

Research Article

Studies on Evaluation of Viscoelastic Material

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ABSTRACT

Pharmaceutical and cosmetic materials range in consistency from fluid to solid. The majority of pharmaceutical formulations are ointments, creams, pastes, and gels. Pharmaceutical gels are the most difficult materials to characterize rheologically because they combine both liquid and solid properties within the same material. Few rheological publications have addressed the dominant viscoelastic nature of a semisolid material in a detailed sense. To understand these complex flows, pharmaceutical gel was tested. In this article, basic rheological terms and an interpretation on the relationship between rheological response and material structure was described.

Key words: Rheology, viscoelastic material, Pharmaceutical gel

INTRODUCTION:

Hooke's and Newton's law are linear laws, which assume direct proportionality between the stress and the strain. The term viscoelasticity is used to describe behavior which falls between the classical extremes of elastic response by the Hookean solids and the Newtonian liquids. The particular response of a sample to applied stress or shear rate in case of certain materials depends on the time scale of the experiment. If the applied stress or shear rate is kept low, the materials will appear to behave viscous, whereas at high stress or shear rates, materials might behave rather elastically. The simultaneous existence of viscous and elastic properties in a material is called viscoelasticity, and one can assume that all real materials are viscoelastic in nature.

In a slow experiment the viscous behavior will dominate, in a short time experiment the material will appear elastic. Viscoelastic materials have

natural times in an interval perceptible by men or at least measurable at a reasonable time. Their natural (or relaxation) times lie between 0.01 and 100 s. The relationship between experiment time and natural time is given by a dimensionless number, the Deborah number De which is calculated as natural time divided by experiment time. If the experiment is faster than the relaxation process the material will appear elastic (high De number), otherwise the viscous part will dominate (low De number). Measurements in the elastic region can give information about the structure, e.g. gel strength or strength of internal bounds; in the viscous region one can get information about the flow behavior which is important for e.g. stirring, pumping or leveling.

Many semi solid pharmaceuticals dosage form and cosmetic manufacturing processes such as new ingredient selections, formulation preparations, material packaging, and shelf storage are associated with a complex flow of

materials. The application and acceptance of semi solid pharmaceutical dosage form and cosmetics are also dependent on the flow properties of the final product. Therefore, rheological measurements, an important route to revealing the flow and deformation behaviors of materials, cannot only improve efficiency in processing but can also help formulators and end users to find pharmaceutical and cosmetic products that are optimal for their individual needs. The basic aim of this paper is rheological measurements of pharmaceutical materials are performed for the following reasons:

1) To understand the fundamental nature of a system, 2) For quality control of raw materials, final products, and manufacturing processes such as mixing, pumping, packaging, and filling and 3) To study the effect of different parameters such as formulation, storage time, and temperature on the quality and acceptance of a final product. In this research work we made an attempt to explore the basic rheological terms and an interpretation on the relationship between rheological response and material structure was described using carbopol gel and diclofenac sodium gel.

MATERIALS AND METHODS

Materials:

Diclofenac sodium obtained as gift sample from Cipla Ltd Mumbai, Carbopol 940 was obtained from Loba Chemic Pvt Ltd Mumbai, Triethanolamine, Sodium Hydroxide all chemical procured from Merck chemicals ltd Mumbai All other reagent and solvent used are analytical grade.

Preparation of pharmaceutical gel:

Diclofenac sodium gel (0.5% w/v) was prepared using carbopol 940 (1% w/v), triethanolamine (0.4%), ethanol and distilled water (Table 1). Diclofenac sodium was dispersed in a mixture of 25%

distilled water and 18.75% ethanol, which was added drop wise into hydrated carbopol 940 containing 6.25% ethanol and 49.3% distilled water, with stirring so as to form a gel.

RHEOLOGICAL CHARACTERIZATION OF PHARMACEUTICAL GEL

Rheological study of formulated gel:

Rheological analysis of formulated gel were performed using a stress control rheometer: Viscotech Rheometer (Rheologica Instruments AB, Lund, Sweden), Stress Rheologic Basic Software, version 5, (Rheologica Instruments, Lund, Sweden) using cone-plate geometry with the diameter of the cone being 25 mm and a cone angle of 1° , operating in the oscillation and static mode. The gap was maintained at 0.5mm.

The following tests then were carried out:

Oscillation stress sweep:

The formulated gel was exposed to increasing stress (1-100 Pa) at a constant frequency 1Hz. This test allows the determination of the linear viscoelastic region (LVR) of the samples, and therefore the consequent choice of the stress value to use in the other oscillation tests.

Oscillation Frequency sweep:

The samples were exposed to a stepwise of increasing frequency (0.1-100Hz) at a constant stress (100 Pa) in the field of linear viscoelasticity.

Creep-recovery:

The test was carried out at stress of 30 Pa, which was maintained constant for 100 s. It was then instantly removed and the recovery was followed for 200 s. The Creep compliance J (1/Pa) (defined as the

ratio between the measured strain and the applied stress) is monitored against time.

Viscometry test:

The sample was exposed to increasing stress (1-100 Pa).

RESULTS AND DISCUSSION

Steady shear flow curves:

A flow curve, viscosity (η) versus shear rate ($\dot{\gamma}$), across a wide range of shear rates

can provide important information about storage stability; optimal conditions for mixing, pumping, and transferring; and end-user applications. The rheological behaviour of the material may change as a result of these forces. If the shear rate changes during an application, the internal structure of the sample will change and the change in stress or viscosity can then be seen. Typical flow curves are shown in figure 1.

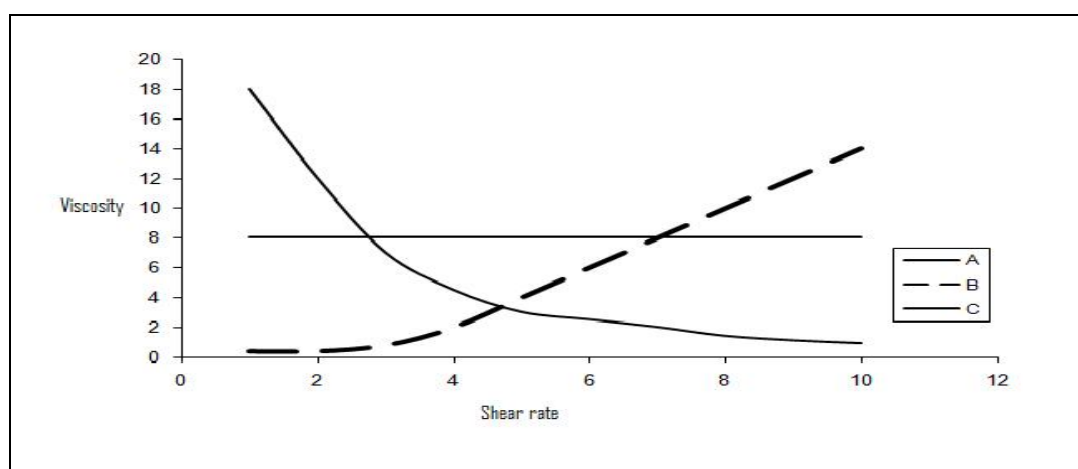


Fig.1. Typical flow curves

Newtonian flow (A curve) is the simplest type, displaying as shear-independent viscosity while the material is sheared. Water and some low-molecular-weight mineral oils are typical examples of Newtonian fluids. Pseudo-plastic or shear thinning fluids (B curve) display viscosity reduction while the shear rate increases. Typical examples of these are colloidal systems. The colloidal structure breaks down while shear rate increases, displaying reduced viscosity. Dilatant or shear thickening flow (C curve), in which viscosity increases with shear rate, is seldom encountered in the pharmaceutical and cosmetics fields.

Dynamic oscillatory experiments:

Although rotational experiments provide information concerning the flow

properties of a system such as thixotropy, and steady flow curve, they are only a part of the complete rheological characterization of a system. Dynamic oscillation testing is a much more powerful tool to understand the secrets of the microscopic structures of a viscoelastic material therefore; it is more attractive and useful from a practical point of view. Strain sweep is utilized to determine the linear viscoelastic region of a material system for performing a subsequent dynamic test. Figure (2) shows the results of strain sweep. The maximum strain up to which G' remains constant is called the critical strain. The critical strain, which indicates the minimum energy needed to disrupt the structure, is dependent on the dispersion quality. Therefore, if the difference in the critical strain of two gels

is known, the different extent of dispersion of particles or ingredients can be measured. The higher the critical strain, the better the system is dispersed. The critical point can also be called dynamic yield stress if a G' versus stress curve is presented. By extrapolating the linear portion, the shear stresses of the same two gels can be read from the separation point. The presence of a dynamic yield stress of suitable magnitude may be used as a criterion to determine whether, for example, a vehicle will maintain suitable semisolid properties under shear. A semisolid has a weak structure, and does not recover this structure after a brief resting period therefore; a dynamic yield value should be used instead of static yield stress to assess film formation and sag resistance of a layer of material applied on a surface. Oscillatory shear measurements can be explained from an instrumentation

point of view: A sinusoidal shear stress (or strain) smaller than the critical value is imposed on a fluid, and the amplitude of the resulting strain (or stress) and the phase angle between the imposed stress and the output strain are measured. In general, the material can respond to this type of deformation through two mechanisms: elastic energy storage and viscous energy dissipation. Quantitatively, these responses can be represented as storage modulus (G'), energy stored per unit volume, and loss modulus (G''), energy dissipated per unit deformation rate per unit volume. Storage modulus (G') is proportional to the extent of the elastic component (contributed by cross linking, entanglement, and/or aggregation) of the system, and loss modulus (G'') is proportional to the extent of the viscous component of the system.

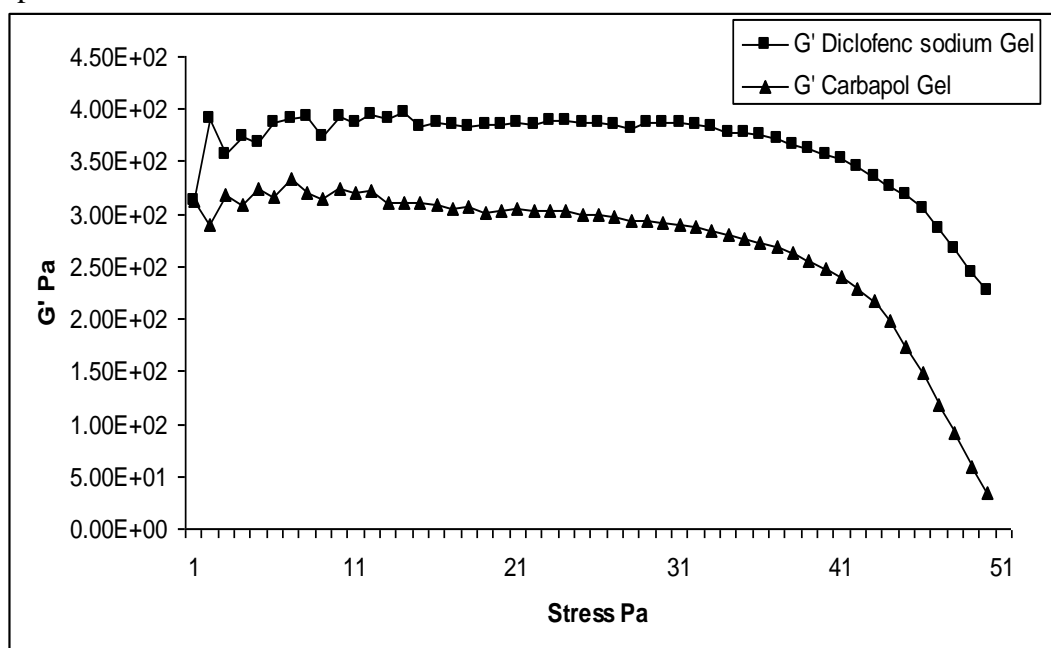


Figure 2 Oscillation stress sweep

Frequency sweep is a useful tool for characterizing the microstructure of a viscoelastic material. Applying a constant strain below the critical value and a frequency ramp reveals the microstructures of a material through the response of that material to different shear rates.

Pharmaceutical gel are cannot relax quickly and are highly elastic at the same frequency range, the storage modulus (G') is higher than the loss modulus (G''), as shown in Figure (3)for the pharmaceutical gel. A semi dilute solution, such as syrup, exhibits a $G' > G''$ scenario at low

frequencies and a $G'' > G'$ scenario at high frequencies. The frequency at crossover

point is a function of the relaxation time of the internal structures of the syrup

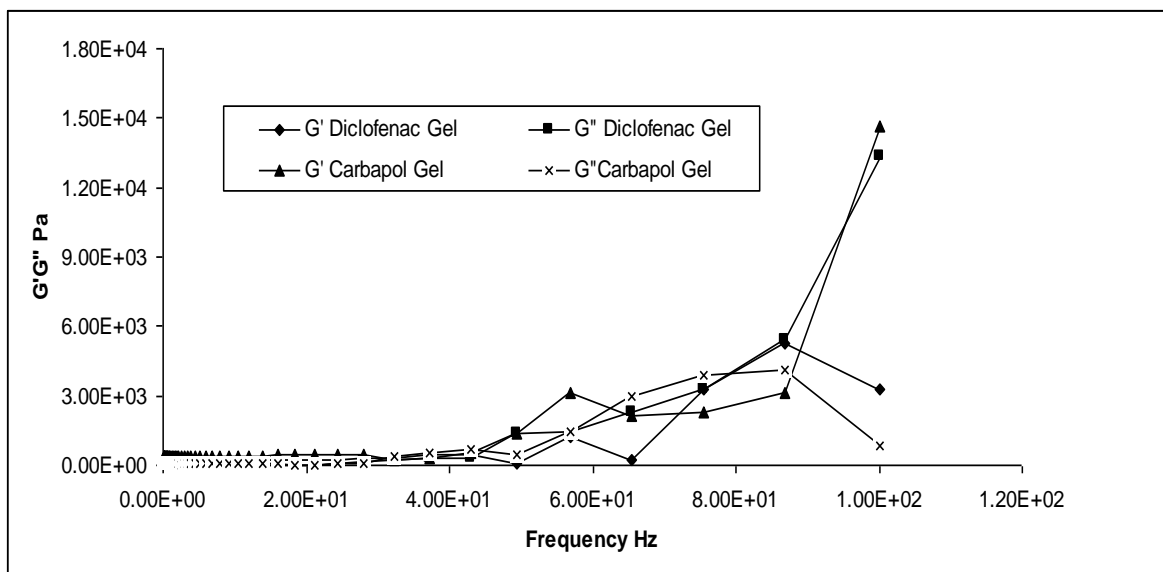


Figure 3 Oscillation Frequency sweep

The creep recovery test is an alternative for obtaining the relaxation time and viscoelastic properties of a material. A constant stress below yield stress is applied to the material and the deformation is monitored with time. Compliance (J) is defined as the reciprocal of modulus, $J = 1/G = g/t$, where G is modulus and g is strain. The value and shape of the creep compliance curve are fundamentally important. Subjected to a constant stress, the strain of an ideal elastic material would be constant and the material would return to the original shape when the stress was

removed. In contrast, an ideal viscous material would show a steady flow, producing a linear response to stress with the inability to recover any of the imposed deformation. Viscoelastic materials (e.g., semisolid pharmaceutical products) will exhibit a nonlinear response to strain and, due to their ability to partially recover structure by storing energy γ ; will show a final deformation less than the initial deformation. Figure (4), which illustrates typical creep behavior of a viscoelastic material, displays a creep recovery test.

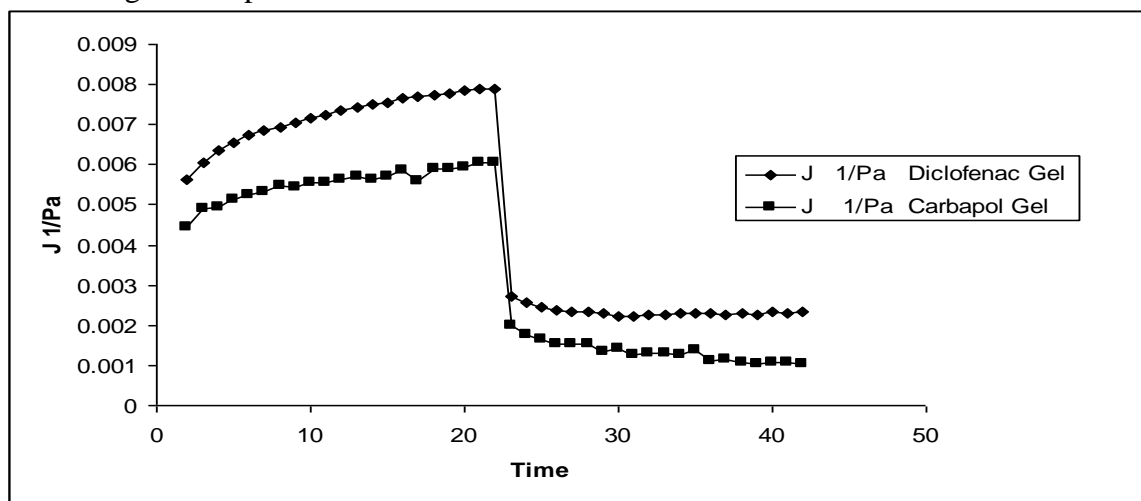


Figure 4 Creep recovery test

In general, the creep compliance-time curve can be subdivided into three regions (Figure 5). Curve A – B is the region of instantaneous compliance, where bonds between the primary structural units stretch elastically. Curve BC is the time-dependent retarded elastic region with compliance JR. Curve CD is the linear region with steady-state compliance J. Some bonds rupture, therefore, the time required for them to reform is in excess of the test period. Thus, the released entities can flow past each other. Upon removal of

the stress, a recovery occurs, and this is represented by DF. There is an instantaneous elastic recovery (DE) with the same magnitude as AB, followed by a retarded elastic recovery equivalent to the retarded region of the creep curve. Some bonds were irreversibly broken in the creep region, and the original structure is never recovered completely. However, the degree of recovery after creep can be represented by the recoverable compliance J.

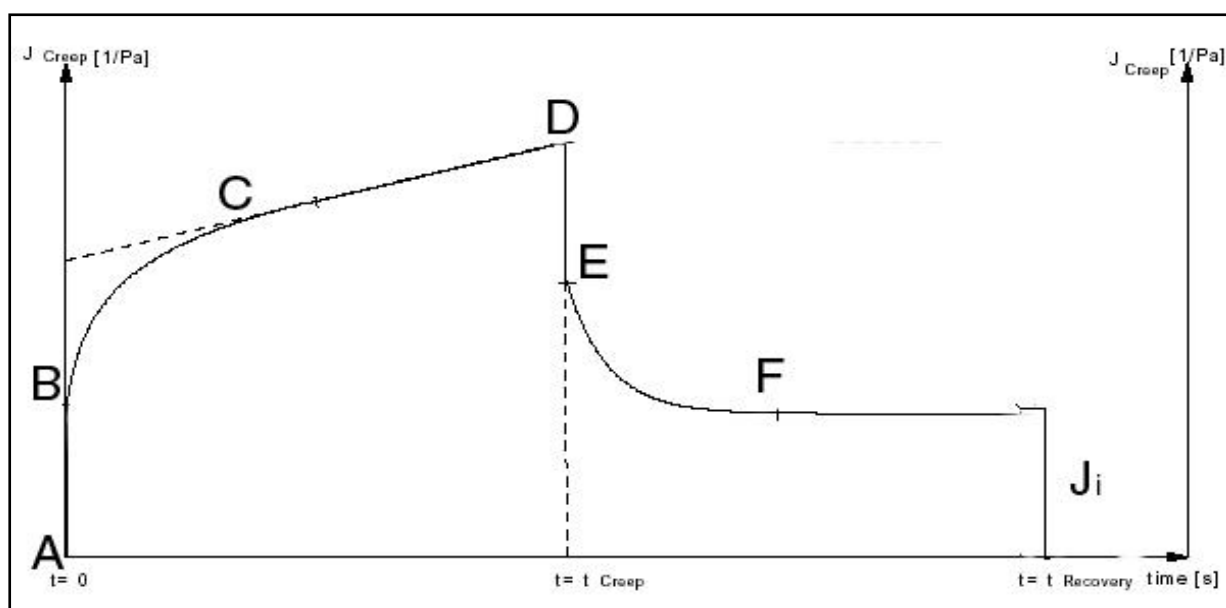


Figure 5 Creep recovery curve of a viscoelastic material as a function of time.

CONCLUSION

This article has reviewed all the important rheological characterizations and the detailed interpretation to correlate the rheological responses with the physicochemical properties of pharmaceutical gel. The rheological characterizations for pharmaceutical and cosmetic semisolids provide important

information for engineers to facilitate their daily production and processing for their products. To day, most formulators also count on rheological results to develop customer-favored products for surviving in the competitive market. Therefore, reliable understanding rheologies are becoming necessary for pharmaceuticals and cosmetics manufacturers

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