Research Article

Miscibility Studies of Agar-Agar/Starch blends using Various Techniques

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ABSTRACT
Miscibility characteristics of agar-agar and starch have been investigated by viscometry, density and ultrasonic velocity techniques at 30°C and 50°C. Blend films of agar-agar/starch were prepared by solution casting method and characterized by differential scanning calorimetric (DSC) technique. Using viscosity data, interaction parameters of Chee's (μ), and Sun's (α) were computed to determine their miscibility. The values obtained from reduced viscosity revealed that blend was semi-compatible at 30°C and compatible at 50°C. The results were then confirmed by differential scanning calorimetric technique. Compatibility in the agar-agar/starch blend compositions may be due to the formation of intermolecular hydrogen bonding between the agar-agar and starch.

Keywords: viscosity, blends, ultrasonic, differential scanning calorimetry.

INTRODUCTION
Polymer blends, i.e. physical mixtures of structurally different polymers which interact with secondary forces with no covalent bonding, has a very important status, scientifically and technologically[1]. This importance arises mainly because blending of polymers may result in reduction of basic cost, improved processing and also enable valuable properties to be maximized. However, manifestation of the superior properties depends upon the compatibility or the miscibility of the homo-polymers at molecular level. Depending upon the degree of molecular mixing, the blends were categorized as totally miscible (compatible), semi-miscible (semi-compatible), immiscible (in-compatible) blends. The mixing of the interacting polymer solutions produces an immediate precipitate or turbidity or homogeneity indicating stronger, weaker or no interaction between the polymer components respectively. In blends, the presence of chemically grafted units is of major importance in providing adhesion between the polymers. Interacting product can be formed from some polymers even without the requirement of a chemical graft; in such cases, weaker secondary forces such as hydrogen bonding plays a dominant role.[2]

Agar is a gelatinous substance derived by boiling from a polysaccharide in red algae, where it accumulates in the cell walls of agarophyte and serve as the primary structural support for the algae's cell walls. Agar is a mixture of two components: the linear polysaccharide agarose, and a heterogeneous mixture of smaller molecules called agaropectin.[3,4]

Starch belongs to the class of organic compounds called carbohydrates and is composed of carbon, hydrogen, and oxygen in the ratio $C_6H_{10}O_5$. These atoms are organized into a simple sugar molecule, D-glucose, or dextrose as it is known commercially. The glucose molecules are, in turn united to form large starch molecules. Thus starch is a polymer made up of a large number of glucose units. [5]

As a part of our research program, we have studied miscibility of agar-agar/starch blends in solution and solid state. The purpose of this study is to characterize the miscibility nature of the agar-agar and starch blends. These homo-polymers are extensively used in food and pharmaceutical industries. Hence blending of these polymers might be enhancing their properties.

MATERIALS AND METHODS

Polymers used for the present study are agar-agar [Merk, Mumbai, India] and starch [Merk, Mumbai, India] which are natural products.

Viscometric method is based on the study of interaction in dilute solutions of two polymers in common solvent. The total weight of the two components in solution is always maintained at 0.2g/dL. Stock solutions of homo-polymers agar-agar, starch and their blends of different compositions (90/10, 80/20, 70/30, 60/40 50/50, 40/60 30/70, 20/80 and 10/90) were prepared in distilled water. The relative viscosities of the polymer blends are determined at 30ºC and 50ºC using Ubbelohde suspended-level viscometer (USLV). Different temperatures were maintained in a thermostat bath with a thermal stability of ± 0.05ºC.

Ultrasonic velocity measurements of blend solution of different compositions were performed by an ultrasonic interferometer technique[6]. During the experiment, different temperature (30ºC and 50º C) is maintained by circulating water from thermostat with a thermal stability of ± 0.05ºC, through the double walled jacket of the ultrasonic experimental cell. The experimental frequency was 2MHz.

Differential scanning calorimeter (DSC) technique is used to detect glass transition temperature of polymer blends. The thin films of agar-agar, starch and their blends were prepared by solution casting method. Films were dried using IR Lamp. DSC measurements were performed in TA Q200 Differential Scanning Calorimeter, under nitrogen atmosphere. During DSC measurements, heating/cooling/heating method was used. In the first cycle of measurements, sample was heated to 90ºC and equilibrated to remove remaining water content in the sample. The sample was then cooled to 20ºC and reheated to 250ºC. The heating/cooling/heating rate was set at 10ºC/min.

RESULTS AND DISCUSSION

Viscometric measurements

From viscometric measurements, reduced viscosities of homo-polymers agar-agar, starch and their blend compositions (90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80 and 10/90) were measured at 30ºC and 50ºC. Reduced viscosities of the pure polymers and their blend compositions are plotted against concentration are shown in Figures 1 and 2 respectively.

The Huggin's plot (Figure 1) of agar-agar/starch and their blend compositions at 30ºC is indicating little higher slope values for 80/20, 70/30, 60/40 50/50, 40/60 30/70, 20/80 and 10/90 blend compositions than 90/10 blend of agar-agar/starch. This may be attributed to mutual attraction of macro molecules in solution, which leads to increase in hydrodynamic volume.[7]

At 50ºC Huggin's plot (Figure 2) of agar-agar/starch and their blend compositions indicating little higher slope value for all the composition. This is may be due to the effect of temperature on mutual attraction of macro molecule in solution.

To quantify the miscibility of polymer blends, Chee[8] suggested the general expression for interaction parameter when the polymers are mixed in weight fractions w_1 and w_2 as

$$\Delta B = \frac{b - \bar{b}}{2 w_1 w_2} \tag{1}$$

where $\bar{b} = w_1 b_{11} + w_2 b_{22}$ where b_{11} and b_{22} are the slopes of the viscosity curves for the components and b is related to Huggins coefficient K_H as,

$$b = K_H [\eta]^2 \tag{2}$$

where $[\eta]$ is intrinsic viscosity
For ternary system, it is also given by

$$b = w_1^2 b_{11} + w_2^2 b_{22} + 2 w_1 w_2 b_{12} \tag{3}$$

where b_{12} is slope for the blend solution.

However, Chee's theory fails to account for the experimental data when intrinsic viscosities of pure components are far apart. In such cases he defined a more efficient parameter to predict compatibility,

$$\mu = \frac{\Delta B}{\{[\eta]_2 - [\eta]_1\}^2} \tag{4}$$

where $[\eta]_1$ and $[\eta]_2$ are intrinsic viscosities of pure component solutions. The polymer blend is miscible if $\mu \geq 0$ and immiscible when $\mu < 0$.

Table 2: Experimental and Theoretical Tg values of starch, Agar-Agar and their blends

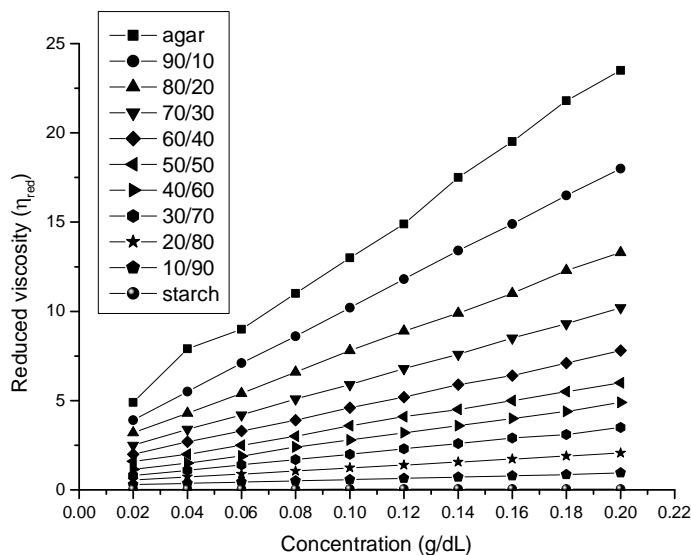| Agar-Agar/ starch blend compositions	Experimental Tg values (°C)	Theoritical Tg values (°C)	
		Fox equation	Wood's equation
Agar-Agar	44.50	-	-
70/30	46.50	48.50	49.51
50/50	50.10	51.70	53.35
Starch	61.20	-	-

Fig. 1: Huggins's plot for 0.2% w/v, agar-agar/starch blends in water at 30⁰C
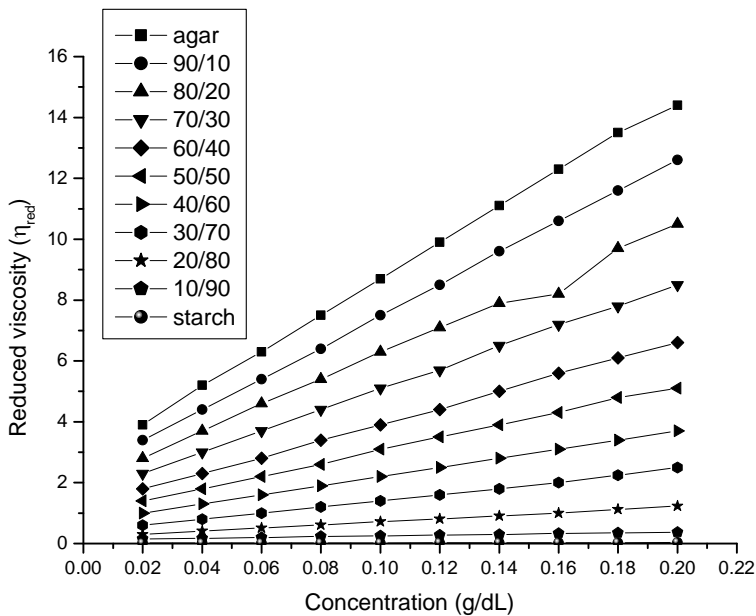

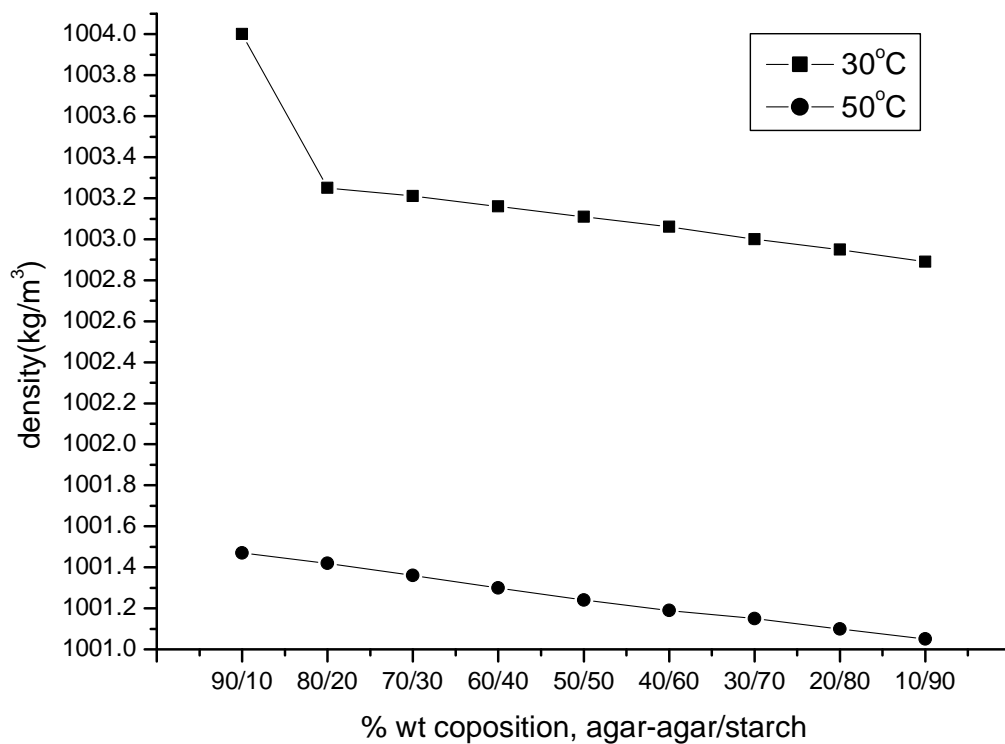**Fig. 2: Huggins's plot for 0.2% w/v, agar-agar/starch blends in water at 50⁰C**

Fig. 3: variation of density with composition of agar-agar/starch blend in water at 30°C and 50°C
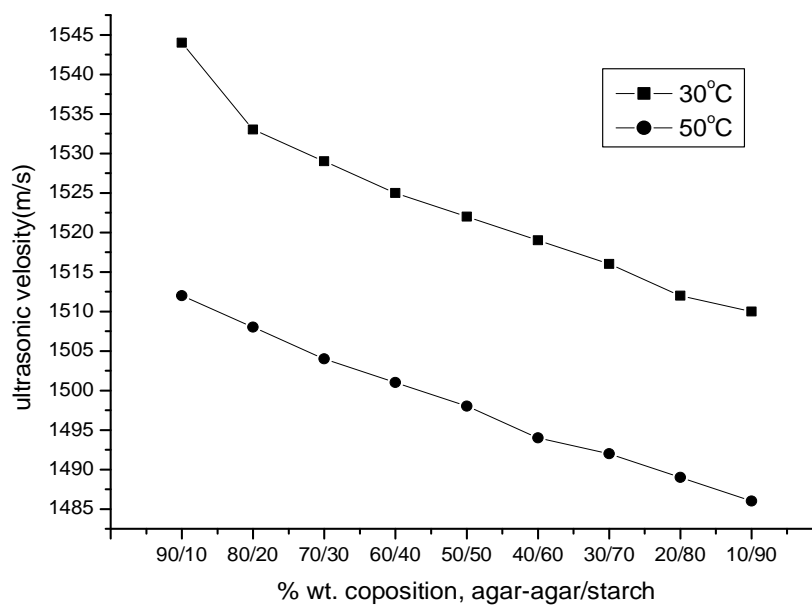

Fig. 4: variation of ultrasonic velocity with composition of agar-agar/starch blends at 30ºC and 50ºC
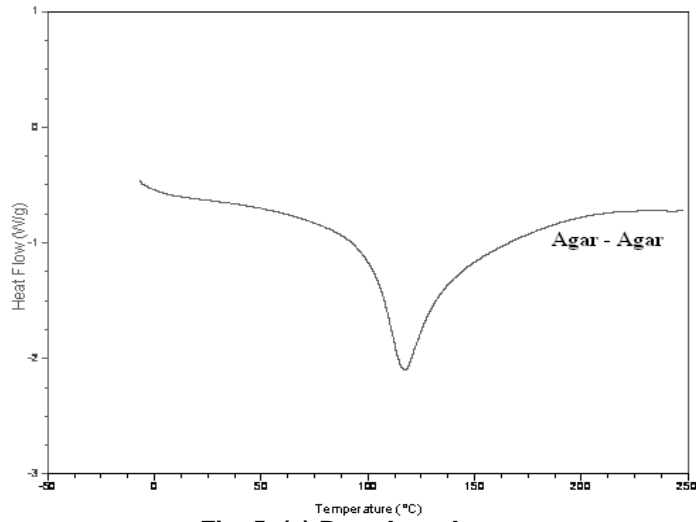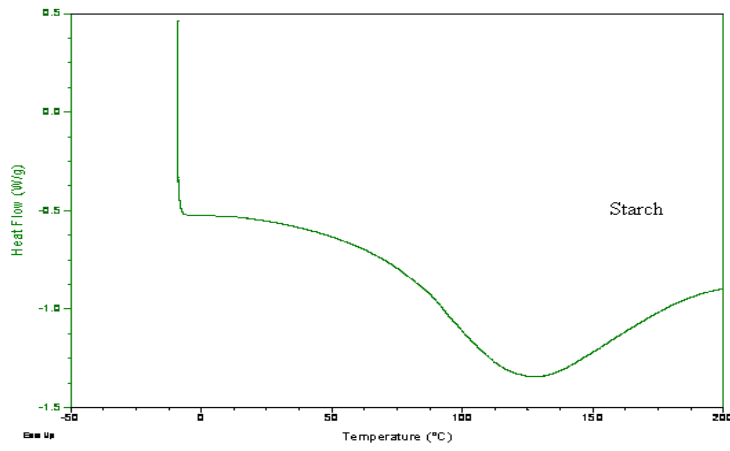
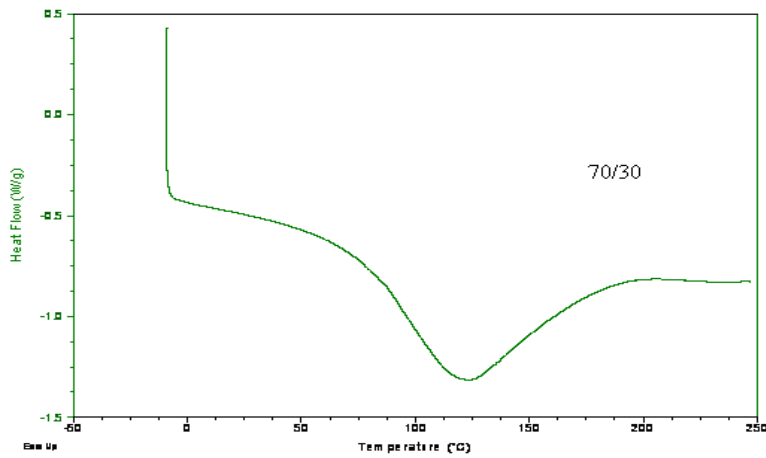**Fig. 5: (a) Pure Agar-Agar**

Fig. 5: b) pure starch

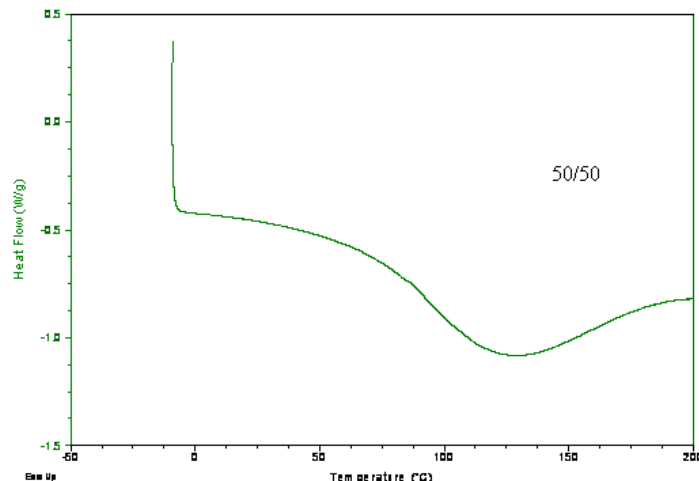**Fig. 5: c) 70/30 Agar-Agar/starch blend**

Fig. 5: d) 50/50 Agar-Agar/starch blend

**Fig. 5: DSC thermograms of (a) Pure Agar-Agar (b) Pure starch c) 70/30 Agar-Agar/starch blend
and d) 50/50 Agar-Agar/starch blend**

CONCLUSION
Based on viscosity, density and ultrasonic velocity measurements, it is concluded that blend of agar-agar/starch is semi-compatible at 30ºC and compatible at 50ºC. It was observed that a raise in temperature of 20ºC has significant effect on the miscibility of agar-agar/starch blend compositions. The Tg value blend compositions are found to be slightly higher than that of theoretical calculated Tg values implying an intermolecular interaction between the polymers. The semi-compatible nature of the blend was also confirmed by DSC studies.

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