Rheology of UHMWPE/ solvent systems: A literature review

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Abstract
The paper reviews the current available literature on the rheological behaviour of Ultra High Molecular Weight Polyethylene (UHMWPE)/ solvent systems. The rheological behaviour of UHMWPE /solvent systems was found to depend on the selection of solvent, shear rate, concentration of polymer, temperature and shear history. The influence of solubility on the rheological characteristics was discussed. The implication of the reports on gel spinning was also discussed.

Key words:
steady shear viscosity, dynamic shear viscosity, viscoelastic properties, miscibility. gel spinning.

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1.0 Introduction:

Ultra-High Molecular Weight Polyethylene (UHMWPE) exhibits a number of exceptional properties, including chemical inertness, lubricity, impact resistance and abrasion resistance.[1]. As a result it has been receiving increasing attention in regards to its application in variety of fields which include biomedical[2, 3] and military[4].

In medical applications, it has been used as a bearing material in the manufacture of artificial joints. Its use in orthopaedics has been the subject of several reviews[5-7].

The extremely high molecular weight and poor melt flow property makes processing of UHMWPE extremely challenging[8].For example, in the manufacturing process of artificial knee joints, UHMWPE powder is initially shaped into primary articles with either square or cylindrical geometries using compression moulding or plunger extrusion techniques. Subsequently, these articles are transformed into artificial knee joints through a turning process[8, 9].

The extrusion of UHMWPE products, including pipes, sheets, and bars, necessitates the use of specially engineered extruders that incorporate a significant quantity of organic compounds to serve as lubricants during the process[8].

In case of UHMWPE fibres, gel-spinning method has been employed as a means of processing UHMWPE due to the fact that UHMWPE cannot undergo melt-spinning like traditional polymers without degrading prior to achieving flow [4]. As per Tam and Bhatnagar [4], gel-spinning processes process can be classified into two main systems: single solvent system and dual solvent system. In the single solvent gel-spinning process, a solvent like decalin is employed to disentangle UHMWPE polymer enabling its spinning through a spinneret with conventional melt-spinning apparatus. The fibre solution is then conveyed through an evaporation chamber, where the solvent is removed to form a gel fibre. During the following drawing process, the remaining solvent may be evaporated, enhancing the tensile strength.

An additional variation of this process involves the formation of gel fibres through the quenching of solution fibres within a liquid bath subsequent to their extrusion through the spinneret and an air gap. The gel fibre is then drawn in an oven to evaporate the solvent and align the polymer molecules, thus producing strong fibres[4].

In the dual solvent system, a low molecular weight solvent functions as the initial solvent, promoting the disentanglement of UHMWPE chains. After the extrusion, the solution fibre is quenched in a liquid bath, to form a gel fibre, which may be stretched. The solvent used in spinning is extracted utilising a second solvent with a low flash point. The initial solvent is thus replaced, and the fibre is drawn in several stages to optimise its mechanical properties.[4]. The manufacture of UHMWPE fibres via the gel spinning technique has been the subject of several studies.[10-18].

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The high performance of UHMWPE fibre is attributable to a combination of high strength (around3.5 GPa) and low density, with a typical value of 970–980 kg/m³[19]. The fibre properties depend on a variety of factors which include, molecular weight [12], gel concentration [13],L/D of extruder[10], spinneret hole size[14], winding speed[11, 15], spinning temperature[16], cooling bath temperature[17],& draw ratio[18].

In gel spinning, the role of the solvent is to disentangle the polymer solution while keeping a minimum number of entanglements for proper spinning of the solution. The peak draw ratio that can be attained, largely depends upon the concentration of the polymer solution. Therefore, the solvent type used in spinning and their concentrations are critical factors[20].

Among the solvents paraffin oil and decalin have been extensively used in industry[21] for gel spinning. There are also several reports where paraffin oil [11, 13-16, 22]& decalin[17, 18, 23] has been used in gel spinning UHMWPE. Other solvents used in gel spinning of UHMWPE include, kerosene[24]; mineral oil, decalin/ 1-dodecanol,lauric acid, stearic acid, peanut oil, olive oil[25]; Sunflower oil, palm oil, orange oil[26]; Polyalphaolefin Oil[27]; Polybutene[21]; camphene[28].

The rheology of polymer solutions can also have a significant impact on spinning processes. Rheological studies can be conducted using various techniques, including steady shear, dynamic shear, and transient tests. While steady shear testing provides insight into the material's viscosity under constant stressor strain, dynamic measurements offer information about the material's viscoelastic properties. Transient testing can be employed to examine the deformation behaviour of the material over time.

As mentioned previously, there are several reviews which deal with medical supplications of UHMWPE.[5-7]. There has also been a report on rheology of UHMWPE blends and composites [29], where there was a limited attention on rheology of UHMWPE solutions. This study reviews the existing literature on the rheology of UHMWPE/solvent systems, to facilitate understanding of UHMWPE flow behaviour during gel spinning.

2. Gel structure

In regards to gel spinning, it is important to note that UHMWPE does not form gels in conventional sense. In UHMWPE, the junction points of the gel networks are composed of crystallites unlike conventional type of gel network, where completely disordered chains are covalently linked together[30].

The gelation process of UHMWPE in solvents like paraffin oil and decalin can be explained by liquid-liquid phase separation, which is influenced by concentration fluctuations. These fluctuations occur as a result of the polymer's crystallization during the cooling of the solution [20]. Gels formed by this mechanism are also thermally reversible [30]. Similar behaviour is noted for other systems such as isotactic polystyrene [31-33],&poly(vinylchloride)[34-37].

Chung and Zachariades [38] indicate that a UHMWPE solution in paraffin oil, with concentrations ranging from 2% to 8% w/w, form a three-dimensional molecular network with secondary bonds at the junction sites.

This can result in the formation of crystalline regions and the development of physical entangled structures with varying lifetimes. Trapped entanglements between crystallites have an apparent infinite lifetime, just like the crystallites. Non trapped entanglements have a transitory lifetime[38].

The parameters employed during the preparation process significantly influence the uniformity of the resultant pseudogels. Non-uniform, gel-like structure appears under non-isothermal conditions. In such cases, the gel is made up of single crystals and fibrils in a shish kebab-like structure, reaching several millimetres in length [39]. In contrast isothermal, quiescent environments, produce a more uniform gel consisting of aggregates of single crystals, and large spherulitic crystals[39].

Moreover, as per the model proposed by Pakshomov et al [40], during the solvent extraction process that leads to the formation of xerogel, the crystal morphology of UHMWPE evolves from a cracked crystal to layered structures composed of multiple coplanar lamellar crystallites. The morphology facilitates the formation of crystalline phase with a high degree of orientation in the process of fabricating high tenacity fibres. The existence of the crystalline cross linked structure in gels can play a significant effect in the flow behaviour of UHMWPE as will be seen in later sections.

3. Solution Preparation

Alekseev [12]demonstrated that the dissolution process of UHMWPE, occurs in two distinct phases: the initial swelling of the polymer followed by the dissolution of the swollen gel particles. When UHMWPE solutions are formulated in petrolatum, the swelling phase occurs at temperatures ranging from 110 to 120°C, while the dissolution phase takes place between 135 and 140°C. Alekseev noted that to achieve a uniform solution, it is essential to gradually heat a suspension of UHMWPE powder in the solvent while maintaining vigorous stirring. If the polymer is subjected to hot petrolatum or heated too rapidly, the swelling process becomes uneven, leading to the formation of aggregates that cannot be dissolved afterward.

Alekseev emphasized the significance of the design of the dissolving apparatus. He indicated that use of typical blade and spiral mixers, along with extruders can have undesirable aspects, including uneven dissolution of particles, dominance of the Weissenberg effect, and limitations in handling higher concentrations of polymers. To address

these concerns, Alekseev suggested the adoption of twin screw extruders and specially designed self-cleaning mixers.

There have also been patents [41] reported which have attempted to address the issues. Development of gel spinning equipment have also been the subject of several patents and has been reviewed elsewhere[42]. The patents involve the use of a solution preparation vessel, mixer with a pump to keep the solution homogenous, and a single crew extruder [43]; twin screw extruder with gear pump [44]; helical intensive mixer, in addition to stirring tanks to create a homogeneous solution before introducing it in extruder fitted with a gear pump [45]; stirring tank, helical mixer, extruder with gear pump and a solvent extraction& recovery system [46]. The challenge of creating a homogeneous solution with flow behaviour suited for gel spinning remain, in this regard rheology studies can play an important role in optimizing gel spinning process as well as design of equipment's.

4. Rheology of UHMWPE/ solvent systems

As stated in the introduction, the proper selection of solvent plays a critical role in gel spinning process. Due to differences in the solubility, it can have remarkably different effect on the rheology of UHMWPE solutions and thus have been the subject of several studies[20, 21, 28, 38, 47-56].

4.1 Steady shear rheology

Steady shear rheology which involves applying a unidirectional deformation under constant shear rate over time[57] is crucial for understanding the flow of UHMWPE solutions, under different shear rates. This is particularly important for processing techniques such as extrusion, where the material is subjected to varying shear conditions. The rheological properties, including viscosity and shear stress, are critical for optimizing these processes.

4.1.1 Steady shear viscosity

Jen and coworkers [28] determined the influence of solvent upon viscosity for 2 % UHMWPE solutions, using a Brookfield viscometer. The shear rate covered ranged from approximately 1-80s^{-1}. They found that the samples exhibited shear thinning characteristics and the solution viscosity was in order of decalin> paraffin oil>camphene; which as per the authors, suggested that camphene may be suitable for spinning as compared the other two solvents.

Chiu and Wang[47] studied the influence of temperature, gel concentration, and shear rate upon viscosity of UHMWPE/ decalin solutions in the shear rate range of approximately 0-10s^{-1}. For 6% UHMWPE solution, in the temperature range between 100-160 °C, they found that viscosity drops with increase in shear rate, especially at high shear rates. At 100°C,a linear decline of viscosity with rise in shear rate was noted which was attributed to the fact that the temperature was below the gel point where phase separation had already occurred. At temperatures above 120ºC, UHMWPE solutions exhibited shear thinning behaviour for shear rates above 1s^{-1}. At shear rates below <1s^{-1}, viscosity was not dependent on the applied shear. It was suggested that the samples undergo shear stress induced orientation, at low shear rates and are fully oriented above 1s^{-1} which results in the decrease in viscosity. As the critical value of shear rate did not depend on temperature, it was suggested that the formation of the oriented structure was also independent of temperature.

In regards to effect of UHMWPE concentration (2, 3, 4, &7%) on viscosity at specific temperature such as at 140 C, and 160ºC, an increase in shear viscosity with concentration was noted at both temperatures. At 140ºC a linear decline in viscosity with increase in shear rate was noted for 2% solution. This was suggested to be indicative of limited structural change in the course of the rearrangement process, as a result of low concentration. For higher concentrations such as at 6 %, viscosity did not depend on the shear rate below the critical value of 1s^{-1} and decreased rapidly above it. Similar behaviour was noted for all concentrations at 160ºC; linear behaviour with shear rate was not observed in any samples.

Jian et al [48] a Brookfield viscometer to study the shear viscosity of UHMWPE / decalin solutions at various temperatures. The experiments were conducted for varying concentrations of UHMWPE at temperatures between 80-190°C. They determined that, a particular temperature, the shear viscosities of gels exhibited a consistent increase with rising concentration above 80°C. Additionally, it was observed that shear viscosity exhibited a modest increase with increasing temperature, particularly at temperatures below 110°C. At temperatures exceeding 110°C, the shear viscosities exhibited a pronounced increase with rising temperatures, attaining a maximum within the range of 120°C to 140°C. The maximum solution viscosity temperature (T_{maxv}) rose from approximately 120°C to 140°C with the increase in solution concentrations from 7 to 18kg/m3. Subsequently, the gel shear viscosities decreased notably when the temperatures exceeded their respective T_{maxv}.

It was suggested that at low temperatures(below 110˚C) only a fraction of the crystals were melted. In the solutions, low interpenetrating mobility resulted in a gel network with loose entanglements. As result a slight increase in shear viscosity was seen as temperatures rose.

They suggested that, in the solutions at temperatures higher than 120°C but not above 140°C, a sizable amount crystals melt, giving UHMWPE chains sufficient interpenetrating mobility to the formation of a stable interconnected gel network. As a consequence, the gel solutions demonstrated maximum shear viscosity at temperatures between 120°C and 140°C.

Furthermore, the reduction in shear viscosity above T_{maxv} was attributed to the total melting of crystals, subsequent partial solvation of UHMWPE molecules, in addition to potential thermal degradation. From the spinning experiments conducted using the same solutions, it was noted that

temperatures lower than120 °C and concentrations lower than 4kg/m^3 were found to be unsuitable for stable spinning. An optimum spinning processing window was suggested based on the viscosity data and spinning experiments. The viscosity window for spinning corresponding to the temperature range 120 to 180°C was 1000 to 1,000,000 cP

Yang and Chen [49] used Brookfield viscometer to study the shear viscosity of UHMWPE / decalin solutions (0.5-3%) solutions in the temperature range 125-165ºCin the shear rate range of approximately 0.1 to 100s^{-1}. Additionally, the impact of introducing 1% aluminium stearate on the shear viscosity of UHMWPE/decalin solutions was investigated. They found that the solutions demonstrated a shear thinning response across the range of shear rates that were measured..In addition they noted that for 2% solution, viscosity could be described with a power law equation $\eta=m\gamma^{n-1}$where m and n are the consistency and flow index respectively .n did not vary with temperature indicating that the non newtonian behavior did not vary much with temperature. The flow index decreased with increase in concentration, tending to level off at concentrations higher than 1.5%. indicating that solution became more non-Newtonian at higher concentrations.

The effect of temperature on viscosity could be characterized by the Arrhenius–Frenkel–Eyring (AFE) equation $m = m_o\exp(\Delta E/RT)$, where ΔE& R are the activation energy of flow, and gas content respectively. The consistency, designated as m, was defined as the viscosity at a shear rate of 1s^{-1}. A master curve was generated for all concentrations using the relation $\eta' = \eta m_s/m_T$ where m_s & m_T are the m at the reference temperature and temperature T respectively. From the parallel lines noted for master curves for all concentration, it was surmised that the activation was not strongly dependent on the concentration.

The concentration dependence of viscosity could also be fitted with a equation $m= kc^a \exp(\Delta E/RT)$, where c is the concentration; α & k are constants. A master curve was generated for both UHMWPE solutions with and without aluminium stearate by plotting m versus the shifted reciprocal of temperature T' obtained using the relation $1/T'=1/T+(R\alpha/\Delta E)ln(c)$. It was noted that the two master curves intersected at T'=300K , and the addition of1% sodium stearate lowered the viscosity of low concentration solutions, while increased the viscosity in high concentrated solutions. The activation energy was observed to be greater in the solution containing stearate than in those in which stearate was absentwhich was attributed to sodium stearate promoting greater polymer- polymer interaction while reducing polymer - solvent interaction.

Ohta and co-workers [50] conducted steady shear viscosity using cone and plate in the shear rate range from 0.5-100$s^{-1}$for 3%& 5% UHMWPE/paraffin wax solution at 160°C. They found the solutions exhibited shear thinning behaviour over the entire range. At high shear rate, they also noted an abnormal brief increase in viscosity which was followed by the solution becoming expelled from the cone & plate gap resulting in a decrease in the shear stress. The nonlinear rheological behaviour was attributed to the accumulated strain during steady shear mode.

Thus from the available literature it can be noted that the viscosity of UHMWPE solutions depend on the selection of solvents. Shear thinning behaviour is seen in UHMWPE solutions in decalin, paraffin wax, paraffin oil & camphene. In case of one study UHMWPE/ decalin solutions[47], shear viscosity was found to be independent of shear rate at low shear rate. This behaviour was found to depend on temperature and UHMWPE content. Additionally, it is important to highlight that the melting of the crystalline macrostructure, along with the resulting entanglements, significantly influenced the viscosity of UHMWPE/decalin solutions at a particular temperature. The shear viscosity of UHMWPE/decalin became non Newtonian with increase in concentration, in addition, the activation energy was found to be independent of UHMWPE concentration[49].

4.1.2. Evaluation of gel point using rotational testing

The viscoelastic nature of UHMWPE/ solvent systems solution undergo significant changes throughout the gel formation process during cooling [47]. Initially, the system behaves like a liquid until it reaches the gel point, when it transitions to a gel. As the gel cools below the gel point, phase separation occurs, removing the excess solvent.[47].

Chiu and Wang [47]determined the gel point of for UHMWPE/ decalin solutions(2-7%) during cooling using a constant stress of 100Pa and controlled cooling of 2°C/min. The authors identified two regions; a high temperature shear thinning region where the viscosity gradually decreased with decrease in temperature followed by a low temperature region where an abrupt increase in the viscosity was noted with decrease in temperature. The drop in viscosity with the reduction in temperature in high temperature region was linked to possible orientation effect due to applied stress. The gel point determined through this process displayed a linear increase with concentration, i.e. it changed from 102 to 108°C as the concentration changed from 2-7%. This was attributed to the increase in entanglement density with the increase in polymer concentration.

However in another experiments reported by the same authors [51]for UHMWPE/decalin solutions (concentrations: 2-7%), the viscosity displayed a continuous increase with decrease in temperature. They determined that the gel point rises from 90.3 to 99.3°C as the UHMWPE content changes from 2 to 7%. The gel point was constant shear stress of 100 Pa., the cooling rate was not specified. The increase in the gel point with UHMWPE content was cross verified by assessing the gel melting temperature through Differential Scanning Calorimetry (DSC). Although the values were lower, a similar trend was noted.

Jen et al. [28]using Brookfield viscometer found the gel points of UHMWPE with decalin, paraffin oil and camphene solvents to be 76.6ºC,102.5ºC and 82.2ºC, respectively and suggested that the high gelation temperature made paraffin oil less desirable for processing.

The gel point determined using steady shear in the reported studies were found to significantly depend on the UHMWPE content in solution. Although gel points determined depended on the mode of measurement for e.g. rheometer or DSC, similar trends were trends were obtained in terms of variation of gel point with polymer concentration . Higher gel points observed for UHMWPE in paraffin as compared to decalin and camphene. In regards to the differences noted shear viscosity trend with temperature in the high temperature region for UHMWPE/ Decalin, in [47]&[51]. It may due to difference in thermal and shear history leading to structural changes. The extent of entanglements in solutions can be significantly influenced by both the thermal as well the shear history, thereby influencing the flow behaviour during the cooling as will be detailed in Section 4.3.

4.1.1.3 Effect on shear stress

There has been limited study on the effect on shear stress of UHMWPE solutions. Chiu and Wang [47] studied the influence of temperature, shear rate and UHMWPE content, and on the shear stress of UHMWPE/ decalin solutions in rotation mode using parallel plate geometry. The shear rate covered was between 0-10 s^{-1}. In regards to relationship between shear stress and shear rate for different temperature(100-160°C), for 6 % UHMWPE solutions , shear stress was found to gradually increase with shear rate at 100ºC.At 120°C, and above a peak in the shear stress versus shear rate curve was noted at $1s^{-1}$ which was linked to process of formation of orientated polymer chains. The shear stress decreased thereafter with increase in shear rate above $1s^{-1}$ which was suggested to be due to lowered resistance to flow as the chains were fully oriented.

In regards to dependence of shear stress upon shear rate for different UHMWPE concentration(2, 4, 6, 7%) and at different temperatures(140°C, 160°C); the shear stress also was found to increase with increase in UHMWPE concentration at both 140°C and 160°C.which was considered to be an indication that shear stress needed for deformation increased with concentration. For all samples tested at 160ºC, a critical value of the shear stress with noted with rise in shear rate for all compositions. For samples tested 140ºC, 2% UHMWPE/ decalin solution exhibited a gradual increase in shear stress corresponding to the rise in shear rate. For 4-7% UMWPE/ decalin solutions, a critical value of shear stress with respect to shear rate was observed. The value of the shear rate corresponding to the critical shear stress at both temperatures ranged between $1\text{-}10s^{-1}$ and followed no particular trend.

Thus studying shear stress as function of shear rate can be a good probe of development of oriented structure or structural development in UHMWPE, it can be used to predict instability in the flow behaviour as was noted in steady shear experiments conducted by Ohta and coworkers [50] mentioned previously which have implications for gel spinning.

4.2. Capillary Rheology

Capillary rheology can be an important tool for measuring the flow behaviour of materials at shear rates beyond the range of the rotational rheometer, prior to testing their applicability at a commercial scale.[58].

Zhang et. al [52] compared the rheological behaviour of dilute solutions of 5% UHMWPE in decalin and paraffin oil using capillary rheology at 150 , 170 & 185 ºC. The shear rate covered ranged from approximately 1-2000 s^{-1}. They found that that UHMWPE/decalin solutions exhibited higher viscosity than UHMWPE / paraffin oil solutions especially temperature below 170ºC and low shear rates, approximately below $100s^{-1}$ at 170°C. At high temperatures, the trend is reversed. Both solutions exhibited shear thinning behaviour. In addition, UHMWPE/decalin solution displayed higher activation energy than UHMWPE/paraffin oil, where the activation energy was calculated using Arrhenius relation. The authors suggested that the higher activation energy resulted in lower entanglement density at 185°C and that was responsible for the lower viscosity for UHMWPE/ decalin as compared to UHMWPE/paraffin oil .

They also noted that the activation energy of the solutions depended on both shear stress and shear rate which was different than other polymers such as polyethylene terephthalate.

Moreover, they observed a discontinuity in η *vs.* $\dot{\gamma}^{1/2}$ curve for 5% UHMWPE/ decalin solution at approximately 70 s^{-1} shear rate, which was deemed indicative of a significant change in the nature of the entanglements within the UHMWPE solution.

Another study [53]investigated the influence of addition of 1% aluminium stearate upon the rheological behaviour exhibited by5% UHMWPE/paraffin oil solutions at 170°C. The study was conducted using a specially designed instrument containing a 3 litre vessel, which was attached to a one hole spinneret of different geometries by means of a tube .

It was found that both the 5% UHMWPE solutions i.e. with and without inclusion of aluminium stearate exhibited shear thinning behaviour within the approximate shear rate interval of $1\text{-}1000s^{-1}$; the incorporation of aluminium stearate resulted in a reduction in shear viscosity. The impact of the geometric dimensions of spinneret orifices, including length-to-diameter ratio (L/D) and entrance angle of the capillary was also investigated for a 5% UMWPE/paraffin oil solution with aluminium stearate. The length-to-diameter ratio (L/D) ranged from 2 to 15, while the entrance angle spanned a range of 6 to 60. From the pressure versus mass flow curves, for different L/D or entrance angle at 170°C,it was determined that increasing L/D ratio or reducing the entrance angle of capillary enhances viscous flow resistance. An analysis of the curves of the first normal stress difference (σ_{11}-σ_{22}) in relation to shear rate (ranging approximately between 5 and 20 s^{-1}), revealed an increase in σ_{11}-σ_{22} as the shear rate increased. The values of pressure recorded at the entry and exit of the capillary were used to determine the Bagley-end correction '*e*,' which was subsequently evaluated

in relation to shear rate. The authors noted that the value of '*e'* increases with shear rate(range approximately 5-20s^{-1}). The authors remarked that as the Bagley-end correction '*e*' and first normal stress difference are indicative of the elastic behaviour, the results reveal that the elastic contribution to spinning solutions in flow is quite pronounced, even at shear rates lower than 20 s^{-1}.

Ohta et al [50]studied the steady shear viscosity of UHMWPE/ paraffin wax solutions (3, 5%) using a capillary type viscometer at 160ºC. Three spinnerets with capillary lengths of 10, 20 and 40 mm. and with equal diameters of 1 mm but different L/D i.e. 10, 20and 40 were carried out. The Bagley plot[59] was utilized to correct the effects of capillary length, while the Rabinowitsch equation[60] was utilized to adjust the shear rate. The shear rate covered ranged was approximately 10-1000s^{-1}. They found that the viscosity increased with UHMWPE content; in addition, the solutions exhibited shear thinning throughout the measuring range.

Fang et al [21] determined the shear viscosity of 2 % UHMWPE / PB solution at 150ºC within the approximate shear rate range of 0-1000s^{-1}. The solution displayed significant shear thinning effects, which could be described by a power law relation .

From the capillary rheology studies, UHMWPE solutions exhibit similar shear thinning behaviour as was noted in the steady state shear studies using Brookfield viscometers and rotational rheometers. The shear viscosity UHMWPE/ decalin solution exhibited higher solution viscosity as compared to compared to UHMWPE/ paraffin oil at low temperatures, as was noted in Brookfield viscometry studies. However, at higher temperatures, this trend was reversed indicating that temperature dependence of shear viscosity must also be taken in to account during selection of selection of solvents for spinning. The spinneret geometry was found to affect the flow behaviour of UHMWPE solutions. The high degree of entanglements resulting from the large molecular weight results in significant elastic effects even at low shear rates[53] which have implication in gel spinning.

4.3. Dynamic shear rheology

Dynamic shear rheology can be used to measure the viscoelastic properties of UHMWPE solutions under oscillatory shear conditions and is an important tool in characterizing its stability during gel spinning.

4.3.1 Complex viscosity of dilute solutions

Complex viscosity (|η*|), obtained via oscillation testing, is a vital parameter that characterizes the flow behaviour of UHMWPE solutions, much like steady shear viscosity. Shi et al[20] determined the complex viscosity of 1% w/v UHMWPE solutions in decalin as well as paraffin oil while cooling it between 150 and 70°C at a frequency of 1 rad/s. They noted that, at temperatures less than 120°C, the viscosity of the solution was much greater for decalin than for paraffin.

Lee et al [54] studied the dynamic rheological properties of UHMWPE / decalin solutions. The complex viscosity for 2%, 6%, 10% UHMWPE/ decalin solutions were determined at three temperatures (110, 130,&150°C) from frequency sweeps using 12% strain. They found the solutions exhibit a shear thieving behaviour for the entire frequency range. The viscosity-frequency curves followed a power-law behaviour given by $\eta = A\,\dot{\gamma}^{n}$ where A, n are a constant& the power law index respectively. The power-law behaviour was noted irrespective of the temperature and UHMWPE content, with the Newtonian plateau absent at low frequencies. Viscosity increased significantly with concentration, with a tenfold increase from 2 to 6%, and then from 6 to 10% at low frequencies at 110ºC. The relationship between viscosity and temperature was represented by the Arrhenius equation $\eta = Ae^{E/RT}$. In the equation, *A, E, R*, and *T* represent a constant, the activation energy for viscous flow, the gas constant, and the absolute temperature, respectively. Linear Arrhenius plots was obtained for the 3 concentrations which was taken as an indication of absence of chain scission during testing. The activation energy increased with gel concentration which was taken as an indication that the temperature dependence of viscosity increased with gel concentration. A master curves of viscosity function versus frequency was generated for all three concentrations from the Arrhenius equation using the relation $\alpha_T = \eta'/\eta'_0 = e^{E/R(1/T-1/T_o)}$ where T_o is the reference temperature, α_T is the shift factor. The curves could be superimposed on a single curve with some deviation noted at high frequencies for the 10% UHMWPE /decalin solution.

A heating/cooling temperature sweep of 2% UHMWPE solution from 110°C to 150°C was also performed at a rate of 2°C/min and at a fixed frequency of 1 rad/s. It was determined the viscosity initially decreased during heating from 100-130ºC, which linked to lowering of the viscosity of the "medium" containing dispersed crystals; it kept constant from 130 to150 ºC which was attributed to formation of extensive physical crosslinks due to meeting of crystals. During cooling step the viscosity remained unchanged from 150 to 120ºC, where its viscosity was similar to heating step. It subsequently increased dramatically after 120°Cas a consequence of crystallization along with phase separation. For higher concentration(6%, 10%) the temperature hysteresis increased, i.e. the viscosity on cooling was lesser than on heating in the melt state which was attributed to attributed to persistence of oriented structures formed during heating.

Ohta and coworkers[50]determined the complex viscosity for 1, 3, 5 %UHMWPE/ paraffin wax solutions at 160°C in the frequency range 0.634 to 10.5 rad/sec. The viscosity increased with polymer concentration. They also noted that the samples exhibited shear thinning behaviour over the measuring range with a small kink in data which shifted to lower frequency with increase in UHMWPE concentration. The power law index (n) of viscosity was determined from a linear fit of the dynamic viscosity as a function of shear rate. The decrease in n values with concentration was considered indicative that the solution exhibits greater non-Newtonian behaviour. The 3 %and 5% viscosity results were combined

with results from steady shear and creep measurements using cone plate geometry, and the viscosity results from the capillary rheology studies. The viscosity data for the two concentrations from the measurements could be plotted on single curves corresponding to each concentration. It was suggested that as the shear viscosity data obtained under the steady shear almost coincided those obtained by the dynamic measurements, it indicates validity of the Cox Merz rule [61] in this system.

Thus complex viscosity, as in case of steady shear viscosity, was found to depend on polymer concentration, temperature and frequency of measurement and selection of solvent .As was noted in the steady shear experiments, the UHMWPE / decalin viscosity was found to higher than the UHMWPE/paraffin oil solution at temperatures less than 120ºC. The complex viscosity dependence on frequency of UHMWPE / decalin, paraffin systems could be fitted with a power law relation. The activation energy of UHMWPE / decalin [54]was found to depend on the concentration of UHMWPE unlike report in [49] for UHMWPE / decalin system, where from the Arrhenius plots it was surmised that the activation energy was independent of polymer concentration. However, it should be pointed out that the study was performed for lower concentration range of UHMWPE(0.5-3%), in addition, activation energy values were not presented. A master curve could be generated for the viscosity function with frequency for the UHMWPE / decalin system [54]. The physical crosslinks formed by melting of crystals play a key role in the temperature dependence of complex viscosity.

4.3.2 Evaluation of gel point using oscillation testing

There have been some reports on evaluation of gel points of UHMWPE solutions using oscillation testing. Fang and co-workers [55] for UHMWPE/polybutene (PB) solutions (2,4&6%) determined the gel point using oscillation testing. The complex viscosity was noted as a function of temperature during cooling and was utilized to evaluate the gel point. The gel point generally increased with polymer concentration, the specific values were not presented. The results were cross verified by noting the melting behaviour of gel using DSC which showed an increase in melting temperature from 114.5, 116, 117.5 ºC for 2, 4 & 6 % solutions respectively. For a particular concentration(4%),it was observed that the gel point exhibited an increase alongside the molecular weight of the solvent,, the authors stated that a similar trend was noted for the other concentrations. In another paper, the authors [21]cross verified the gel point obtained from oscillation testing during cooling from 150 to 100ºC for 2% UHMWPE/ PB solution with the crystallization temperature obtained from DSC.

Thus as in the case of rotational testing, gel point was found to be dependence on the concentration of UHMWPE was confirmed. Moreover, the molecular weight of solvent was also found to influence the gel point, thus it is an additional factor to consider when selecting solvents for spinning.

4.3.3 Viscoelastic property of UHMWPE solutions using oscillation testing

The measurement viscoelastic parameters, such as storage and loss modulus, can play an important aid in optimizing the spinning parameters as the fibre formation process is significant influenced by the viscoelastic properties of the solution.

Fang et al[21] conducted an oscillation frequency sweep of a 2% UHMWPE/PB solution. The experiments were carried out at a fixed strain of 1% and 5%, keeping the temperature at 150ºC. The found that the both storage and loss modulus increased with frequency. It was observed that at frequencies lower than 1 Hz, the loss modulus (G″) is greater than the storage modulus (G′), indicating a dominance of viscous characteristics in the solution. They asserted that the UHMWPE solution should be suitable for spinning in this frequency region by curtailing elasticity, thus allowing for the development of high-strength fibers. Furthermore, they indicated that in the high-frequency region (greater than 1 Hz), where the storage modulus exceeds the loss modulus, elastic effects prevail. Consequently, spinning in this domain may lead to significant die swell, potentially resulting in fibers with increased defects. In regards to variation with % strain, G´, G″ and viscosity were higher for sweeps conducted at 1 %, than 5% strain .

In another paper, Fang et al [55]investigated the viscoelasticity of the 2% UHMWPE/ Polybutene(PB) and compared it with UHMWPE/paraffin oil solution using frequency sweeps. They reported that, at a concentration of 2% UHMWPE and using solvents of comparable molecular weight, the spin dope containing PB showed enhanced G', G", and |η*|, at 150°C. This suggests that, under equivalent extrusion conditions, the UHMWPE/PB spin dope is more capable of yielding continuous filaments, and that further decreasing the concentration may improve the strength of the resulting fibre. For UHMWPE/paraffin, (*G′*), was higher than the *G″* over the entire frequency range which would suggest that elastic nature was dominant in the frequency range. For UHMWPE/ Polybutene(PB) similar behaviour could be seen; In addition, a crossover point could be seen at the beginning of the frequency sweep. In the both cases the modulus increased with increase in frequency.

Chiu and Wang [47]studied the viscoelastic properties UHMWPE/decalin system. In the experiment, the viscoelastic properties of UHMWPE / decalin system at UHMWPE concentrations of 2%, 4%, 6%, and 7%, conducted at temperatures of 120°C, 140°C, and 160°C. Strain sweeps were performed from 1 to 100% and frequency at 2 Hz.

During strain sweep of 6% UHMWPE/ decalin system at different temperature, it was observed G' exhibits a plateau region at low strain levels. Subsequently, a significant decline was noted as strain increased, particularly at a critical point of approximately 45%.

They proposed that the molecular chains which orient themselves with increase in strain rates at low strain rates, form physical crosslink interaction force at the critical strain value. When the strain is increased beyond this point, the polymer chains will be drawn out of the entangled area and start to slide. As a result, the crystalline region starts to break down, which causes G' to drop dramatically.

Furthermore, it was noted that the G' values achieved during strain sweeps at 140°C were greater than those obtained at 120°C and 160°C. They attributed it to the gel forming a shish kebab structure at the temperature due to the stress-induced crystallization. G' at 120°C was lower than at 160°C. The authors proposed that the incomplete formation of crystals at 120°C resulted in a low G'. Moreover, they suggested that at 160°C, which is higher than the crystals' melting point of 147°C, the crystal domains are destroyed, resulting in a lower G' value.

Furthermore, during the strain sweep conducted at various UHMWPE concentrations at 140ºC, it was noted that as the content of UHMWPE increased, the critical strain value shifted to higher ranges. Additionally, the storage modulus (G') exhibited an increase with rising UHMWPE content. The authors attributed the increase in the critical point to presence of a greater number of entangled crystals at higher concentrations which cannot be easily pulled out from the entangled region thus contribute to increase in the critical point.

Chung &Zachariades[38] conducted dynamic frequency and temperature sweep experiments for 2-5% UHMWPE/ paraffin oil system (referred as pseudogels). During the frequency sweep on4% UHMWPE / paraffin oil gels at 25°C, it was noted that the G' and G" were frequency dependent. G' exhibited a decline in the low frequency range, subsequently reaching a plateau in the intermediate frequency range, before experiencing a rapid increase in the high frequency range. G" exhibited similar trend with respect to frequency In addition the modulus also varied as the number of consecutive runs .i.e. the G' and G" exhibited lower values at from second run onwards, with loss modulus exhibiting lower shear sensitivity. This shear history dependence of the viscoelastic properties was less pronounced at 0°C which was linked to low mobility of the chains. The effect of entanglements with short life times (from section 2) was linked to the initial decrease in G' at low frequency and overall decrease in G' in subsequent scans. The plateau region was associated with the presence of crystals and the confined entanglements in among them, which collectively exist in a state of pseudo-equilibrium. This state depended on the gel concentration, temperature, frequency. and the shear history. The authors reported that similar behaviour was noted for the other concentrations, data was not shown.

Moreover, it was observed that the dynamic shear modulus of 3% UHMWPE/paraffin oil gels exhibited a hysteresis response when subjected to thermal cycling from -20°C to 100°C. It was observed that during the heating cycle ranging from -20 to 110°C, the storage modulus (G') showed a significant decrease as the temperature increased to -10°C. The authors indicated that this finding is contrary to the expected behaviour of cross-linked gel systems, which typically exhibit a constant G'. The observed behaviour was linked to a rise in the mobility of temporary entanglements. As the temperature beyond 60ºC, G' further decreases sharply due to deformation of crystals resulting in reduction of trapped entanglements. The authors assert that this process results in a reduction of the overall level of entanglements by the conclusion of the heating cycle.

During cooling G' initially exhibited similar value as the heating cycle. Upon further cooling, G' values exhibited a rapid decline, ultimately reaching a minimum and increasing thereafter reaching a modulus value much lower than what was noted at the beginning of the heating cycle at -20°C.

The initial decrease was once again associated with the disentanglement effect observed at elevated temperatures, where the crystals were deformable. The authors noted that this behaviour is contrary to most polymer systems where storage modulus exhibits higher values during cooling due to decreased chain mobility, it was suggested that the disentanglement effect offset the expected increase in G' with cooling. As the temperature was lowered below 40°C, it was suggested that the reduced deformability of the crystals, would lead to the entrapment of a greater portion of entanglements thus contribute to resisting the decline of storage modulus. In addition, it was proposed that the reduction of temperature to -20°C led to a significant decrease in chain mobility, which subsequently resulted in an increase in the G'. The final G' value measured during the cooling phase did not attain the initial value noted during the heating phase. This discrepancy was attributed to the permanent loss of some confined entanglements throughout the thermal cycle, leading to an irreversible reduction in G'.

They also observed that the hysteresis behaviour of the G" was less pronounced. Additionally, the researchers reported that during the temperature sweep ranging from -20°C to 100°C, there was a notable increase in the storage modulus (G') with increasing concentration. This increase was associated with a higher density of entanglements and an elevated level of crystallinity in the more concentrated solutions. In addition consistent decrease in the G' could be seen with increase in temperature which may due to increased mobility of the chains as mentioned above.

Qiao et al [56]studied viscoelastic properties of UHMWPE swollen by petrolatum in 1, 4, 10% concentrations. Dynamic time sweeps were performed for 60 min at 150ºC with 10% strain. They found that G'> G" storage modulus was higher than the loss modulus without any change over time which was taken to be an indication of indicating the stability of the petrolatum. G' decreased with increasing solvent content which was considered to be an indication that the elasticity and strength of UHMWPE was reduced.

On carrying dynamic temperature sweeps in the range 140-180 ºC , the authors reported that the modulus has a weak

dependence on temperature , the data was not presented. The authors concluded that UHMWPE flow properties have a weak dependence on temperature.

For the three concentrations, dynamic strain sweeps were performed across a strain range of 0.1% to 100%, with the frequency held constant at 10 rad/s. They found that with the increase in strain, G', after initially remaining constant, decreases after a critical value which taken to be an indication of breakdown of the macrostructure at the non-linear strain. G' also decreased with the rise in petrolatum content which was attributed to the increase in the degree of disentanglement with petrolatum content thus promoting reduced elasticity.

Furthermore, the storage modulus decrement was determined using G'_0 i.e. the plateau storage modulus in the linear strain region and G'_y i.e the decreased storage modulus at a certain nonlinear strain using the relation, $(G'_0 - G'_y) / G'_0$. As the nonlinear strain increased and the petrolatum content decreased, there was a corresponding rise in the values of storage modulus decrement. It has been suggested that reducing the quantity of petrolatum or increasing the proportion of UHMWPE in samples could result in diminished chain flexibility. This decrease in flexibility may subsequently increase the degree of macrostructural damage, leading to elevated values of storage modulus decrement.

The authors conducted dynamic frequency sweeps ranging from 100 rad/s to 0.1 rad/s at a temperature of 150ºC for the three concentrations. It was noted that both G' and G" decrease with the increase in petrolatum content as was noted in dynamic time and strain sweeps. Both G' and G" showed an increase with increasing frequency, with G" showing less of a frequency dependence at high UHMWPE content. At lower frequencies, G" was found to be greater than G'; however, as frequency continues to increase, a crossover point is observed between G' and G". The crossover point ($G' = G''$) which was denoted as the gel point signified the transition from viscous to elastic behaviour. The disentanglement time, denoted as t_d , and derived from the inverse of crossover frequency, ω_c, was associated with the relaxation time of a segment situated within two entanglement points. The data revealed that as the levels of petrolatum increased, there was a corresponding decrease in relaxation time and a lower crossover point modulus. Consequently, it was concluded that the addition of petrolatum caused improved chain disentanglements, enabling the segments to relax more quickly. It was suggested that the process led to the formation of more loosely held chain networks, which in turn resulted in a decrease in the elastic modulus.

Ohta and coworkers[50] studied the frequency dependence of 1,3,&5 % UHWMPE paraffin wax dilute solutions at 160ºC. The frequency range was tested was between 0.634 to 10.5 rad/sec with 5% strain. They found that G' and G'' increase with frequency, and also increased with UHMWPE content. While the authors did not elaborate on the trend, it is evident that the 1% and 3% solution curves showed a higher G" compared to the G' at the low values of frequency, with a crossover point emerging as frequency increased. This crossover point was observed to move to lower values of frequency with the rise in UHMWPE content. For the 5% solution, the crossover point is positioned very close to the onset of the frequency sweep, making it difficult to determine accurately.

In addition, the authors noted the linear Han plots of log G"versus G' shifted with increase concentration. As the Han plot generally do not show and concentration or temperature dependence in miscible or compatible systems; however they show deviation from linear behaviour due to polydispersity, it was suggested that the shift in Han plot with concentration was due to wider polydispersity by considering paraffin as low molecular tails of polyethylene. It addition they noted that the plots exhibited a slope greater than ½ which was also taken as evidence of effect of polydispersity as was reported by Han & Kim[62].

From the results, it can be noted that the viscoelastic properties such G' and G"of the UHMWPE solutions depend selection of solvent and the concentration of polymers. It can also depend on the, strain rate, frequency, as well as the temperature of measurement. While in regards to frequency, G' in particular tended to continuous increase with frequency at higher temperatures when the sample are in melt state as was noted for the UHMWPE/ PB [21, 55], petrolatum[56], and paraffin wax systems[50]. At lower temperatures, the entanglements confined by crystals can cause G' values to remain constant for a particular frequency range, as was noted for the UHMWPE/ paraffin oil system at 0 and 25ºC [38]. The viscoelastic properties are also shear history dependent due to the effect of trapped entanglements between crystalline regions. The dependence of the modulus on the shear history can be less pronounced lower temperatures. G' was more sensitive to the shear history than the G". In regards to effect strain rate it can be noted that for UHMWPE /decalin [47], paraffin wax [50] & petrolatum systems [56],the G' significantly reduces with the rise in strain above a critical value due to breakdown of the entanglement network.

It can be noted that the G" was higher that G' at low frequency for many systems, this trend was revised at higher frequencies, with crossover point exhibiting a dependence on concentration of UHMWPE.

In regards to solvents, it can be noted that the UHMWPE/ PB exhibited higher G' and G" as compared to UHMWPE / paraffin oil which may the result of higher degree of entanglements. It also important to note that during temperature sweeps while G' of UHMWPE/ petrolatum system shows weak dependence with temperature, G' of UHMWPE/decalin gels decrease with increase in temperature[38]. The difference may be due to differences in degree of disentanglement by the solvent. In the UHMWPE/ petrolatum system, chains being more tightly held similar to a covalently bonded gel network system.

4.4. Creep recovery tests

The creep recovery test is an important tool to measure response to applied stress over time. Ohta and coworkers[50] carried out creep recovery experiments for 3 & 5 % UHMWPE / paraffin wax at 160ºC. The applied creep stress was varied from 0.5 to 30 Pa.

While the steady shear viscosity was obtained from the linear fit from the strain time curves. The creep compliance $J_e(\sigma)$ was calculated from the relation: $J_e(\sigma)=S_r/\sigma$ where S_r is the recoverable strain and σ is creep stress.

It was noted that steady shear viscosity showed shear shinning behaviour in the shear rate window of 10^{-4} to $10^{-2}s^{-1}$ i.e. the Newtonian plateau was missing even at low shear rates. The shear viscosity also increased with UHMWPE concentration.

The authors also determined that steady shear viscosity was related to the concentration through the relation $\eta_{(\gamma)} aC^{a_{(\gamma)}}$ where α, *C* are the power law index and the concentration respectively. Using the shear viscosity values of the 3 & 5% solution, α was determined versus shear rate. Upon plotting α against the shear rate, it was determined that the value of α lies between 3.4 and 3.5, as the shear rate tends toward zero.

They also studied the creep stress dependence on $J_e(\sigma)$. The creep compliance for each concentration was almost constant for the creep stress range with the 3% UHMWPE./ paraffin wax solution displayed higher values of $J_e(\sigma)$ than the 5 % solution.

By interpolation of σ= 0, the zero shear creep compliance J_e^0 of 3 % & 5% UHMWPE/ paraffin wax solution was determined to be 10^{-1} Pa^{-1} and 3x 10^{-2} Pa^{-1} respectively. After using the relation of the concentration dependence of creep compliance $J_e^0 = J_e^{00}\varphi^{-m}$. The J_e^{00}, the creep compliance of non-dense system of the UHMWPE, was determined to be 10^{-5} Pa^{-1} which was close to an earlier report value of 10^{-5} Pa^{-1} for monodisperse high molecular weight polystyrene[63]. The *m* value was determined to be 2.4±0.2. It was suggested that the large values and recoverable strain of UHMWPE solution was a result of extremely large molecular weight between entanglement points (M_e).

5. Conclusions

From the available literature, it appears that among the commercially utilized solvents in gel spinning i.e., decalin and paraffin oil, decalin exhibits higher solvent viscosity at low temperatures below 170°C which suggests that UHMWPE is more readily disentangled by paraffin oil. However, as UHMWPE solutions in decalin have a greater temperature dependence than those in paraffin oil, the trend is reversed at higher temperatures.

In experiment conducted by [21],it was observed that during the crystallization of UHMWPE gels containing decalin, solvent was expelled from the gels. Conversely, the gels with paraffin oil exhibited no substantial solvent loss, while those with PB experienced a moderate loss of solvent. It was attributed that to the fact that paraffin oil exhibits greatest affinity with polyethylene due to their similar alkyl main chains although the chain lengths differ[20].The authors also noted that high level of interaction would make the process of extraction of solvent more difficult during gel spinning process.

The gel point observed during cooling under both rotation and oscillations testing were found to depend on the concentration of UHMWPE. The type of solvent used for the disentanglement process also affected the gel point. Gel points were higher in case of paraffin oil than decalin and camphene.

A broad viscosity window in the range of 1000 to 1000000 cP corresponding to the 120°C to 180°C was reported to suitable for gel spinning for the UHMWPE/ decalin system.

It was determined that both the steady shear and dynamic shear viscosity are dependent upon the shear rate and the frequency at which measurements are taken.. In regards to UHMWPE/PE-Wax [50] system both steady shear and complex viscosity appears to coincide with which would suggest that Cox- Merz rule may be valid for the system.

In general, shear thinning behaviour was noted in both steady state and dynamic shear for UHMWPE systems especially at high shear rate and could be modelled using power law equation [49, 50, 54], The temperature dependence of viscosity could be modelled with Arrhenius equation [49, 52, 54]. The activation energy was found to depended on the concentration of UHMWPE except in[49].

Aside from the findings presented in [47] regarding UHMWPE/decalin solutions, the majority of cases exhibited a lack of a Newtonian plateau at low shear rates. The lack of a Newtonian plateau at low shear rates would render the startup process for gel processing highly challenging. [54]**.**The presence physical crosslink between crystals was found to greatly affect the viscosity of UHMWPE a different temperatures. The concentration dependence of shear viscosity could be described by power law type equation for UHMWPE / decalin [49] and UHMWPE / paraffin wax system[50]

Capillary rheology studies have shown that changes in spinneret geometry, including enhancing the length-to-diameter ratio (L/D) or lowering the entrance angle of the capillary, promotes to a greater resistance to viscous flow. The viscoelastic properties such as storage and loss modulus of UHMWPE / solvent systems determined under oscillation tests depended on the type of solvent. polymer content; shear history; temperature and frequency of measurement. The presence of entanglements between the crystalline regions also played a significant role in the viscoelastic behaviour of UHMWPE in terms of frequency and temperature.

6. Implications for gel spinning:

From the reports it can be surmised that the use of capillary rheology studies remains a useful tool in optimizing the processing parameters due to the fact that the shear rates that are measured in capillary rheology are closer to the shear

rates observed in spinning. Miscibility of solvent with the polymer remains important parameter tor determining the level of disentanglement as well as the ease of extraction of solvent from fibres. Measurement of viscoelastic properties such as storage and loss modulus through parallel plate rheology also play a guide in diagnosing issues such as non-formation of continuous filaments. In this regard, there are reports where the dynamic rheological properties have been used to predict the melt spinnability of polymers[64], and PAN/ CNT systems[65]using experimental spinning data. However, there have been no reports which validate the predications made in viscoelastic property studies with experimental spinning behaviour for UHMWPE. It may also be due to the complex rheological behaviours which occur during spinning and remains a challenge for the future.

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