**INTRODUCTION**

Development of novel biomaterials for drug delivery which forms a part of the so-called novel drug delivery systems has always been exhilarating. Using nanotechnology, it is possible to tailor materials at the atomic and molecular scales to meet the desired outcomes.\(^1\) The necessity of elucidating the mechanical behavior of those materials which would be subjected to load or stress during its application is inevitable. **Methods:** Rheological characterization was done by studying viscosity and yielding. Rheological modeling was also carried out. **Results:** The viscosity and yield stress were inversely dependent on the eugenol concentration. The gels followed Herschel–Bulkley and Bingham rheological models. **Conclusion:** Nanodroplets are colloidal systems and the microstructural changes in the Carbopol based nanodroplet gels were unveiled using rheometry.

**Key words:** Flow curve, microstructure, nanodroplet, rheological model
Jiangsu, China. Water used for the study was of Reagent grade I, Millipore, Molsheim, France.

Preparation of eugenol nanodroplet gels
The preparation of the NDGs are similar to microemulsion and nanoemulsion gels which have been widely reported. The composition of the NDGs is as given in Table 1. A mixture of Tween 80 and ethanol were prepared which acts as the surfactant and cosurfactant systems for the formation of nanodroplets. To this eugenol was added and mixed thoroughly. The nanodroplets of eugenol were obtained by the addition of water to it and stirred with a magnetic stirrer. The ratio of Tween 80 to ethanol was kept at a constant value of 5:1 in all the formulations. The gels were prepared by dispersing 1% Carbopol 940 in the nanodroplet formulations and subsequent neutralization with triethanolamine. The prepared gels were further subjected to flow curve studies by rheometry.

Flow and deformation properties of nanodroplet gels
Rheological characterization of the gels was carried out using Anton Paar Physica MCR 51 Rheometer, Graz, Austria. RheoPlus software, Anton Paar, Graz, Austria, was used for the instrument handling and data analysis. During the experiments, the temperature was set at 25°C for all the samples. The system employed was a parallel plate with a diameter of 19.957 mm. The gap was 1 mm.

Viscosity and yielding
The flow curve was obtained for the NDG samples by applying a shear rate of 0.1-100/s. Shear stress and viscosity were measured with the change in shear rate. The yield stress values of the NDGs from their flow curves were determined using RheoPlus software (Anton Paar, Graz, Austria).

Rheological modeling
Rheological models are used to characterize flow properties in an effort to determine the ability of a sample to perform specific functions. Shear stress and shear rate data of the eugenol NDGs was fitted into various rheological models. The data were fitted into Newtonian, Ostwald (Power law), Bingham, Herschel-Bulkley, and Casson rheological models using RheoPlus software (Anton Paar, Graz, Austria).

Newtonian model: It is a shear rate independent model and obeys a simple relationship between shear stress and shear rate as given in equation (1):

\[ \tau = \eta \dot{\gamma} \]  

where \( \tau \) is the shear stress, \( \eta \) is the viscosity and \( \dot{\gamma} \) is the shear rate.

Ostwald model: This model is also known as power law model and is one of the most used models. The model is represented by the equation (2):

\[ \tau = K \dot{\gamma}^n \]  

where \( \tau \) is the shear stress, \( K \) is the consistency index, \( n \) is the flow behavior index and \( \dot{\gamma} \) is the shear rate. The consistency index is a measure of viscosity index of the system whereas the flow behavior index is an indication of the shear thinning behavior of the sample. The non-Newtonian behavior of the sample is assumed as the value of \( n \) shows variation from one.

Bingham model: The Bingham model is given by the equation (3). The model is applicable to samples which possess a yield point and plastic viscosity which are independent of the shear rate. Samples following this model behave as solids at low shear rates and as a viscous fluid at the high shear rates.

\[ \tau = \tau_y + \eta_p \dot{\gamma} \]  

where \( \tau \) is the shear stress, \( \tau_y \) is the yield value, \( \eta_p \) is the plastic viscosity and \( \dot{\gamma} \) is the shear rate.

Herschel-Bulkley model: This model is useful when the yield point and viscosity are dependent on the shear rate. The model is explained by the equation (4):

\[ \tau = \tau_y + K_{HB} \dot{\gamma}^n \]  

where \( \tau \) is the shear stress, \( \tau_y \) is the yield value, \( K_{HB} \) is the consistency index, and \( \dot{\gamma} \) is the shear rate.

Casson model: This model is given by the equation (5):

\[ \tau^{0.5} = \tau_y^{0.5} + K_c \dot{\gamma}^{0.5} \]  

where \( \tau \) represents the shear stress, \( \tau_y \) represents the yield value, \( K_c \) represents the consistency index (Casson viscosity) and \( \dot{\gamma} \) represents the shear rate.

RESULTS AND DISCUSSION

Flow and deformation properties of nanodroplet gels
From the flow curve measurements, the viscosity and yielding properties of the NDGs were evaluated. The data were further fitted with various rheological models to identify their flow behavior.

Viscosity and yielding
The eugenol concentration in the NDGs was found to have an influence on both the shear stress and viscosity. From the plot for viscosity [Figure 1], it is obvious that the samples did not exhibit any Newtonian flow as there is no plateau phase. The

| Code | Eugenol (%w/w) | Tween 80 (%w/w) | Ethanol (%w/w) | Water (%w/w) | Carbopol (%w/w) |
|------|----------------|-----------------|----------------|--------------|-----------------|
| NDG1 | 5 | 50 | 35 | 1 |
| NDG2 | 10 | 50 | 30 | 1 |
| NDG3 | 15 | 50 | 25 | 1 |

NDG: Nanodroplet gel
viscosity of the all the samples were observed to be dependent on the shear rate. The effect was most pronounced in the case of NDG1 containing 5% eugenol. As the slope of a middle portion of the curve for NDG1 is more, it can be assumed that the microstructural attractive forces are more for this gel containing 5% eugenol. This can be considered as a reason for its enhanced rigidity compared to other NDGs with higher eugenol content. Some materials resist flow when subjected to a stress below a critical value. This critical stress is called as yield stress, and these materials are considered to be yield stress materials.[18] Though the importance of yield stress is under question, it is still considered to be a characteristic parameter for semisolids.[19] The NDGs were observed to have yield stress values which are inversely proportional to the eugenol concentration. The yield stress values determined from the flow curves were 53.88 ± 0.90 Pa, 13.64 ± 0.01 Pa, and 3.21 ± 0.001 Pa for NDG1, NDG2, and NDG3, respectively. There was a significant difference in the yield stress values among all the NDGs (P < 0.001).

The decrease in viscosity for the NDGs, as observed in Figure 1, can be explained with the help of illustrations shown in Figure 2. The Carbopol based gels are formed when the polymer swells (as a result of uncoiling of polymer molecules and subsequent molecular extension) after the addition of triethanolamine. It is known that the electrostatic repulsion of the carboxyl (−COO−) groups present on the extended chains impart rigidity to the gel structure.[20] The presence of eugenol NDs can cause screening of the electrostatic repulsive forces (indicated by dotted lines with double arrow) and decreases the rigidity of the gel structure. The length of the line is a measure of the magnitude of electrostatic repulsion. The + sign indicates the positively charged ions from triethanolamine. The effect becomes pronounced when a shear rate is applied as it causes the polymer chains to come closer without any impedance due to the fact that the repulsive electrostatic force between carboxyl groups is masked by nanodroplets (NDs). This can explain a decrease in viscosity on applying shear rate. The decrease in viscosity for NDGs are in the order of NDG3 > NDG2 > NDG1. This further confirms the above said mechanism as a decrease in viscosity was directly proportional to eugenol content in NDGs. Another aspect of this issue might be that as the eugenol content increases an equivalent volume of water gets replaced from the formulations which cause a less volume of aqueous phase available for the proper swelling of Carbopol polymer. This also can lead to decreased viscosity as a result of reduced rigidity of the gel structure in NDGs with higher eugenol content.

Figure 3 shows a plot of shear stress versus shear rate. Throughout the study regime, it was found that the shear stress is dependent on the shear rate. This implied a fluid nature of the NDGs rather than having a solid nature.[21] It can be attributed to the fact that at these shear rates the Carbopol polymer chains undergo alignment in the direction of flow.[9] The presence of eugenol NDs also aids in this process, and the net result will be the sum of their individual effects.

Rheological modeling

The correlation coefficients [Table 2] indicated that 5% and 10% eugenol NDGs follow Herschel-Bulkley model while Bingham rheological model was most fitting to NDG3 containing 15% eugenol. It was noticed that yield value and consistency coefficient are in the order 5% > 10% > 15% and is independent of the rheological model studied. The Bingham behavior of the 15% sample is clear from the flow behavior index of 1.0943 (almost unity) for Herschel-Bulkley model. At n = 1, the Herschel-Bulkley model is equivalent to Bingham model.[22] Herschel-Bulkley model can be visualized as an idealization of the viscoplastic behavior of the NDGs.[19]

CONCLUSIONS

This work elucidated the effect of eugenol on the microstructural changes in its NDGs when subjected to mechanical stress. The concentration of eugenol was found to have a significant effect on the flow and deformation of its NDGs. From the flow curves, it was observed that both the viscosity and yield stress was inversely dependent on the eugenol concentration in the NDGs. Both the viscosity and shear rates were found to be dependent on the shear rate. The samples NDG1 and NDG2 were found to follow Herschel-Bulkley model whereas NDG3 with 15% eugenol

| Table 2: Fitting of various models to the rheological data of eugenol nanodroplet gels |
|-------------------|----------|-----------------|-----------------|-----|
| Rheological model | NDG      | Yield value (Pa) | Consistency coefficient (Pa sⁿ) | Flow behavior index (−) | R²  |
| Newtonian         | NDG1     | —               | 2.4785           | —               | 0.8688 |
|                   | NDG2     | —               | 1.5228           | —               | 0.9663 |
|                   | NDG3     | —               | 0.4446           | —               | 0.9677 |
| Pseudoplastic/    | NDG1     | 63.6270         | 2.0513           | —               | 0.8958 |
| Ostwald/power     | NDG2     | 2.8287          | 1.8433           | —               | 0.9559 |
| law               | NDG3     | 0.5467          | 0.4453           | —               | 0.9885 |
| Bingham           | NDG1     | 80.4060         | 0.0336           | 1.9894          | 0.9583 |
| (plastic)         | NDG2     | 2.9165          | 2.9649           | 0.8469          | 0.9981 |
|                   | NDG3     | 0.8904          | 0.3088           | 1.0943          | 0.9782 |
| Herschel-Bulkley  | NDG1     | 58.2620         | 0.7127           | —               | 0.8340 |
|                   | NDG2     | 1.4370          | 1.1481           | —               | 0.9925 |
|                   | NDG3     | 0.3055          | 0.5625           | —               | 0.9808 |

NDG: Nanodroplet gel
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followed Bingham rheological model. The study results pointed toward the necessity of future investigations on the role of other components in the topical NDG formulation.

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Conflicts of interest
There are no conflicts of interest.

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