

Article

## Green Polymers in Personal Care Products: Rheological Properties of Tamarind Seed Polysaccharide

Alessandra Semenzato <sup>1,\*</sup>, Alessia Costantini <sup>2</sup> and Giovanni Baratto <sup>2</sup>

<sup>1</sup> Dipartimento di Scienze del Farmaco, University of Padova, Via F. Marzolo, 5, 35131 Padova, Italy

<sup>2</sup> Unired Srl, Spin off-University of Padova, Via N. Tommaseo 69, 35131 Padova, Italy;  
E-Mails: info@unired.it (A.C.); gianni.baratto@unired.it (G.B.)

\* Author to whom correspondence should be addressed; E-Mail: alessandra.semenzato@unipd.it;  
Tel.: +39-49-827-5356; Fax: +39-49-827-5366.

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**Abstract:** Tamarind seed polysaccharide (TSP) is a xyloglucan of vegetable origin, recently proposed for the cosmetic and pharmaceutical market as a “green” alternative to hyaluronic acid. In this study, TSP water dispersions, at different concentrations, were characterized by means of rheological measurements, both in continuous and oscillatory flow conditions. The results were compared with those of hyaluronic acid of two different molecular weights. The results pointed out the close rheological behaviors between TSP and hyaluronic acid with comparable molecular weight. Afterwards, the structural features of binary and ternary polysaccharide associations prepared with TSP, hyaluronic acid (very high MW) and dehydropolysaccharide gum, a modified xanthan gum, with high stabilizing properties, were investigated. The rheological properties were significantly affected by the polysaccharide ratios in the mixture, suggesting that the combination of TSP with other polymers can lead to a modulation of the texture and functional properties of cosmetics.

**Keywords:** polysaccharides; moisturization; xyloglucan; rheology

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### 1. Introduction

The use of polysaccharides in cosmetic formulations is growing, together with the increasing attention of manufacturing companies toward green raw materials and product sustainability.

Polysaccharides are complex carbohydrates with many hydroxyl groups and generally interact strongly with water, according to their chemical composition. They are widely used in food, cosmetic and pharmaceutical industries, because they can provide good mechanical properties for applications as fibers, adhesives, hydrogels or drug delivery agents [1].

In personal care products, these multipurpose polymers are used as thickener and stabilizing agents (*i.e.*, xanthan gum, cellulose) or as moisturizing ingredients that can also improve the skin feel of the product (*i.e.*, hyaluronic acid, guar derivatives) [2].

Tamarind seed polysaccharide is obtained from the endosperm of the seed of the tamarind tree, *Tamarindus indica* L., an economically important tree in the Indian subcontinent [3].

Tamarind seed polysaccharide is a xyloglucan, formed by a linear  $\beta$ -(1,4)-D-glucan backbone, partially substituted at the O-6 position of its glucopyranosyl residues with  $\alpha$ -D-xylopyranose. Some of the xylose residues are  $\beta$ -D-galactosylated [4]. Xyloglucan water dispersions show high viscosity and broad pH tolerance [5]. Therefore, they are used as a texturizing agent and a thickener in food and pharmaceutical products [6].

Toxicological studies indicate that xyloglucan is very well tolerated by conjunctival cells and can reduce drug-related toxicity, probably due to its mucin-like structure. Moreover, xyloglucan seems to promote corneal wound healing due to its greater interaction with the integrin recognition system than hyaluronate [7]. The similarities between xyloglucan and hyaluronic acid, from both a physical and a biological perspective, suggest this polysaccharide as a “green” alternative to hyaluronic acid [7,8].

In this study, we investigated the rheological properties of xyloglucan aqueous dispersions, prepared with a new raw material (TSP), recently introduced and intended for personal care products (Xilogel<sup>®</sup>-Indena).

The results were compared with those of two microbial hyaluronate products of different molecular weights. Besides, the rheology of the binary and ternary associations of TSP with different polysaccharides was studied with the aim of optimizing the effects on the cosmetic properties.

## 2. Experimental Section

### 2.1. Materials

Xilogel<sup>®</sup> (Tamarind seed polysaccharide): MW, 600–700 kDa; Indena S.p.A., Milan, Italy; TSP (in the text); T (in the graphs).

Phylcare LW (Low Molecular Weight) (sodium hyaluronate): MW, 400–1000 kDa; Shandong Freda Biochem Co. (Jinan, China); HA (in the text and graphs).

Phylcare HW (High Molecular Weight) (sodium hyaluronate): MW, 1800–2200 kDa; Shandong Freda Biochem Co.; HB (in the text and graphs).

Amaxe XT<sup>™</sup> (Dehydropolysaccharide gum): MW, >10 kDa; National Starch (Bridgewater, NJ, USA); A (in the text and graphs).

## 2.2. Methods

All samples were dispersed in distilled water, gently stirred overnight, until complete and homogenous swelling. Before carrying out the rheological analysis, all samples were stored at 23 °C for at least four days.

Rheological analyses were performed in continuous and oscillatory flow conditions using a rotational rheometer, Rheoplus Anton Paar MCR 101, at fixed temperature  $23 \pm 0.05$  °C, equipped with a cone-plate geometry CP50-1 (fixed gap 0.098 mm) (Anton Paar GmbH, A-8054 Graz, Austria).

The viscosity at rest ( $\eta_0$ ) was calculated by fitting the flow curves of the different samples, obtained in stationary conditions as a function of shear rate, with the Carreau–Yasuda model that describes the shear thinning behavior of materials [9].

The viscoelastic properties,  $G^*$  (complex modulus),  $G'$  (elastic modulus) and  $G''$  (viscous modulus), were measured at fixed oscillation amplitude, within the linear viscoelastic region of each material, by varying the oscillation frequency. The trends of  $G'$  and  $G''$  as a function of frequency, measured in linear conditions, are the “mechanical spectra” of the material and describe its structural properties [1].

## 3. Results and Discussion

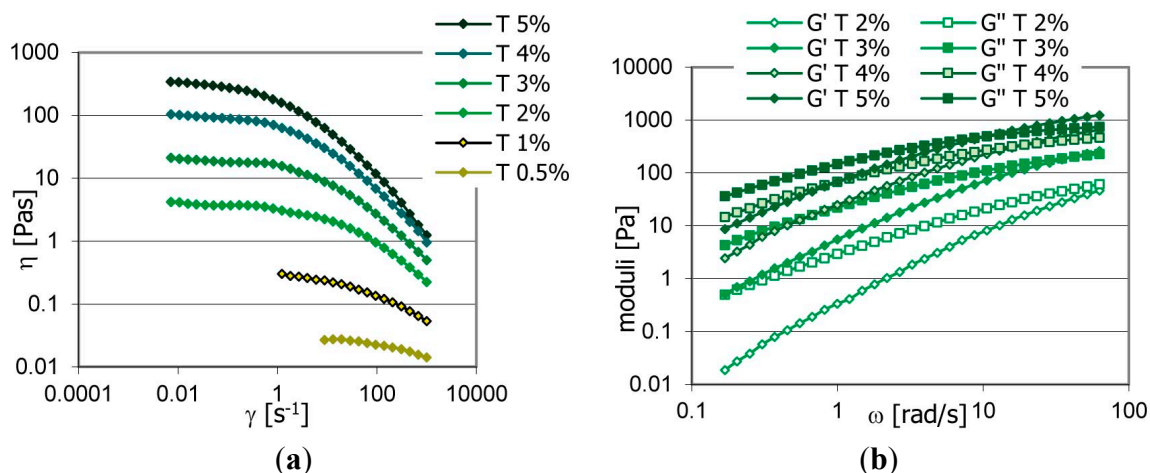
### 3.1. Rheological Characterization of TSP vs. Hyaluronic Acid

The rheological properties of TSP aqueous solutions have been measured both in continuous and oscillatory flow conditions at different concentrations in the range 0.5%–5% w/w.

The viscosity trends as a function of shear rate of TSP solutions are shown in Figure 1a.

The viscosity of TSP solutions increased with the polymer concentration in conjunction with the shear-thinning behavior, as a result of firmer interactions between the polysaccharide chain and the solvent.

The viscoelastic properties as a function of frequency, using a fixed oscillation amplitude within the linear viscoelastic range, showed a sol-gel transition as a function of TSP concentration (Figure 1b).



**Figure 1.** (a) Viscosity trends vs. shear rate; (b)  $G'$  and  $G''$  trends as a function of the frequency of tamarind seed polysaccharide (T) samples at different concentrations.

TSP solutions of up to a 2% concentration showed a liquid-like behavior, with the viscous modulus  $G''$  greater than the elastic modulus  $G'$ , in all of the frequency ranges investigated, and both of the moduli significantly dependent on frequency. By increasing the polymer concentration, the elastic character of the systems increased, and  $G'$ , the elastic modulus, became higher than the viscous modulus, when high frequencies were applied.

The mechanical spectra of the TSP concentrated solutions (3%–5% w/w) showed a crossover point between the moduli patterns characteristic of the viscoelastic materials. As expected, the frequency value correspondent to the crossover point decreased by increasing the polymer concentration (crossover point-frequency values: T3% 40.4 rad/s, T4% 19.2 rad/s, T5% 10.5 rad/s).

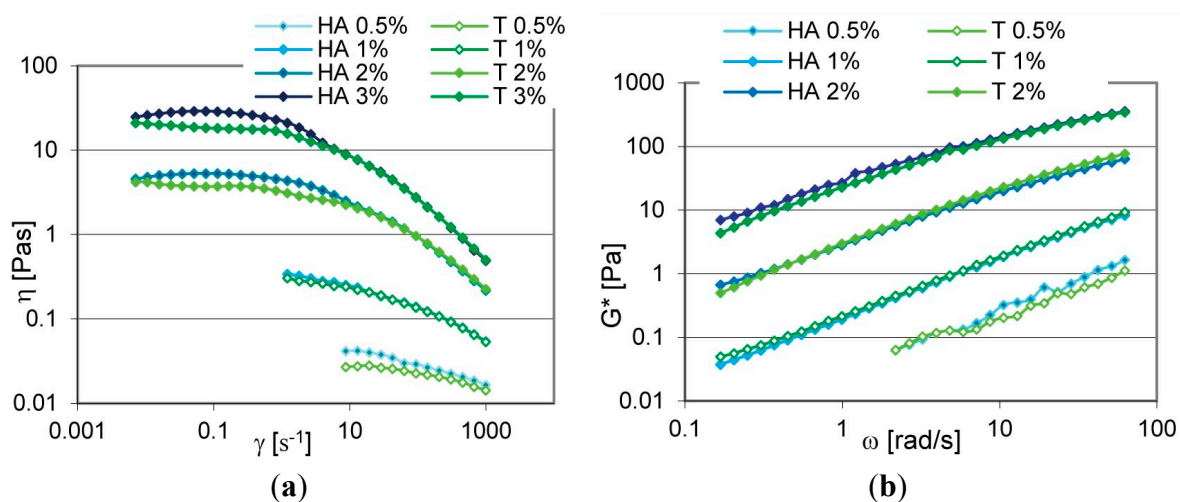
The rheological properties of TSP were compared with those of hyaluronic acid using two different raw materials with different molecular weights: HA (400–1000 kDa) comparable with TSP, and HB (1800–2200 kDa).

In Figure 2, the viscosity curve as a function of shear rate (continuous flow conditions) (Figure 2a) and the viscoelastic properties (oscillatory flow conditions) (Figure 2b) within the linear viscoelastic region of HA and TSP aqueous dispersions, prepared at the same concentrations, are compared.

The flow curves showed an increase of viscosity and the shear-thinning behavior as a function of the concentration for both TSP and HA aqueous dispersions in the range 0.5%–3% w/w (Figure 2a).

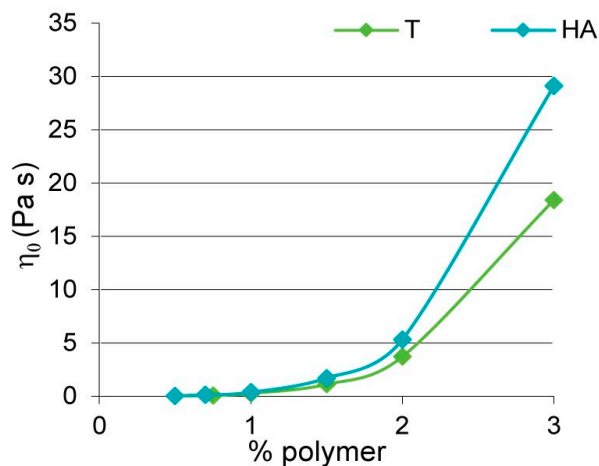
In oscillatory flow conditions, all of the samples presented a liquid-like behavior with similar absolute values of the complex modulus  $G^*$  as a function of polymer concentration (Figure 2b).

The  $G^*$  patterns were dependent on the frequency, confirming the significant viscous character of the structures that both polysaccharides are able to form in water.



**Figure 2.** (a) Viscosity trends vs. shear rate; and (b)  $G^*$  trends as a function of the frequency of TSP and HA aqueous dispersions at different concentrations.

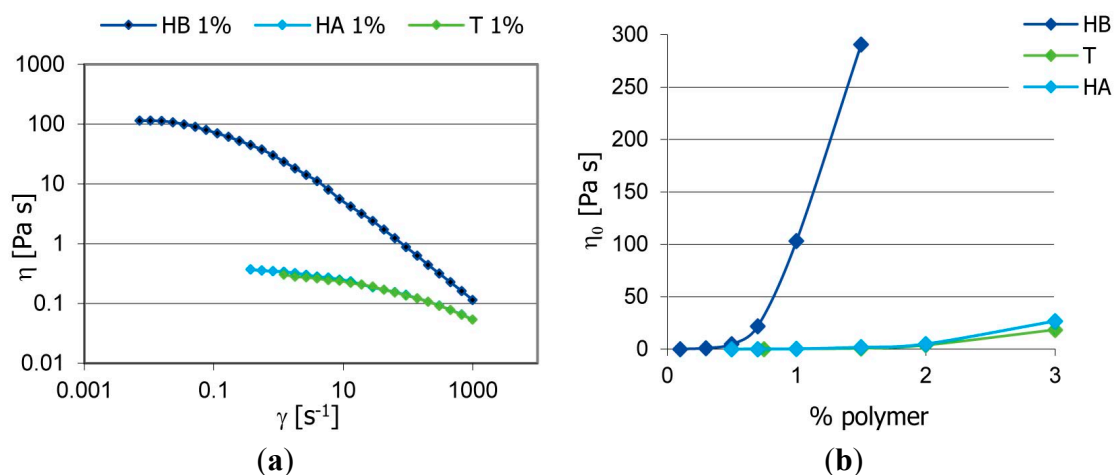
By plotting the viscosity at rest ( $\eta_0$ ) values, calculated with the Carreau–Yasuda model [9] vs. polymer concentration (Figure 3), we obtained similar trends (up to the 2% w/w) for the two polysaccharides.



**Figure 3.** Viscosity at rest ( $\eta_0$ ) values as a function of polymer concentration.

At higher concentrations, HA aqueous dispersions were more viscous than those of TSP, suggesting a better swelling capability of hyaluronate, in concentrated water dispersions.

Even though hyaluronate and xyloglucan are polymers with different chemistries obtained from different sources (microbial and vegetal), the rheological properties of their solutions, in the concentration range investigated, were very similar, suggesting that the molecular weight represents the most relevant factor affecting their swollen structures. It is reasonable to think that the similarity in the rheology of the polysaccharides' solution can produce comparable sensorial and moisturizing effects in personal care products. In Figure 4a, the flow curves of TSP, HA and HB aqueous solutions (1% w/w) are compared. As expected, the rheological behavior of hyaluronic acid is significantly affected by the molecular weight. The HB sample shows an increment of viscosity at low shear rates, higher (two magnitude orders) than those of HA and TSP, together with a more marked shear thinning behavior.



**Figure 4.** (a) Viscosity trends vs. the shear rate of HA, HB and TSP at 1% w/w; (b)  $\eta_0$  values as a function of polymer concentration.

By plotting the zero viscosity values, calculated with the Carreau–Yasuda model vs. polymer concentration (Figure 4b), the influence of the polysaccharide's molecular weight in the rheology is more evident. HB water dispersions showed a more significant dependence on polymer concentration compared to TSP and HA samples.

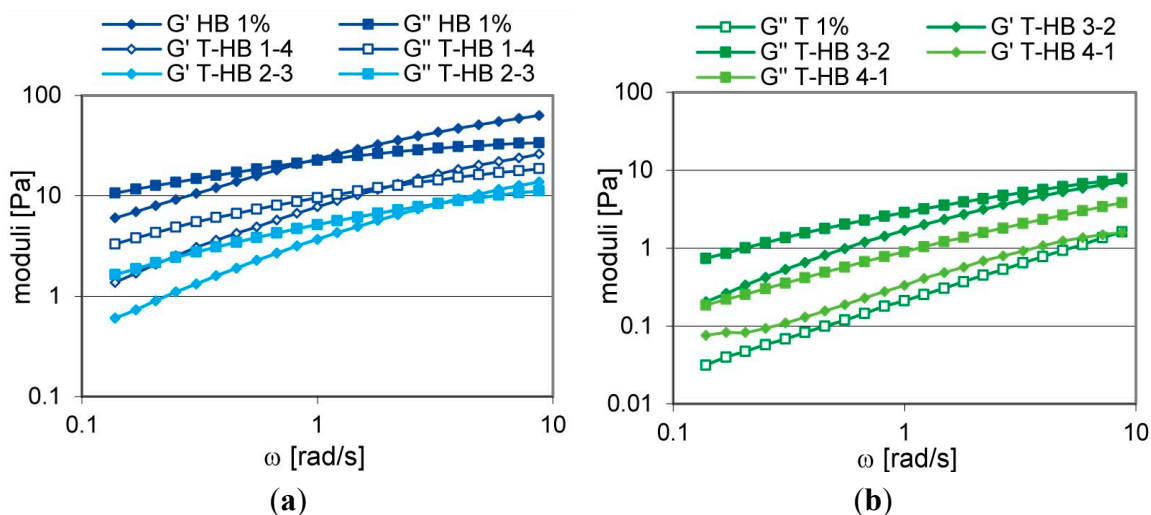
### 3.2. TSP Association with Other Polysaccharides

It is well known that polysaccharide associations can be used in cosmetic formulations to improve the stability in time and to optimize the spreading properties of products. Both properties depend on the rheology of the systems. In fact, stability is strictly related to the elastic character of the material, while spreading is related to the viscous nature.

Figure 5 shows the moduli trends as a function of the frequency of 1% polymer solutions prepared using TSP-HB mixtures at different ratios, in comparison with those of each single polysaccharide (HB and TSP 1%).

It clearly appears that by mixing the two polysaccharides in different ratios, an interesting modulation of the viscoelastic properties can be easily obtained. All of the mixtures showed different viscoelastic properties, depending on the relative ratios of the two polysaccharides.

The mechanical spectra of the dispersions prepared using only TSP or HB represented the two boundary behaviors. TSP 1% solution had a relevant viscous character. By increasing the HB relative ratio in the mixture, the elastic character of the polymer dispersions progressively increased, HB 1% being the sample with a more evident viscoelastic character.



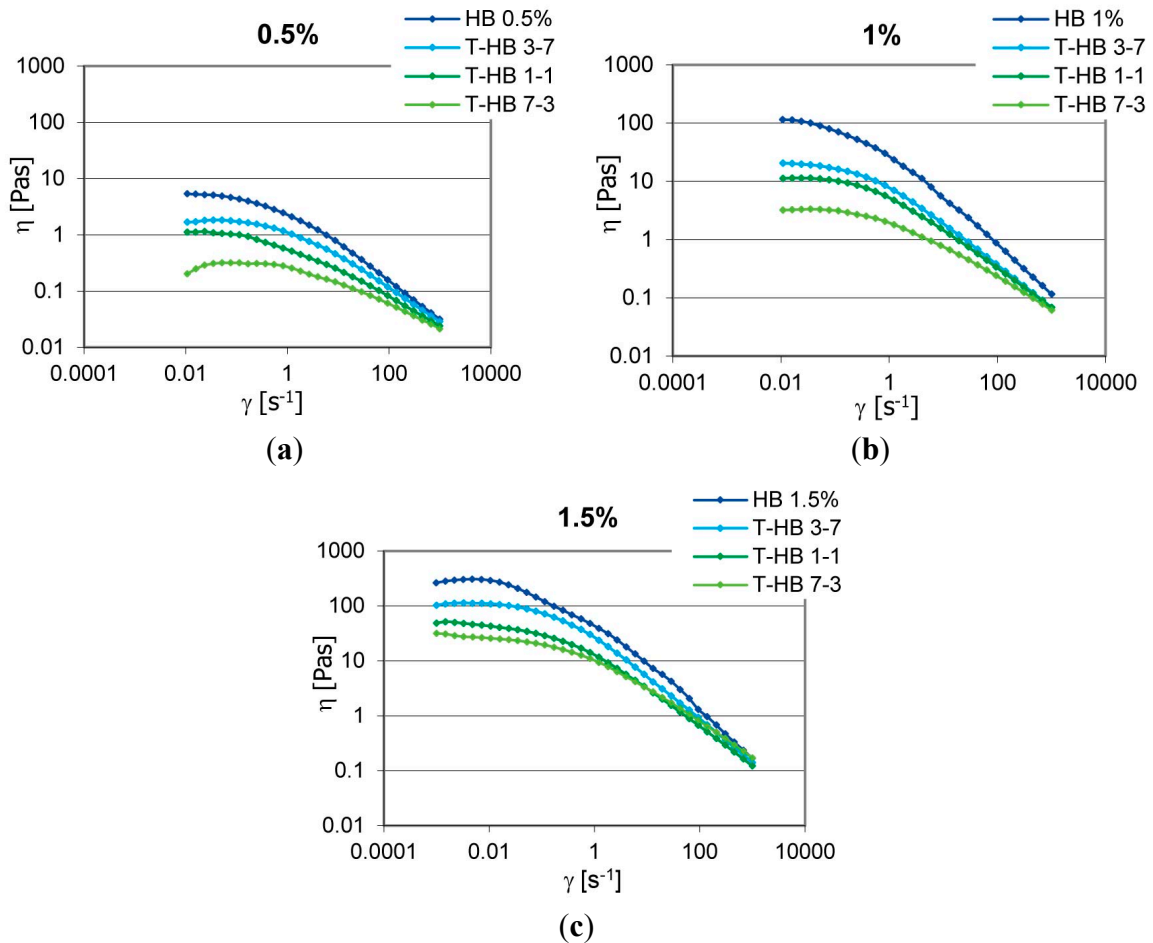
**Figure 5.**  $G'$  and  $G''$  trends as a function of the frequency of TSP-HB mixtures in different ratios: (a) 0:1, 1:4, 2:3; (b) 1:0, 3:2, 4:1 (1% w/w).

As expected, the association between TSP and HB can modulate also the flow properties of the gels. The viscosity trends as a function of the shear rate of various binary systems, prepared by mixing TSP and HB at different ratios (7:3, 1:1, 3:7), at different total polymer amounts (0.5%-1%-1.5% w/w), are reported in the following graphs (Figure 6).

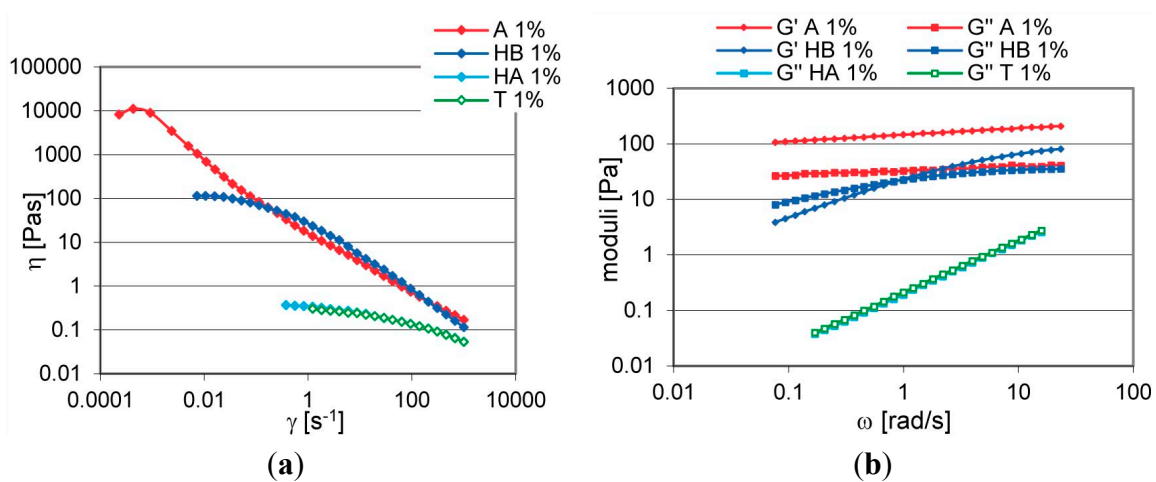
In order to improve the elastic character of the mixtures, we studied the rheological behavior of ternary polysaccharide mixtures formed by TSP, HB and dehydropolysaccharide gum (A). As a matter of fact, the increase of the elastic character improves the stabilizing properties of the polymer blend.

The flow curves and the viscoelastic properties of the TSP, HA, HB and A (1% w/w water dispersions) are shown in Figure 7. Each polysaccharide had a peculiar and characteristic rheological pattern dependent on its swelling capability and on the nature and strength of its interactions with water molecules. The aqueous dispersion of dehydropolysaccharide gum (A) showed very high

viscosity at rest (two magnitude orders higher than HB) and the most marked shear thinning behavior (a rapid decrease of viscosity with increasing shear rate) (Figure 7a).



**Figure 6.** Viscosity trends vs. the shear rate of T-HB mixtures at different polymer concentrations: (a) 0.5%; (b) 1%; (c) 1.5%.

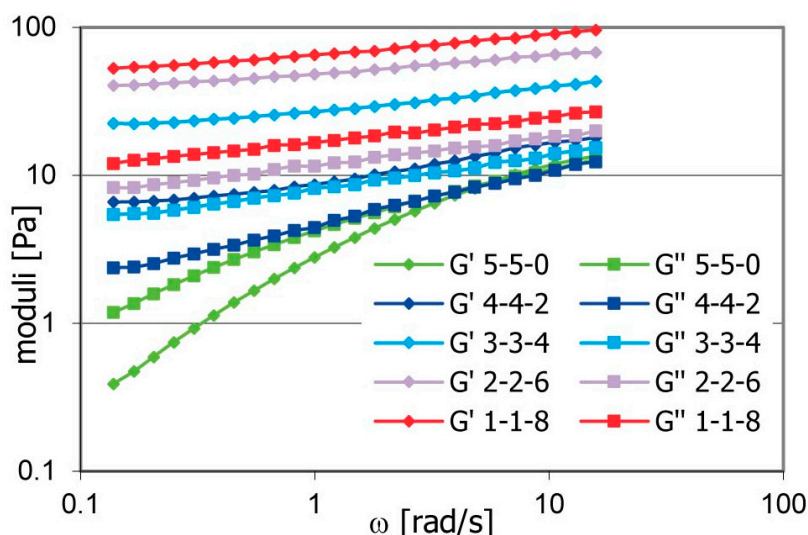


**Figure 7.** (a) Viscosity trends vs. the shear rate; (b)  $G'$  and  $G''$  trends as a function of frequency of A, HB, HA and TSP (1% w/w).

The mechanical spectra of sample A (Figure 7b) showed an elastic modulus ( $G'$ ) higher than the viscous modulus ( $G''$ ) in all of the frequency ranges investigated, with trends of both moduli being slightly dependent on frequency. This pattern of the viscoelastic properties, typical of structured materials, such as gels, is known as “weak gel behavior” [1].

These rheological data justify the different uses of the three polysaccharides in personal care products. The marked elastic character of A gels suggests a prevalent use as a stabilizer agent. The marked viscous character of TSP and HA water dispersions can improve both spreading and skin feel, while the viscoelastic behavior of HB gels in which there is a good balance between elastic and viscous properties can be used as thickening agent and also to improve the skin feel and spreading properties of cosmetics. Besides TSP or HA, HB and A can be used in combination in order to optimize the cosmetic properties.

A series of ternary gels (1% w/w) was prepared by increasing the relative amount of A and keeping fixed the ratio of TSP and HB. The mechanical spectra of the different samples are shown in Figure 8. As expected, the elastic character of the samples increased as a function of the dehydropolysaccharide gum (A) amount in the polymer mixture.



**Figure 8.**  $G'$ ,  $G''$  trends as a function of the frequency of ternary gels prepared with T-HB-A at different ratios (1% w/w).

The mixture containing only TSP and HB (5-5-0) showed a liquid-like behavior, with both moduli strongly dependent on the frequency. All of the ternary mixtures presented a “weak gel” behavior with  $G'$  and  $G''$  that became less dependent on the frequency as a function of the increasing concentration of A in the mixture. Furthermore, the absolute values of rheological parameters were consistent with the relative amount of A in the mixture, so that the mixture 1-1-8 showed the highest values of both elastic and viscous moduli.

We found good compatibility among the three polymers that can be easily associated with cosmetic formulations. The combinations of gels were clear and homogeneous and showed different rheological behaviors that can be used to optimize the sensorial and functional properties of the cosmetics, when the viscous properties are significant, and/or to improve their stability over time, when the elastic character is more marked.



#### 4. Conclusions

The investigation of the rheological properties of polysaccharide aqueous dispersions represents a powerful tool to optimize their use in personal care products.

Hyaluronate and xyloglucan, with a similar molecular weight, show very close rheological properties when used in the concentration range 0–2%, both in continuous and oscillatory flow conditions.

Tamarind seed polysaccharide can be considered as a substitute of hyaluronic acid in green cosmetic products.

The rheological study of polysaccharide binary and ternary mixtures allows the optimization of the attributes of gels and rationalizing the concentration of each polymer in finished products.

#### Acknowledgement

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#### Author Contributions

Alessandra Semenzato designed the study and wrote the paper. Alessia Costantini performed the experiments and data analysis presentation. Giovanni Baratto gave his contribution to the discussion of the data and the paper revision.

#### Conflicts of Interest

The authors declare no conflict of interest.

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