charged groups in the micelle; promoting micelle growth and reducing the energy required for their formation [26].

A low concentration of surfactant increases absorption possibly due to enhanced contact of the drug with the absorbing membrane. Concentrations above CMC will either produce no additional effect or will cause decrease absorption depending on the nature of the drug including its water-solubility or whether non-

absorbable micelles are formed [26]. While the release of a poorly soluble drug from a dosage form may be enhanced by the presence of a surfactant which impart wetting, inhibition of absorption may occur if a soluble drug is incorporated into surfactant micelles [27].

Even though the hemicellulosic gums only showed mild to moderate surface activity, studying their surface properties is important for establishing the optimum concentration for striking a balance of effect on solubilization and absorption for different types of drugs. For instance, while a low concentration of SCMC (< 0.10 % w/v) must be used to ensure absorption of a soluble drug, higher concentrations of the hemicelluloses are permissible to ensure adequate absorption of the same type of drug. Also, while a higher concentration (> 0.25 % w/v) of the hemicelluloses must be used to ensure absorption of poorly soluble drug, as low as 0.10 % w/v of SCMC will ensure solubilization and absorption of the same type of drug.

Hydrophile - lipophile balance

Phenol index is directly related to HLB value [4] and was found to be in the order SCMC > PRG > AFG. HLB value is a measure of the relative hydrophilicity of surfactants and ranges from 0 to 20 [28]. According to the classification by Davies [28], surfactants having HLB values of 8 to 18 are oil-in-water emulsifiers. Therefore, the three gums are oil-in-water emulsifying agents. The HLB values of the polymers ranged from 9.74 (AFG) to 14.04 (SCMC) showing that AFG is the least hydrophilic while SCMC is the most hydrophilic.

V. Conclusion

Afzelia and prosopis gums are xyloglucan hemicelluloses. They possess better flowability and lower inter-particulate cohesion compared to SCMC. Prosopis gum is likely to form a more viscous dispersion compared to afzelia gum if used at the same concentration for liquid or semi-solid formulations. Sodium carboxymethylcellulose is a more effective and a more efficient surfactant compared to the two hemicellulosic gums. It is also more hydrophilic than the two gums. The surface activity of PRG is better than that of AFG and the former might enable better drug delivery.

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