VISCOELASTIC PROPERTIES AND RHEOLOGICAL CHARACTERIZATION OF TOPICAL HERBAL FORMULATIONS

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Abstract:- *The current research paper details the determination of the viscoelastic properties and rheological characterization of some topical herbal formulations. Glyceryl monostearate SE is the monoester of glycerin and stearic acid. It is an emulsifier. Mont nova 68 is another glucolipid emulsifier which was derived starting materials of vegetable origin. Many commercial cosmetic products such as, creams and lotions contains these materials as they aid in providing viscosity, stabilization and suspension properties to the final products. Preparation and source of the emulsifiers can affect the final cosmetic products and this need to be acknowledged thoroughly before finalizing the formula. Shear at the time of dispersion and mixing is such a factor that can affect the behavior of the emulsifier. It was found that many emulsifiers were affected by shear depending on the method of dispersion used. Shear sensitive emulsifiers can be used in commercial production if low shear mixing is employed but this might push the dispersion times longer and production costs higher.*

Key words: DV-II +Pro Viscometer, Rheometer, Shear rate, Shear stress, Viscoelasticity, Emulsion, Amplitude sweep, Flow curve, Oscillation

1. INTRODUCTION:

Many research papers were already published reporting the effectiveness of transdermal delivery of various drugs using an emulsion preparation with Nano-metric droplets size (20-200 nm). The investigations revealed that such dosage forms possess influential solubilization capability, thermodynamic stability, controllable droplet size, enhanced permeability, *etc.* (1, 2, 3 & 4). The present research was conducted with 3% of Glyceryl monostearate SE, 3 % Mont nova 68, 4 % of glycerin and coconut oil. With 85% of water, oil in water formulations were prepared and subjected to viscosity and rheological characterization. Two different grade emulsifiers were evaluated at room temperature. Different Schiff base active compounds were taken for the study as they provide rich sensory feel, high clarity to the final product and possess anti-oxidant activities to the facial and skin creams, sunscreen products etc.

Generally, micro- and nano-emulsions deliver poor rheological properties because of their very low viscosity. This makes them behave as Newtonian fluids or semisolids of high fluidity and due to this they become pharmaceutically inapplicable and commercially unacceptable as topical products (5). Addition of thickening agents or gel-network forming substances is highly recommended to overcome these problems (6).

Glyceryl monostearate SE is the monoester of glycerin and stearic acid. Mont nova 68 is a Glucolipid emulsifier derived from vegetable origin. Carbomers (poly-acrylic acid polymer), gums (polysaccharides), semi-synthetic cellulosic derivatives, *etc*, are extensively used in pharmaceutical and cosmetic applications to provide properties such as: emulsification, stabilization and rheological control (7).

Cosmetic creams are produced by mixing two immiscible liquids with different polarities. These mixtures are highly instable causing creaming, sedimentation, flocculation, Ostwald ripening, coalescence, and phase inversion (8) etc. These unwanted effects can be suppressed by addition of emulsifier and this represents an often used method of how to stabilize a structure of emulsion: continuous carrier liquid and the other one are homogeneously distributed within the type of distinct droplets. Addition of an emulsifier helps in two ways—decreases interfacial tension between both liquids and stabilizes the dispersed phase against coalescence. Type of emulsifier to be used is generally decided final process development steps of a new cosmetic cream. Generally 0.5–5% of the final formula is contributed by the emulsifier and this raises a question on how its usage affects the rheological characteristics of cosmetic-lotion final formulations.

Theoretical determination of rheological characteristics is highly complicated. Pal [9] describes that emulsion viscosity is dependent on these ten entry parameters: shear rate, time, viscosity of continuous and dispersed phase, density of continuous and dispersed phase, particle radius, concentration of particles, thermal energy, and interfacial tension [10]. He had proposed an analytical expression for the viscosity of dilute emulsions in the presence of emulsifiers. However, cosmetic creams in general are emulsions with high-water content (70–90%) and low viscosity, often oil-in water type. Creams of water-in-oil type are of low significance cosmetically. Experimental determinations of rheological

characteristics are well explained and documented and they can be used for predicting the properties like spreadability or pouring of cosmetic lotion from a bottle.

Rheological properties are coupled, not detached [11] and the rheological behavior of cosmetic products is one of the most significant features from technical and aesthetic points of view. Cosmetic products are meant not only to be easy to use, but also to meet appeal to the customer and the rheological properties discussed are often directly related to the product's appearance and to its performance.

Recent research of cosmetic emulsions and creams has given good weight to the rheological analysis, but only some studies evaluated the connection with sensory analysis. Paper [12] had applied rheological measurements to four sun creams with different consistencies and established significant correlation between the rheological measurement results and has illustrated the use of rheological characterization for research, development and quality control. Paper [13] reported a good correlation between rheological parameters of the consumer products. Three oil-in-water cosmetic emulsions were studied exploitation easy and periodical shear physical science tests. Due to recent high demand for natural cosmetics, [14] investigated the effect of the plant extracts and the influence of solvent on the product flow properties. [15] has reported statistically significant relationships between rheological parameters of cosmetic emulsions, studying body lotions and face creams. Rheological studies were also used for the determination of the optimal content of the active ingredient as applied, [16], who analyzed the Dead Sea salt content in cosmetic emulsions.

The agenda of this study is to study and establish relation between the small influential changes in the composition of a cosmetic emulsion to its rheological properties. For this, three cosmetic emulsions, water-in-oil / oil-in-water body creams, with different ratio of emulsifier were prepared. Rheological evaluation was performed on these samples. Obtained results were compared with the sample ingredients and the role of emulsifier is assessed. A relationship among the detected characteristics was specified to find out a connection among the used methods compared to viscosity and rheological properties.

2. Materials and methods:

The research was performed using Brookfield DV II +Pro Viscometer, equipped with LV-4 spindle, 20 rpm, T-96 spindle, 2.5 rpm and Anton Paar Rheometer, equipped with CP 50 spindle.

Materials:

Table-1: Products with different Schiff base active compounds and concentrations.

Product	A	B	C	D	E	F	G	H	I	J
%Active	0.1% (D)	0.05 %(D)	0.05% (E)	0.1% (E)	0.2% (E)	0.2% (E)	0.1% (D)	0.1% (E)	0.1% (D)	0.1% (E)

Apparatus:

Constant temperature water bath.
Brookfield Viscometer, DV II +Pro.
Anton Paar Rheometer (MCR-302).

Formula product preparation:

Table 2: Composition of Schiff base active compounds with multiple emulsions.

Sl,No	Name of the material	% composition	Phase
1	Glycerin monostearate SE grade	3.0 %	Ist-Oil phase
2	Coconut oil	4.0 %	
3	Montanova-68	3.0 %	
4	Glycerin IP	4.0 %	IInd-Water phase
5	Purified Water	Adjusted to 100.0%	
6	Euxyl PE 9010	0.5 %	IIIrd-Phase
7	Perfume Orange fresh	0.5 %	
8	Schiff base active compounds	0.1 %	

Preparation of Oil-in-water type Multiple Emulsions.

Several pre-formulation studies [8] helped us in the selection of the most appropriate primary emulsion for the further development of Oil-in-water multiple emulsion system. Composition of the selected emulsion is given in Table 2. All multiple emulsions were produced by three-step emulsification procedure which is described as follows [3].

Phase-I (Oil phase): Primary emulsion was prepared in a stainless steel vessel by emulsifying the oil phase with the aqueous phase in the presence of Coconut oil. Both phases were heated at 80^{0}C for 10 minutes in a digital water bath with continuous stirring until a clear solution was formed.

Phase-II (Water phase): Secondary emulsion was also prepared in a separate stainless steel vessel. Glycerin in the presence purified water were mixed by heating both phases at 80^{0}C for 10 minutes in a digital water bath with continuous stirring using an overhead stirrer at 2000 rpm for 10 minutes.

Phase-III: Third phase was prepared by addition of Euxyl PE 9010, Perfume orange fresh and Schiff base active compounds in a separate stainless steel vessel and mixed well with a stirrer and then sonicated.

Phase-I was slowly added to phase II. Homogenization of the aqueous phase with oil phase was achieved by heating both phases at 80^{0}C and mixing with an overhead stirrer, at 2000rpm for 10 minutes. The speed of the stirrer was then reduced to 1000 rpm for 10 minutes and finally the emulsion was cooled down to room temperature while maintaining a stirring speed of 500 rpm for further 10 minutes. Phase-III was then added slowly and the mixture was further stirred at a speed of 700 rpm for 10 minutes. 0.025 % of citric acid was added at this point to adjust the pH from 5.5 to 6.5. A soft cream is formed at the end and this product was allowed to stand at room temperature in a dark place for 48hrs. Viscosity and rheology studies were performed on this product after 48hrs.

Test procedure for viscosity measurement:

Clean and dry 100 ml glass borosil beaker was taken and the sample was transferred into the beaker.
Care was taken to not introduce any air bubbles. Beaker was covered with aluminum foil and kept in a calibrated water bath (25 ^{0}C ± 1 ^{0}C) for 1 hour for the temperature to equilibrate. Sample temperature was measured by the temperature probe attached to the viscometer and then viscosity was measured by using spindle LV-4, at speed 20 rpm and T-96 spindle at speed 2.5 rpm.

The spindle was dipped at center position of beaker up to the mark on the spindle. Constant reading on spindle was measure after a minute. The results were tabulated here in table.3.

Table-3: Real time viscosity at 25^{0}C, LV-4 spindle, 20 rpm.

Sample	LV-4 spindle, 20 rpm.	T-96 spindle, 2.5 rpm.
A	10850	159000
B	16940	162000
C	15860	151000
D	16070	152000
E	7920	153000
F	12930	154000
G	5810	160000
H	7010	162000
I	9460	158000
J	11540	161000

Test Procedure for Flow curve determination:

Rheological measurements were performed immediately after pressure treatment using a controlled stress and strain Rheometer (Anton Paar MCR 302, Germany). Parallel plate geometry (50 mm diameter) was used and the gap between the two plates was 0.1 mm. Before each test, the sample was placed between the Rheometer plates for 5 min allowing the stress relaxation and temperature equilibration (temperature was kept constant at 25°C). Physical Rheometer Data Analysis software (Rheo compass, version V1.11:173, Germany) was used to obtain experimental data. A rheogram of the samples was plotted using shear rate and shear stress at various revolution rates of the spindle (PP-50).

The Real time viscosity values of (Table-4).

Sl.No	A	B	C	D	E	F	G	H	I	J
Viscosity in mPa.s	10,910	17,121	15,929	16,164	8,007	13,051	5,852	7,062	9,552	11,608

Amplitude sweep test:

Amplitude sweep test, as an oscillatory test is defined by a variable amplitude and constant frequency.
The term 'sweep' stands for an operate with a variable parameter. Either of the shear stress (CSS) or the shear deformation (CSD) is controlled during the test. These tests generate information about the flow behavior of a substrate especially its stored elasticity, the LVE deformation range, marked as area between the points of the parallel running curves of G' and G" and their transition. The inflection or transient point denotes the yield point.

On the other hand, frequency sweep test is designed on a variable frequency and constant amplitude which usually is conducted with controlled shear deformation (CSD). However, the yield stress is to be determined first in order to assure that measurements are carried out within the LVE range. Curves of the storage modulus G', the loss modulus G" and also the complicated viciousness $|\eta^*|$ square measure displayed as a operate of the angular frequency ω.In the other way, the complex viscosity $|\eta^*|$ can be replaced by tan δ. Both generate information related to the viscous behavior, respectively the portion of viscosity in relation to elasticity. Frequency sweep tests are helpful in investigating short-term and also long-term behavior. Thus, cyclic adaptations of frequencies might be applied, e.g. frequency changes of farm implements [17].

The LVE range (linear viscoelastic) analysis is used for determining yield stress derived from amplitude sweep tests, which have either deformation γ (controlled shear deformation, CSD) or shear stress τ (controlled shear stress, CSS) as default. Calculations of frequency sweep tests are based upon a Carreau equation (Carreau-Yasuda) and they are generated automatically during the tests [18].

Oscillatory shear responses (G' or coefficient of elasticity, and G" or loss/viscous modulus) were determined at low strains over the frequency vary of zero.001–100 rad/s. The linearity of viscoelastic properties was verified for all the materials at different conditions and different stages.

3. EXPERIMENTAL RESULTS & DISCUSSION:

Viscosity properties:

The ten different Schiff base herbal active formulation's viscosity was studied at real time, 25 ± 1^0C by using Brookfield DV-II +Pro viscometer.

The initial viscosity profiles of herbal formulations are plotted in Fig-1. At 25°C there is a difference in viscosity in product E, G and H. Viscosity of products E, G and H are in the range of 5,000 cps to 8,000 cps. For products A, B, C, D, F, I and J, the viscosity values are similar and in the range of 9,000 cps to 17, 000 cps. As per general cosmetic formulations, soft skin cream is considered to be acceptable with a viscosity value not less than 5, 000 cps.

Hence it is stated that all the formulations prepared were possessing acceptable viscosity values and are acceptable for usage.
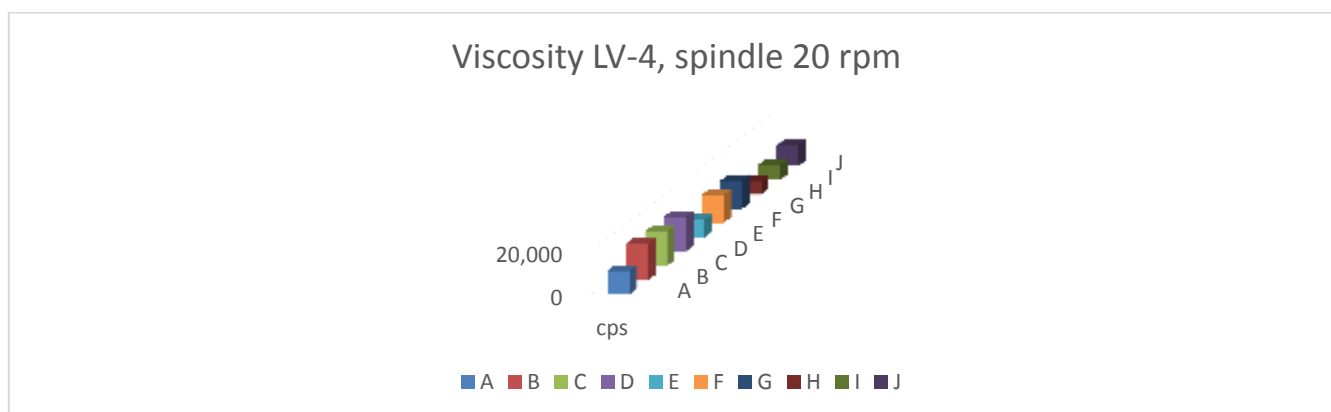
Fig,1: Viscosity data of Formulations:

Flow curve:

A graph plotted as viscosity versus shear rate is called as flow curve and across a wide range of shear rates Newtonian flow is the simplest type, displaying as shear-independent viscosity while the material is sheared. Water and a few low-molecular-weight mineral oils square measure typical samples of Newtonian fluids. Pseudo-plastic or shear dilution fluids show body reduction whereas the shear rate will increase. Colloidal systems are the typical examples of this type. The colloidal structure breaks down as shear rate increases, thereby showing a reduction in viscosity. Dilatant or shear thickening flow, wherein the viscosity increases with shear rate, is often observed in the pharmaceutical and cosmetics manufacturing.

Often the biggest changes in viscosity just take place within the range of low shear rates and for evaluating the behavior in low shear-rate range, it is beneficial to use a log-log plot for the diagrams of flow curves and consistency curves. The advantage of evaluating these diagrams on a logarithmic scale is that a very large range of values (several orders of magnitude) can be accompanied and illustrated clearly in a simple single diagram.

Steady state viscosities of ten formulations were measured at a temperature of 25°C. For clarity, the flow curves for sample's increasing shear rate with decreasing viscosity were depicted in Fig. 2 to 11. For a shear rate with constant temperature, viscosity of these products did not change appreciably. The temperature stability or inertness can be attributed to the elastic or cross-linked structure of the emulsions. Thermal fluctuations or increased thermal mobility of the polymer chain strands are suppressed by the cross-link junctions. Therefore, viscosity does not change appreciably with constant temperature.

The flow curves for constant temperatures were fitted with Ostwald's model (19) $\tau = K \gamma^n$. The fluidity or power law index n in this equation represents departure from Newtonian behavior (n = 1 for Newtonian fluids) and is a measure of pseudo plastic or shear thinning extent of the fluid. It can be interpreted as the rate of change of structure with shear rate (γ) (20). The gel network structure can be changed due to deformation induced changes in shapes of the microgel particles, alignment of polymer chain segments, and decrease in the number of entanglements between polymer chain segments and side chains. In support of the mentioned statement, the values of n will be lower for the stronger emulsions. This is because of increased non-covalent forces of attraction between adjacent particles, which in-turn will increase stability and lifetime of the temporary entanglement junctions.

The Viscosity v/s shear rate at 25°C flow curve profiles of herbal formulations were plotted in Fig-2-11. There was no much difference observed in viscosity and shear rate of flow curve profile for the products A, B, C, D, E, F, I and J. For the products G and H, viscosity was found to be slightly decreasing, but there was difference in shear rate. For all the products, the viscosity drop points were determined to be greater than 10 shear rates. This shows that at 25°C, the flow cure profiles of cosmetic creams formulated with different Schiff base active compounds in the concentration range of 0.05 % to 0.2 % and at pH-range of 5.5 to 6.5 are stable and not prone to viscosity changes. All the products are said to be stable and there will be no emulsion breakage.
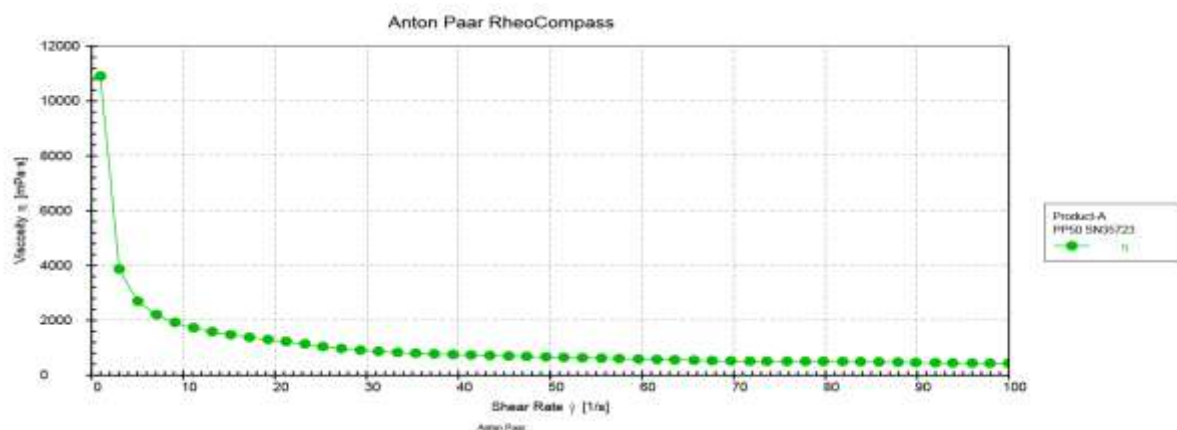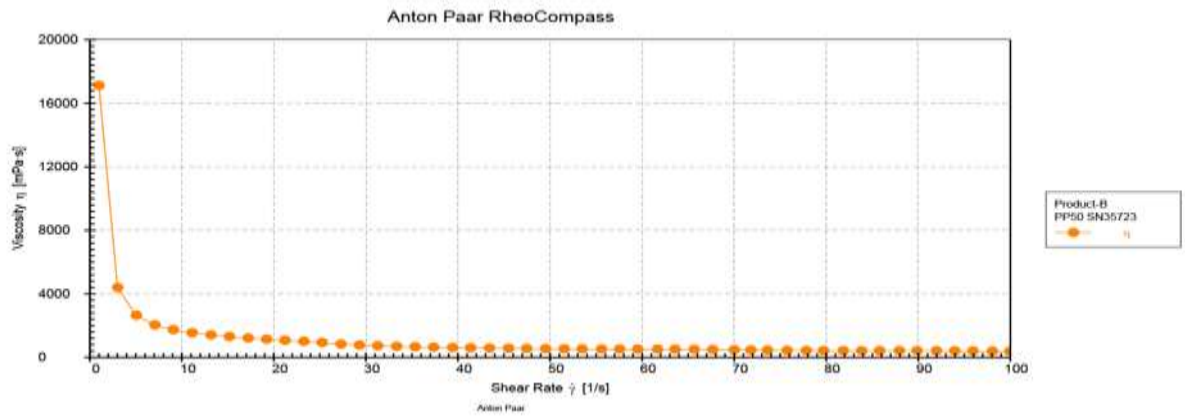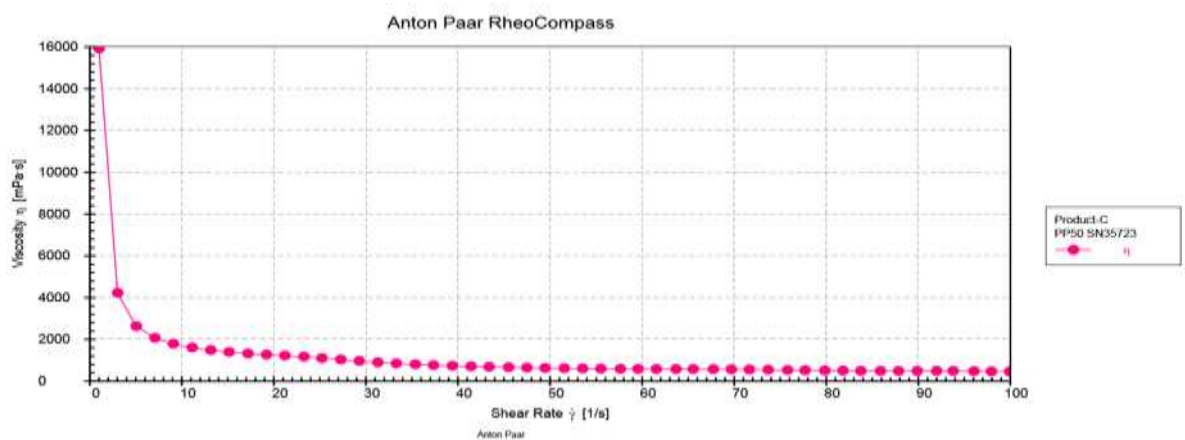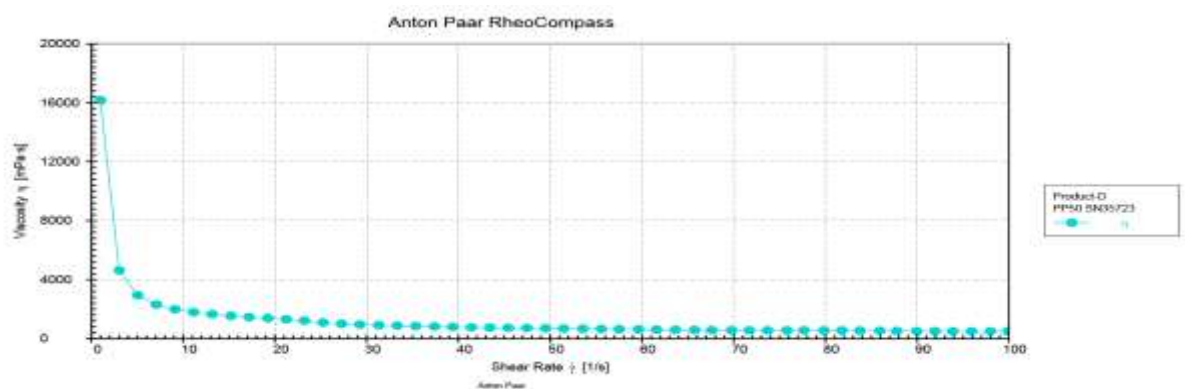

Fig 2: Product A:

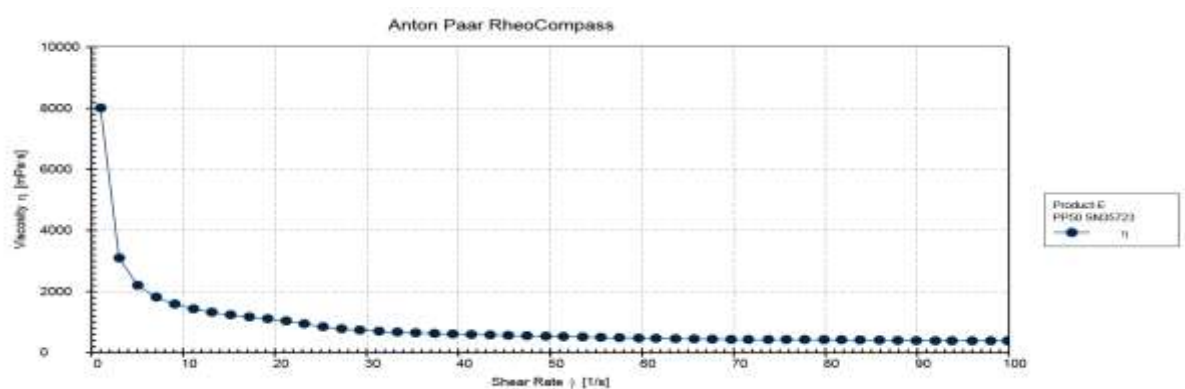Fig 3: Product B:

Fig 4: Product C:
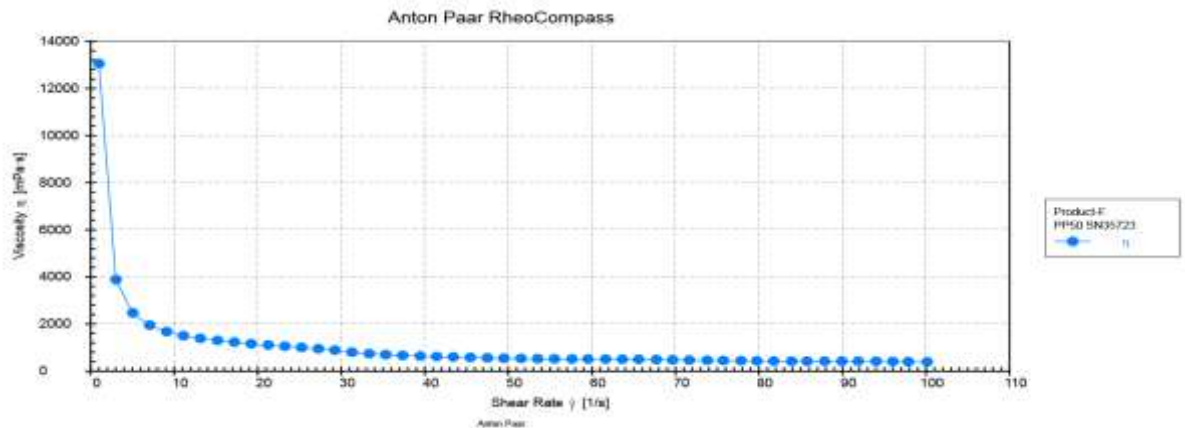

Fig 5: Product D:
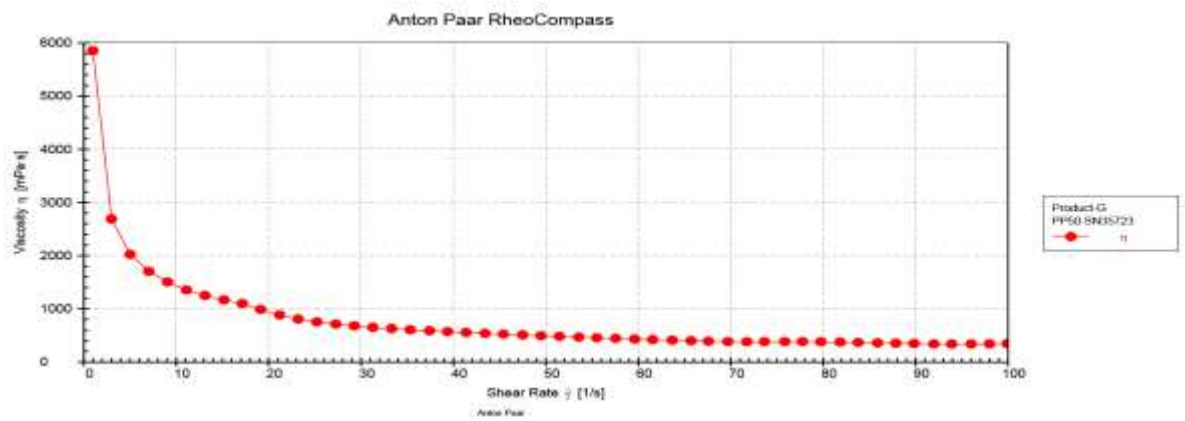
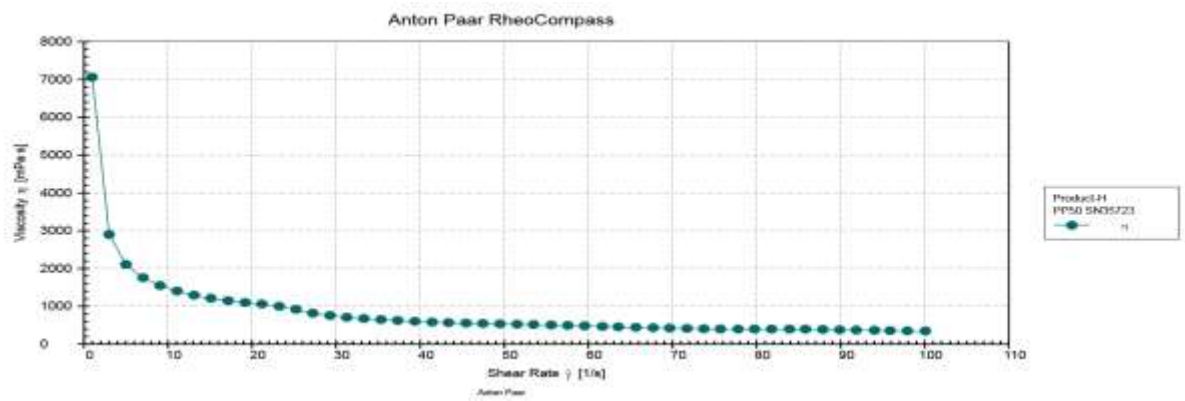

Fig 6: Product E:

Fig 7: Product F:
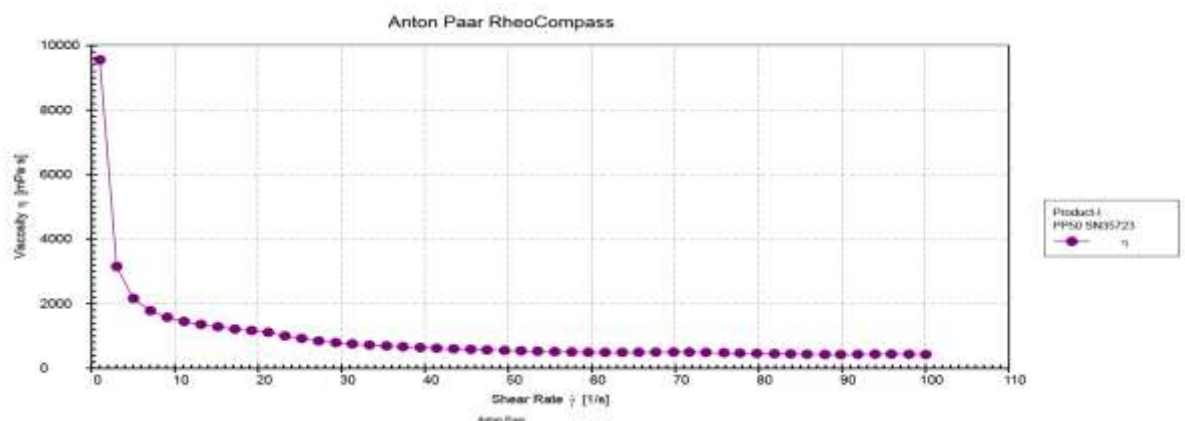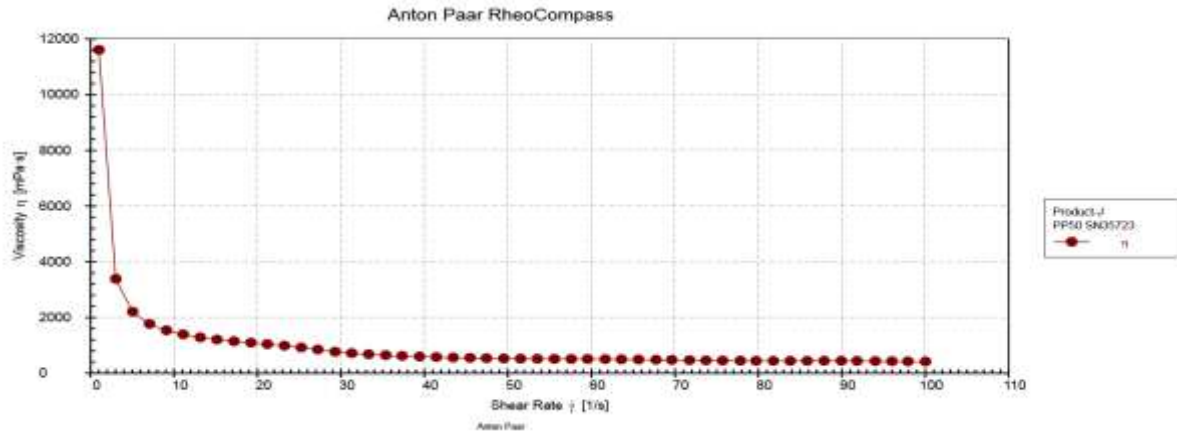

Fig 8: Product G:

Fig 9: Product H:

Fig 10: Product I:

Fig 11: Product J:

Amplitude sweep Test:

Strain sweep experiments were generally performed at constant periodical frequencies with enlarged strain from zero.001 to 10. Little differences in the G" and tan (δ) [tan(δ) =G"/G'] profiles of these materials were observed at different constant frequencies (0.01 Hz, 1 Hz, 100 Hz) (Fig. I to IV). The observations in turn state that the gels' responses are elastic in the frequency range of 0.01 to 100 Hz.

The storage modulus G' (G prime, in Pa) represents the elastic portion of the viscoelastic behavior, which quasi describes the solid-state behavior and stability of the sample. The loss modulus G'' (G double prime, in Pa) characterizes the viscous portion of the viscoelastic behavior, which can be referred to as the liquid-state behavior of the sample.

Viscous behavior is a result of the internal friction between the components of a flowing fluid and in turn between the molecules and particles. This friction generates frictional heat in the sample, and consequently, transforms the deformation energy into heat energy. This energy is absorbed by the sample, used up by internal friction processes and will no longer be available for the subsequent behavior of the sample material. This loss of energy is also called energy dissipation. In contrast, the elastic portion of energy is stored in the deformed material by extending and stretching the super structures present internally without overstressing the interactions and without overstretching or destroying the material. The material when released from stress, this unused stored energy drives the reformation of the structure into its original shape.

Storage modulus G' represents the stored deformation energy and loss modulus G'' characterizes the deformation energy lost (dissipated) through internal friction when flowing. Viscoelastic solids with G' > G'' have a higher storage modulus than loss modulus. This is due to links inside the material. Chemical bonds or physical-chemical interactions are a great example of this behavior. On the other hand, viscoelastic liquids with G'' > G' have a higher loss modulus than storage modulus. This is because of no such strong bonds between the individual molecules as compared to the previous case.

As evident from Fig. 12 to 21, the elastic contribution at low strain is more dominant than complex modulus. For all product at strain of around 100 percent, the loss modulus (G") is a smaller amount than 2 hundredth of the coefficient of {elasticity|modulus of elasticity|modulus} that indicates the total elasticity of the system. In this case, the gel network can occur as closely packed hard sphere dispersion. At higher strains, the elastic structure breaks down and further, the elastic modulus decreases steeply with increasing shear strain shear stress (Fig. 12 to 21).

The 25°C strain sweep experiments were performed at constant oscillating frequencies with increased strain from 0.001 to 10. Little variations within the G' and tan (δ) [tan (δ) =G"/G'] profiles of those materials were determined at totally different constant frequencies (0.01 Hz, 1 Hz, 100 Hz) (Fig.12 to 21). The observations further depict that the emulsions' responses are elastic. In the frequency range of 0.01 to 100 Hz, at 10 degree strain, sweep experiment of all ten samples are plotted in Fig-12 to 21. The elastic structure breaks down and further the elastic modulus decreases steeply with a rise in strain. A crossover strain (γc) can be identified over which the gels behave predominantly as liquid.
This is as a result of G" becomes lesser than G' [tan (δ) < 1]. As the emulsions' concentration is same in all ten samples, the breakdown strain is similar. Collapse of the gel structure at such low strains shows a closer packing of the microgel particles (21), and these smaller spheres lead to a lower breakdown strain.

Yield stress is defined as the minimum stress applied before the material starts to flow (22). This is an important parameter for evaluating the ten products. The cross linked microgel structure, where individual particles are closely

packed with their neighbors is responsible for yield stress. The magnitude of the yield stress represents the strength of the closed pack structure. For the material to start flowing, the yield stress should exceed this strength of the closed pack structure. All ten products yield stress value is more and hence they possess good stability.
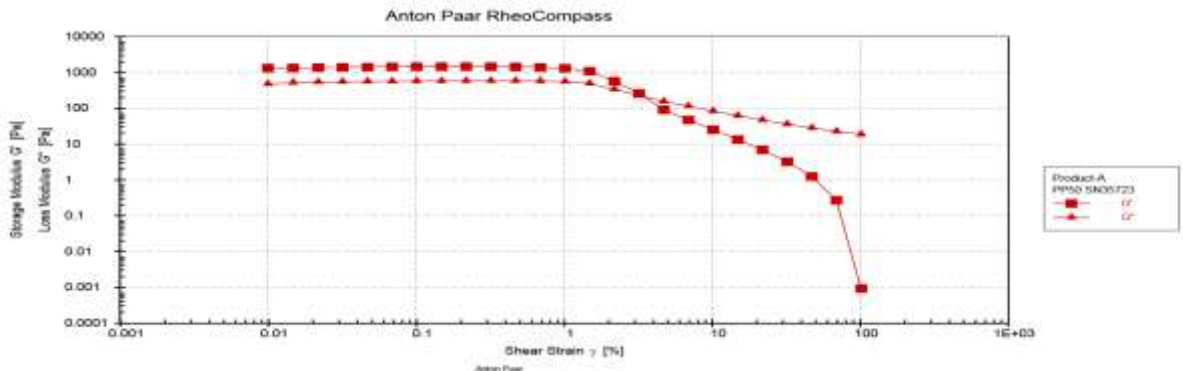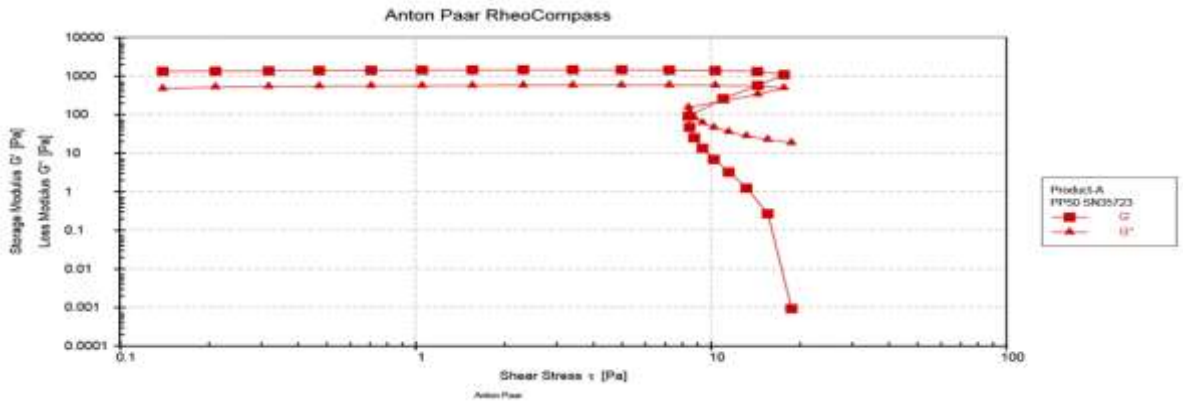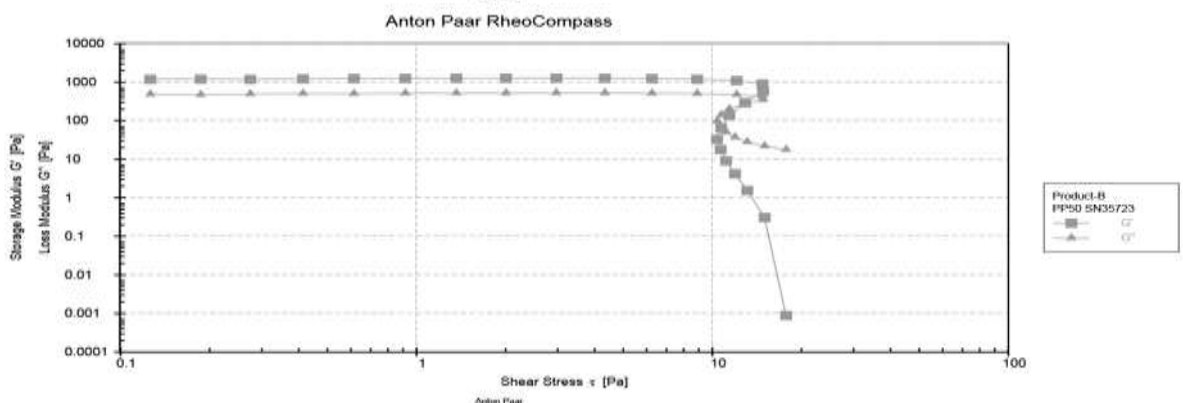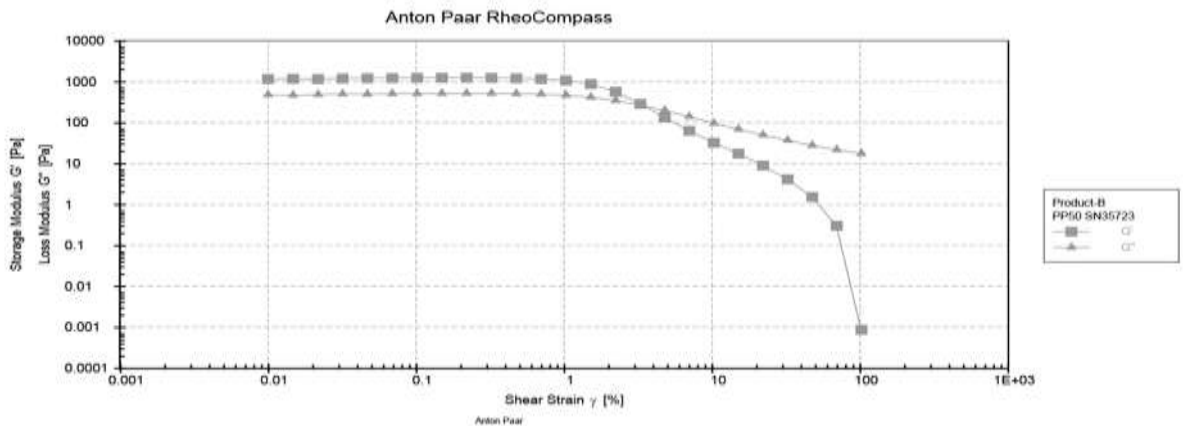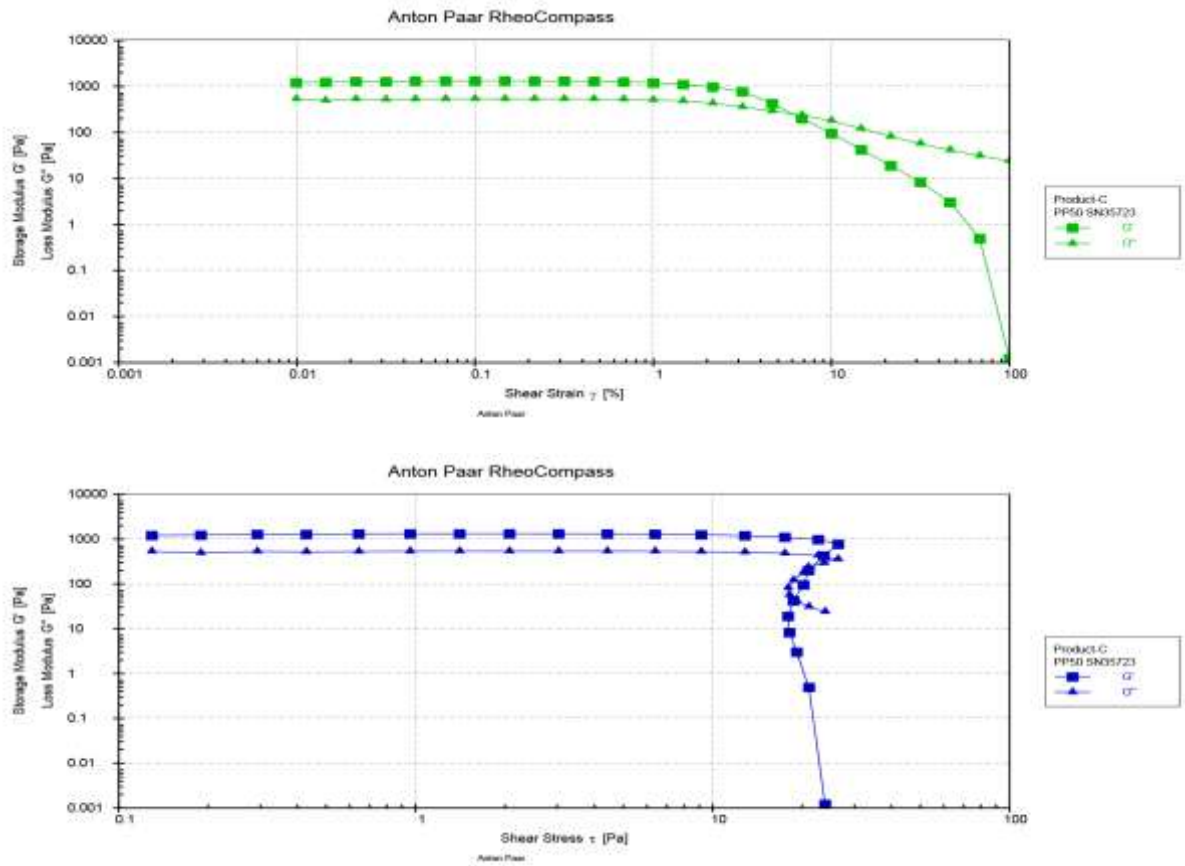

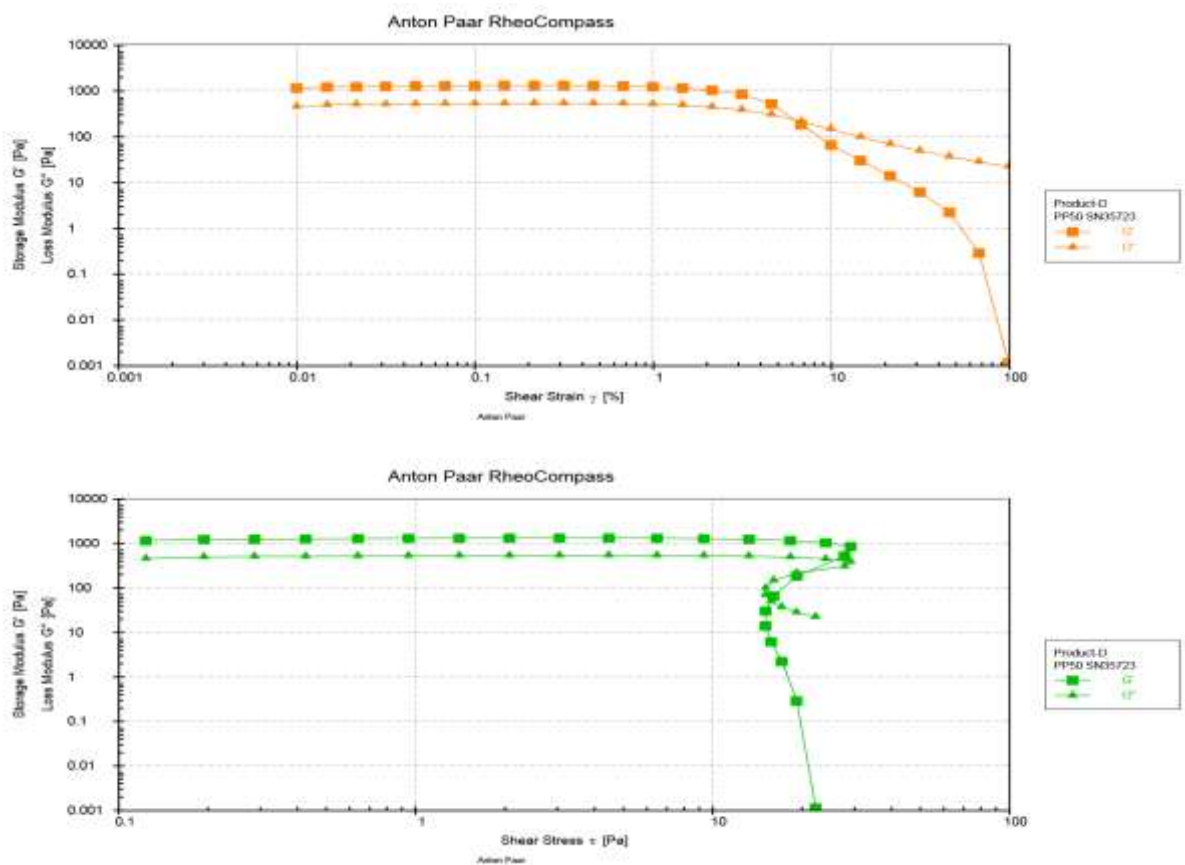Fig 12: Product A:

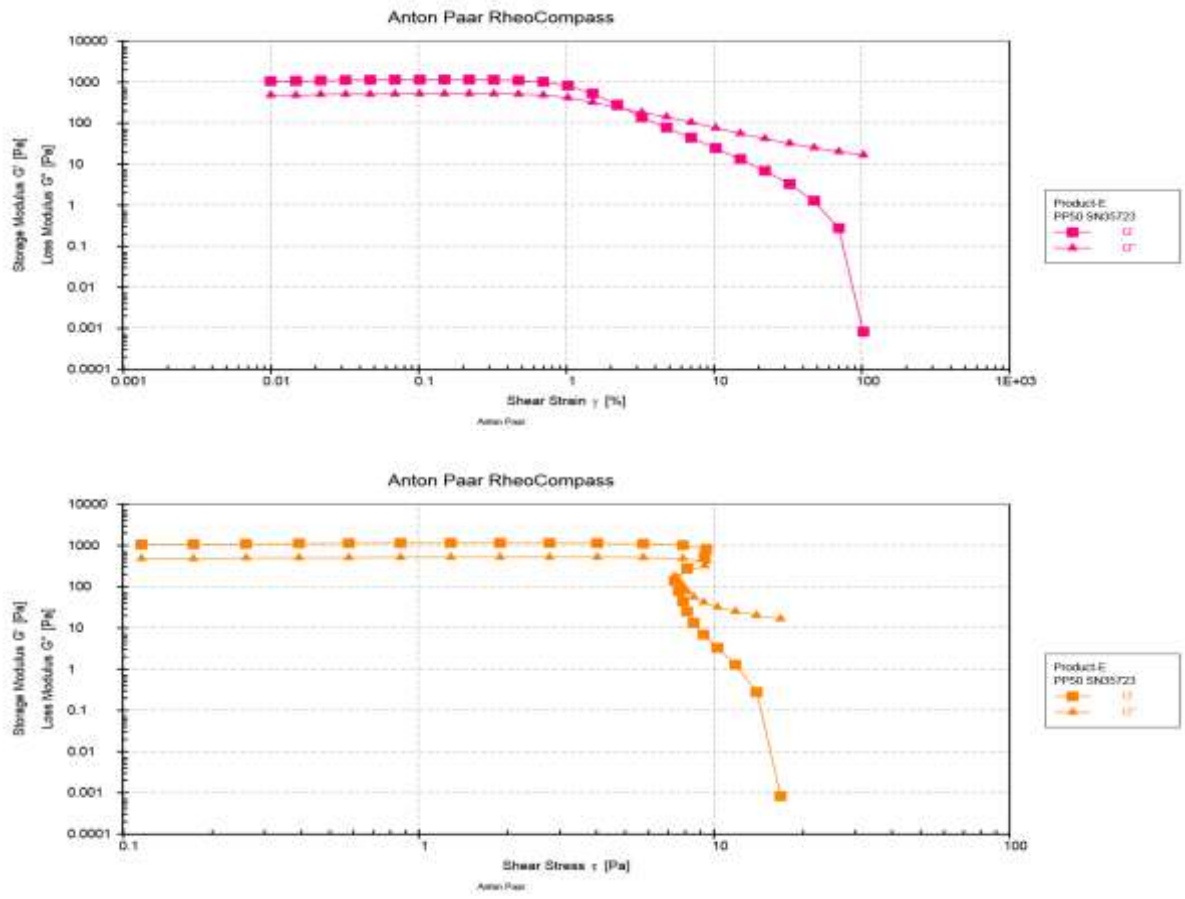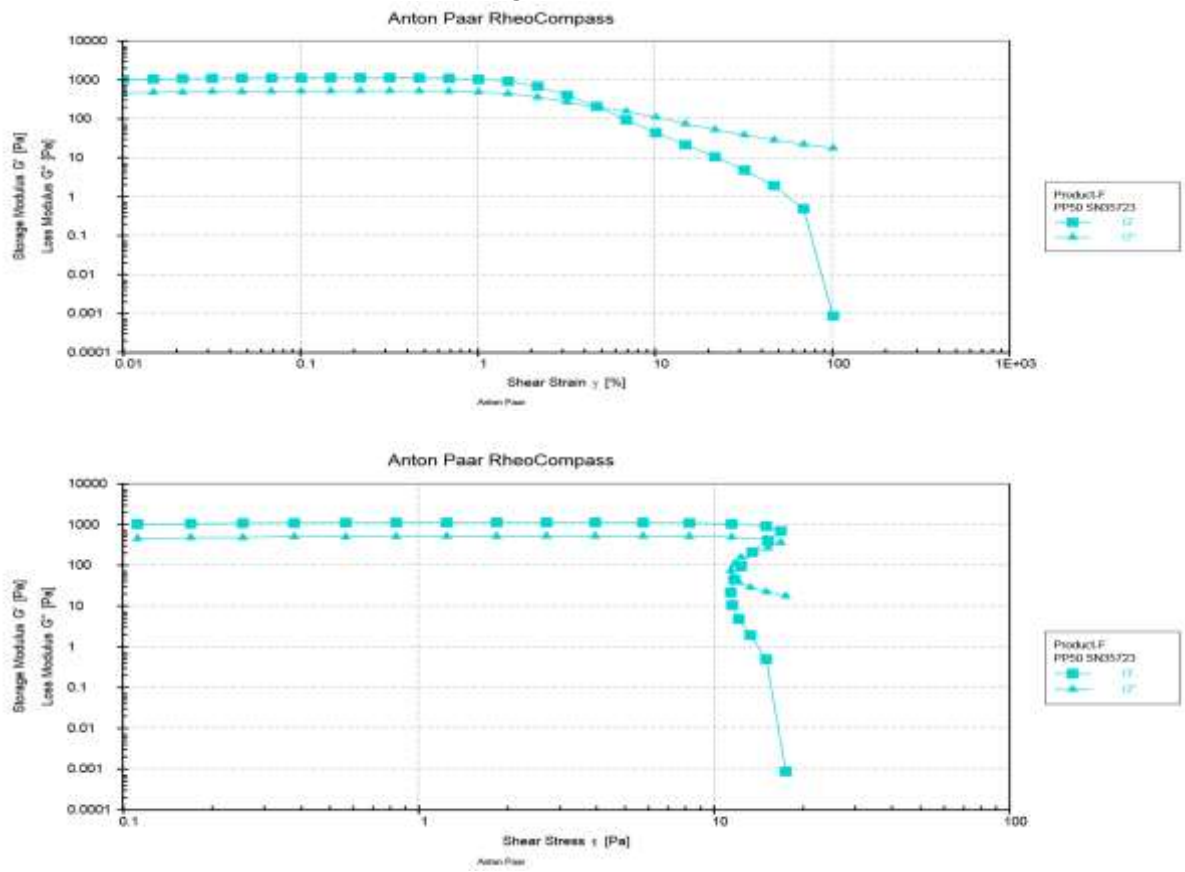Fig 13: Product B:

Fig 14: Product C:

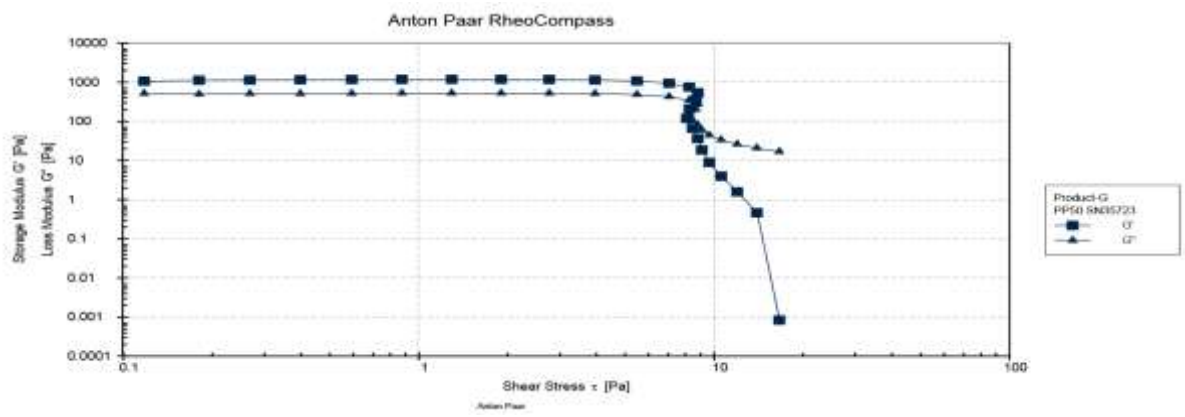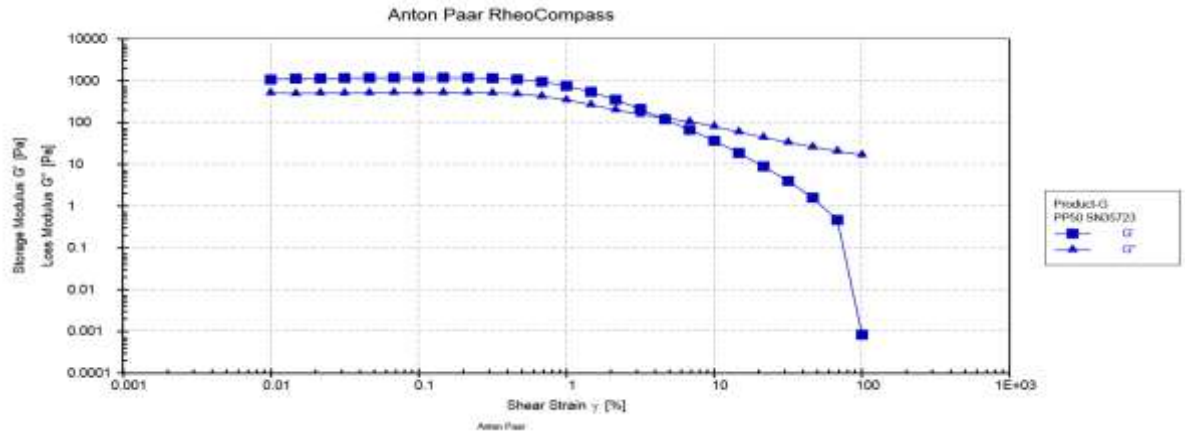Fig 15: Product D:

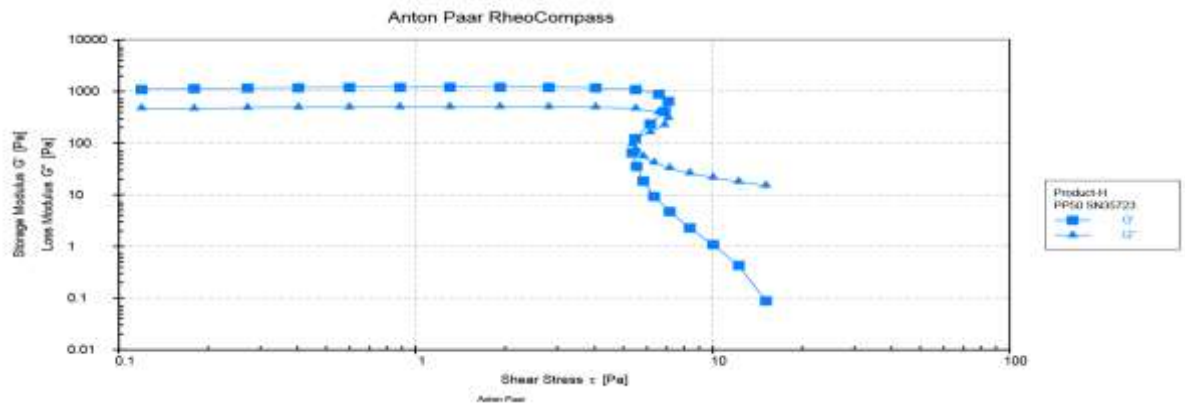Fig 16: Product E:

Fig 17: Product F:
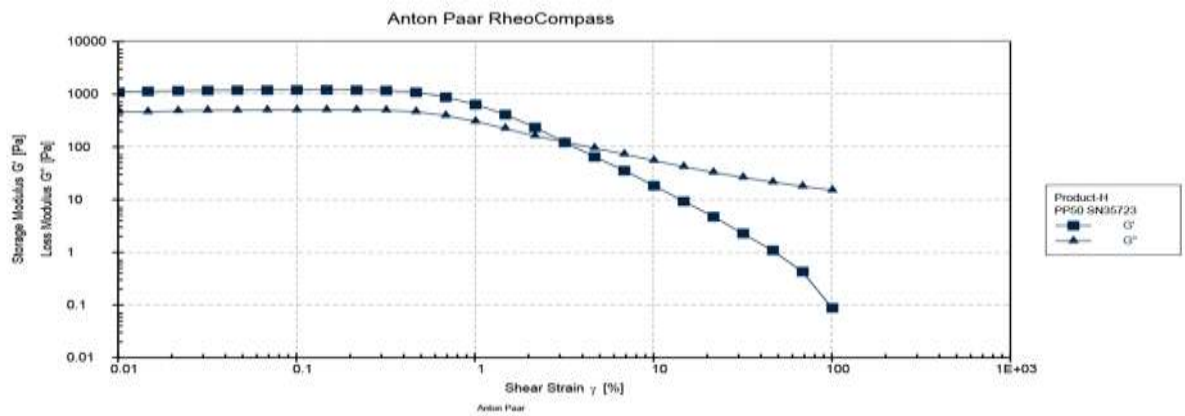

Fig 18: Product G:

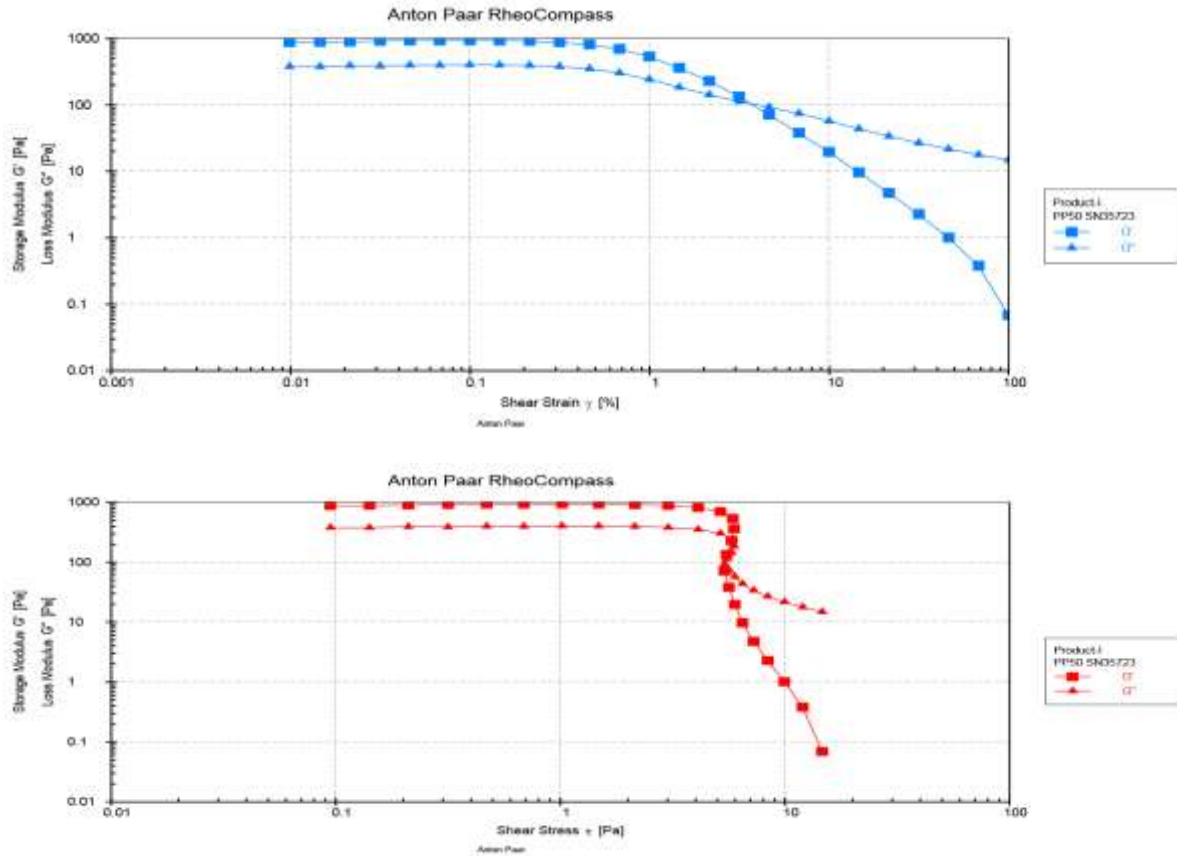Fig 19: Product H:
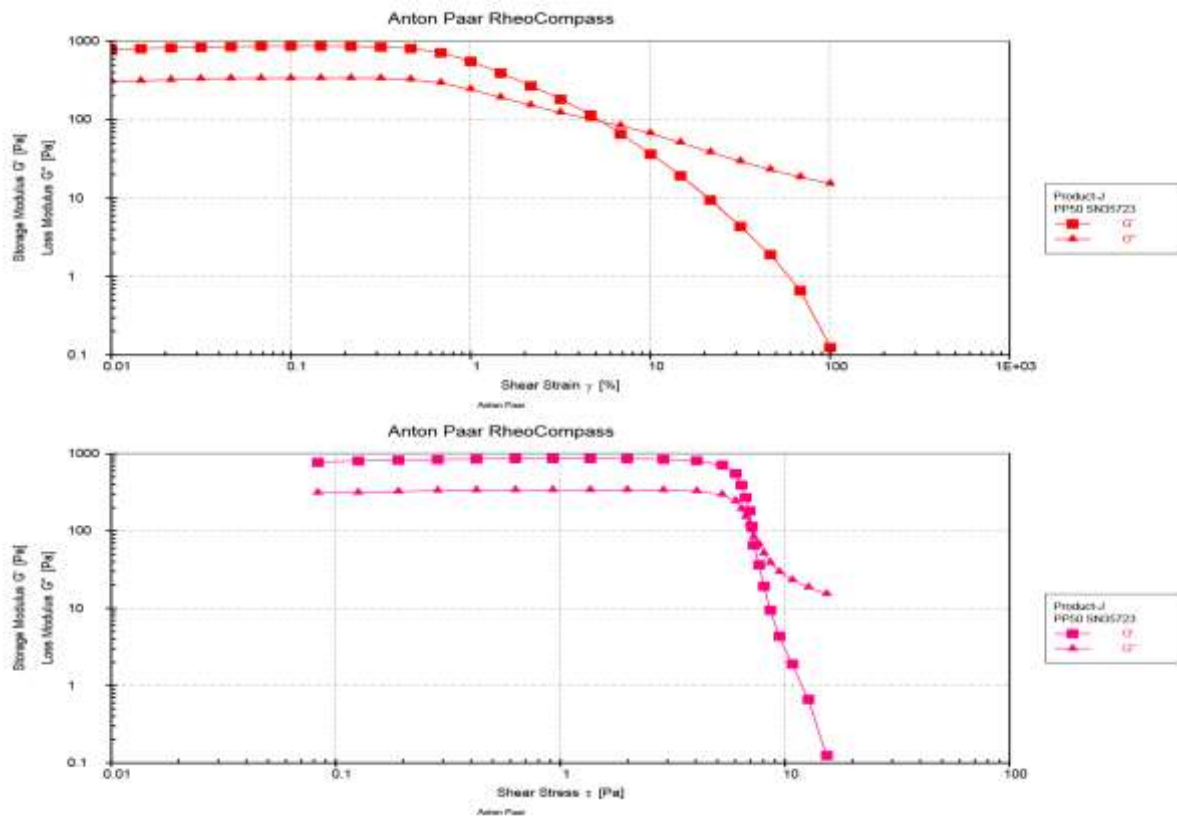

Fig 20: Product I:

Fig 21: Product J:

4. CONCLUSION:

In the current study, 0.05 to 0.2% of Schiff base active compounds in Oil-in-water emulsion were formulated along with two modern emulsifiers. Stability characteristics of 10 different emulsion samples at room temperature were studied and

satisfactory data was observed. These 10 emulsion samples were found to be resistant to phase separation. The pH scale price was at intervals the bounds of traditional skin pH scale vary. An inverse relationship was found between the shear stress and viscosity at the room temperature studied. It is stated that varying storage conditions have no impact on any of the physicochemical characteristics of the 10 different formulations studied. The formulations can achieve long-term stability even at elevated temperatures. Further studies can be taken up for exploring these formulation models for the development of various types of skin rejuvenating cosmetic herbal products.

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