

# Effect of TEOS on the rheological properties of polyvinylidene fluoride and poly(vinylidene fluoride-co-hexafluoropropylene)

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**Abstract:** The influence of TEOS on the rheological properties of PVDF and poly(vinylidene fluoride-co-hexafluoropropylene) was investigated. The addition of TEOS to low molecular weight PVDF results in pseudoplastic behavior. The exception is PVDF containing 5 wt%. TEOS, which shows dilation behavior. Similar behavior has high molecular weight PVDF with the addition of 2 wt.% TEOS and low molecular weight copolymer with and without TEOS. The influence of temperature on the viscosity and activation energy of the tested PVDF solutions and the influence of TEOS on the average molecular weight were also examined.

**Keywords:** TEOS, PVDF, viscosity.

## Wpływ TEOS na właściwości reologiczne polifluorku winylidenu i poli(fluorku winylidenu-co-heksafluoropropylenu)

**Streszczenie:** Zbadano wpływ TEOS na właściwości reologiczne PVDF oraz poli(fluorku winylidenu-co-heksafluoropropylenu). Dodatek TEOS do PVDF o małej masie cząsteczkowej skutkuje właściwościami pseudoplastycznymi. Wyjątek stanowi PVDF zawierający 5% mas. TEOS, który wykazuje właściwości dylatacyjne. Tak samo zachowuje się PVDF o dużej masie cząsteczkowej z dodatkiem 2% mas. TEOS oraz kopolimer o małej masie cząsteczkowej z dodatkiem i bez dodatku TEOS. Zbadano także wpływ temperatury na lepkość i energię aktywacji badanych roztworów PVDF oraz wpływ TEOS na średnią masę cząsteczkową.

**Słowa kluczowe:** TEOS, PVDF, lepkość.

Polyvinylidene fluoride (PVDF) is a non-reactive fluoropolymer that, due to its similar polarity, is soluble in dimethylformamide (DMF). This is a solvation process

that depends on the temperature and concentration of reagents [1-3]. DMF forms hydrogen bonds with the polar groups of PVDF. The number of hydrogen bonds and the strength of the interactions influence the solubility and degree of crystallinity of PVDF in DMF [4].

Two of the most popular orthosilicates are tetramethyl orthosilicate (TMOS) and tetraethyl orthosilicate (TEOS). The two silicates have a wide variety of uses, but most commonly are used as binders or crosslinking agents for inorganic materials. They are both colorless, clear liquids. According to Fig. 1, which depicts the structures of both silicates, TEOS is often preferred over TMOS since it only yields ethanol when hydrolyzed whereas TMOS releases hazardous methanol [5]. For usage as a mixing agent, tetraethyl orthosilicate (TEOS) is chosen due to its reactivity and well-known chemical characteristics [6]. Additionally, it supports increasing mechanical and thermal qualities as well as the permeability of the membrane [7, 8].

The viscosity of the polymer solution depends on many factors. These variables include the molecular weight,

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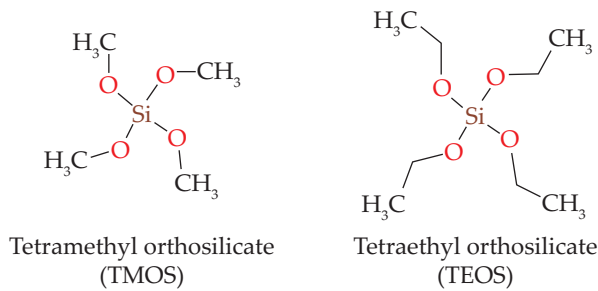
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**Fig. 1. Structure of TEOS and TMOS**

shape, and degree of hydrophilicity, as well as how the molecules of polymer molecules react with the solvents [9]. The molecular weight ( $M_w$ ) of a polymer is one of its most essential properties. Even though it is not a definite method and needs the measurement of constants, viscosimetry is one of the most efficient and straightforward ways to determine the molecular weight of polymers. Equations modeled by Mark-Houwink Sakurada as a function of average molecular weight describe the intrinsic viscosity [10]. Several methods, including fractionation of high molar mass polymers, have been developed to estimate average molar mass of high molar mass polymers via viscosity determination [11].

By analyzing the complex process of polymer flow, many physical structures can be studied, from the micro to macro scale, such as the molecular arrangement of the polymer chains, the interactions between the chains, and how they move in the solvent.

Many hypotheses have evolved throughout the years, with varied degrees of success. It is now possible to examine the mobility of polymer chains in the diluted and concentrated/melt stages, even though there are still some difficulties in the semi-dilute area of polymer solutions because of the high correlation fluctuations. In this field, interactions between polymers and their solvents are both important. Since polymer rheological processes are kinetically controlled, the influence of temperature

on flow has been studied ever since. It was discovered rapidly that the shear viscosity of a polymer fluid has a general Arrhenius-type dependency with temperature because simple shear is the simplest experimental setup to use Equation 1, De Guzmán (1913) wrote the first draft, which Eyring (1935 - 1936) later developed:

$$\eta = Ae^{\frac{E_a}{RT}} \quad (1)$$

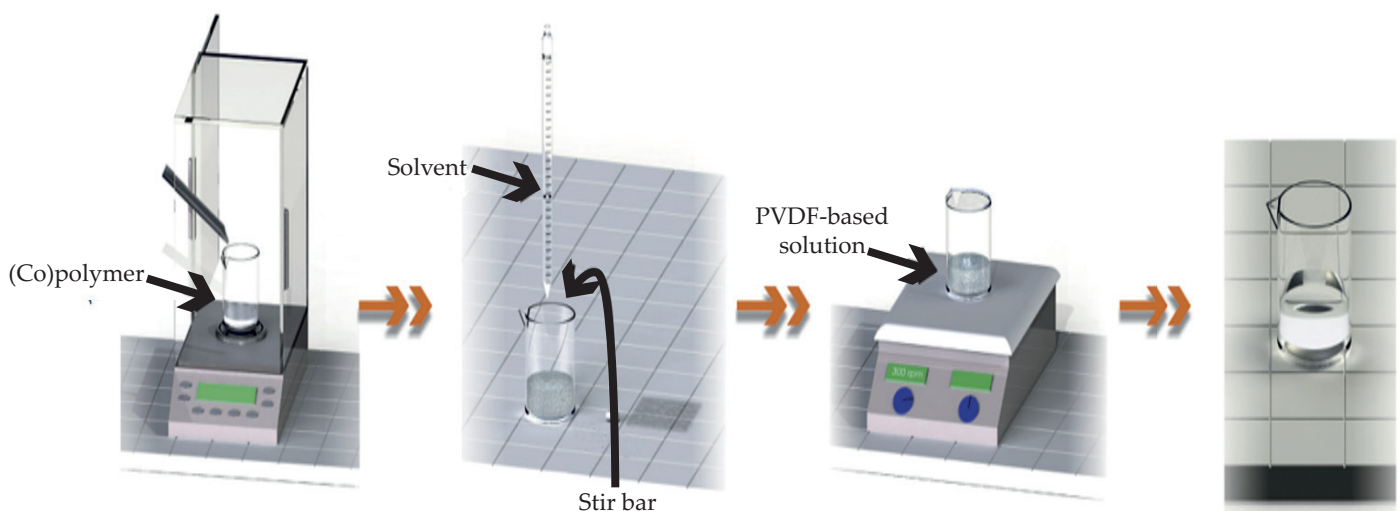
where  $\eta$  represents viscosity,  $E_a$  stands for activation energy,  $T$  for absolute temperature,  $R$  for molecular gas constant, and  $A$  for Arrhenius constant. There is no negative sign in front of  $E_a$  because the original Arrhenius equation was derived from the rate of occurrence, but this equation is derived from viscosity [12, 13]. The concept of activation energy is a fundamental aspect of chemical reactions, and it plays a crucial role in determining the reaction rate. Activation energy is the minimum amount of energy required for a chemical reaction to occur, specifically to initiate the transformation of reactants into products. In other words, it represents the energy barrier that must be overcome for the reaction to proceed [14-16].

The aim of this work was to investigate the effect of TEOS on the rheological properties and activation energy of HMWHP-PVDF, LMWHP-PVDF, HMWCP-PVDF and LMWCP-PVDF.

## EXPERIMENTAL PART

### Materials

Poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP or HMWCP-PVDF Solef<sup>®</sup>21216,  $M_w$ : 600,000 g/mol), poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP or LMWCP-PVDF Solef<sup>®</sup>21510,  $M_w$ : 300,000 g/mol), polyvinylidene fluoride (PVDF or LMWHP-PVDF Solef<sup>®</sup>6010,  $M_w$ : 352,000 g/mol), polyvinylidene fluoride PVDF or HMWHP-PVDF Solef<sup>®</sup>6020,



**Fig. 2. Scheme for obtaining a PVDF solution in DMF [18]**

**Table 1. Composition of different polymer dope solutions**

| Polymer    | PVDF wt% | TEOS wt% | DMF wt% |
|------------|----------|----------|---------|
| LMWHP-PVDF | 10       | 0        | 90      |
|            | 10       | 0.5      | 89.5    |
|            | 10       | 1        | 89      |
|            | 10       | 2        | 88      |
|            | 10       | 5        | 85      |
| HMWHP-PVDF | 10       | 0        | 90      |
|            | 10       | 0.5      | 89.5    |
|            | 10       | 1        | 89      |
|            | 10       | 2        | 88      |
|            | 10       | 5        | 85      |
| LMWCO-PVDF | 10       | 0        | 90      |
|            | 10       | 0.5      | 89.5    |
|            | 10       | 1        | 89      |
|            | 10       | 2        | 88      |
|            | 10       | 5        | 85      |
| HMWCO-PVDF | 10       | 0        | 90      |
|            | 10       | 0.5      | 89.5    |
|            | 10       | 1        | 89      |
|            | 10       | 2        | 88      |
|            | 10       | 5        | 85      |

$M_w$ : 670,000 g/mol) obtained from Solvay Specialty Polymers (Bollate, Italy) were dried for a few minutes at nearly 60°C before use to remove any moisture. Tetraethyl orthosilicate 99 wt% and 99.5 wt% pure solvent *N,N*-Dimethylformamide (DMF) was purchased from Sigma-Aldrich (Merck, Burlington, USA). PVDF and its copolymers were dissolved in dimethylformamide (DMF) by using mechanical stirring. To avoid polymer breakdown, the co-polymer was adequately dried, and dissolving temperatures were kept below 50°C. The dissolution time was 30 minutes to 3 hours without TEOS. With TEOS, the dissolution time was increased, Li-Yun *et al.* [17] also observed the same. Transparent and homogeneous solutions were obtained by following the method [18]. In Fig. 2, the first step was to weigh the PVDF, and in the second step, the solvent was added with a magnetic stir bar. In the third stage, the glass beaker was sealed, then the PVDF was dissolved using a magnetic stirrer, and in the last stage, the result was a transparent, homogeneous solution. Table 1 shows the percentages of LMWHP-PVDF, HMWHP-PVDF, LMWCP-PVDF, and HMWCP-PVDF with different concentrations of TEOS.

## Methods

### Dope solution viscosity

Viscosity was determined using a Brookfield model DV-III digital rheometer with an SC4-31 sample adapter

(Stoughton, MA, USA) at room temperature (25°C) as a function of shear rate.

### Rheological characteristic

The power law was used to analyze the rheological characteristics of the PVDF/DMF/TEOS solution, using Equation 2 [19]:

$$\tau = \kappa \dot{\gamma}^n \quad (2)$$

Where  $\kappa$  is the consistency index ( $\text{Pa} \cdot \text{s}^n$ ),  $\tau$  is the shear stress (Pa),  $\dot{\gamma}$  is the shear rate ( $\text{s}^{-1}$ ),  $n$  is the flow behavior index (dimensionless), and  $\dot{\gamma}$  is the shear rate.

### Calculation of activation energy

The activation energy of polymer solutions was calculated using Eq. 3.

$$\eta = A e^{\frac{E_a}{RT}} \quad (3)$$

where:  $\eta$  – viscosity,  $E_a$  – activation energy,  $T$  – temperature,  $R$  – molecular gas constant,  $A$  – Arrhenius constant.

## RESULTS AND DISCUSSION

### Intrinsic viscosity and average molar mass

The intrinsic viscosity was calculated using the formulas below.

Relative viscosity:

$$\eta_r = \frac{\eta}{\eta_0} \quad (4)$$

where  $\eta$  the dope solution's viscosity and  $\eta_0$  pure solvent's viscosity.

Specific viscosity:

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1 \quad (5)$$

Intrinsic viscosity:

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \quad (6)$$

Equation 4 was used to convert the apparent viscosity into relative viscosity, which was then transformed again using equation 5 to obtain the specific viscosity. The graph between  $\eta_{sp}/c$  and  $c$  was plotted to determine the intrinsic viscosity by using Equation 6. It was chosen to use concentrations of 8, 10 and 12 wt% of PVDF. The relationship between the intrinsic viscosity and the polymer's average molecular weight has been found to be direct. With increasing intrinsic viscosity, the average molecular weight grows gradually. Moreover, the molecular weight directly affects various properties of the polymer, such as its mechanical strength, flexibility,

**Table 2.** Rheological data of the investigated polymers

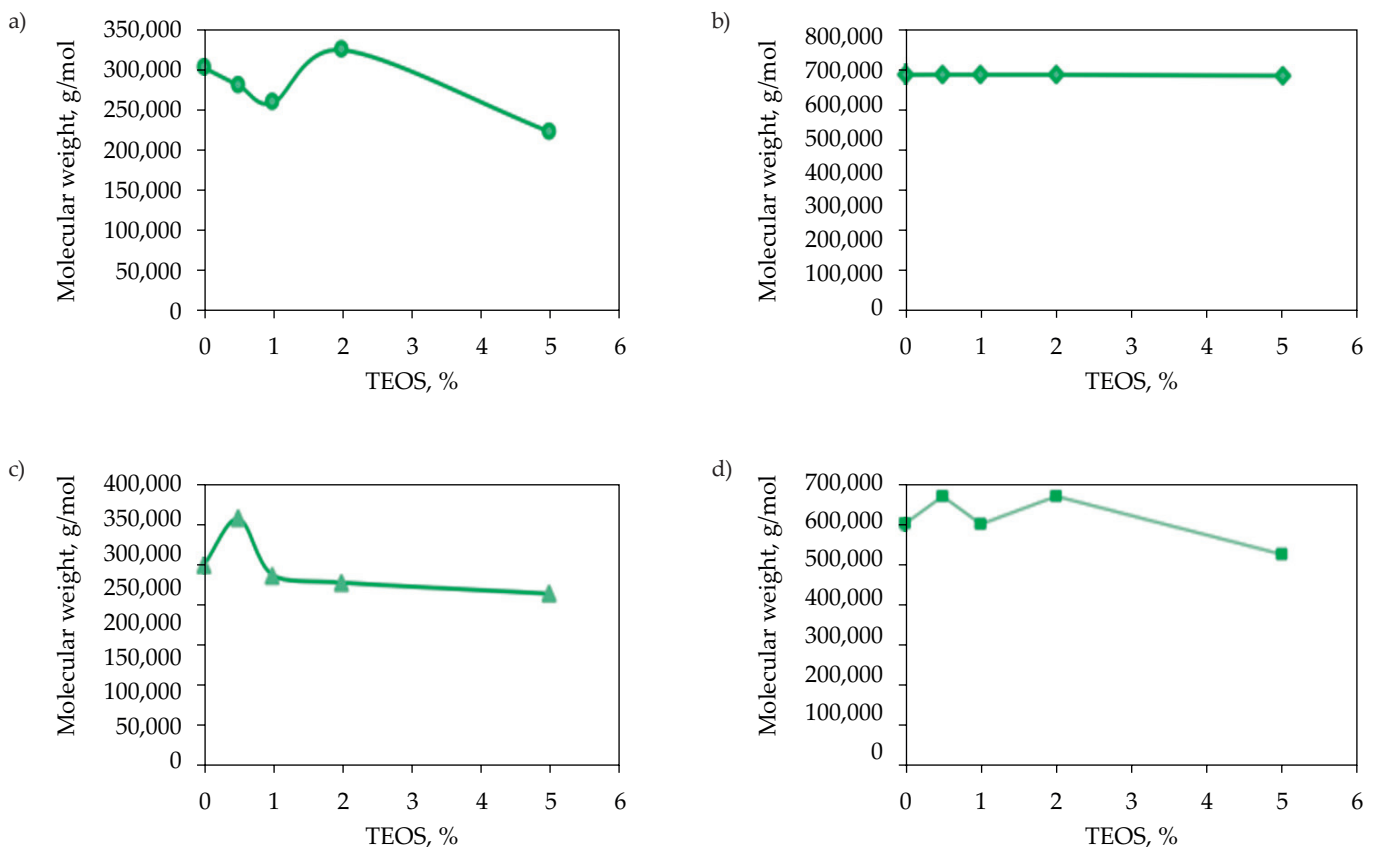
| Polymer    | PVDF wt% | Relative viscosity Pa·s | Specific viscosity Pa·s | $\frac{\eta_{sp}}{c}$ | Intrinsic viscosity dL/g | Molecular weight g/mol |
|------------|----------|-------------------------|-------------------------|-----------------------|--------------------------|------------------------|
| LMWHP-PVDF | 8        | 70.65                   | 69.65                   | 9.26                  | 0.20                     | 301,338                |
|            | 10       | 138.05                  | 137.05                  | 14.58                 |                          |                        |
|            | 12       | 245.56                  | 244.56                  | 21.70                 |                          |                        |
| HMWHP-PVDF | 8        | 544.30                  | 543.30                  | 70.52                 | 0.34                     | 668,991                |
|            | 10       | 1329.11                 | 1328.11                 | 141.2                 |                          |                        |
|            | 12       | 2990.51                 | 2989.51                 | 264.56                |                          |                        |
| LMWCP-PVDF | 8        | 56.12                   | 55.12                   | 7.33                  | 0.12                     | 282,756                |
|            | 10       | 111.18                  | 110.18                  | 11.83                 |                          |                        |
|            | 12       | 169.62                  | 168.62                  | 15.01                 |                          |                        |
| HMWCP-PVDF | 8        | 494.30                  | 493.30                  | 65.73                 | 2.97                     | 596,562                |
|            | 10       | 1125.80                 | 1124.80                 | 120.00                |                          |                        |
|            | 12       | 2983.00                 | 2982.00                 | 264.00                |                          |                        |

and thermal properties. The viscosity average molecular weight was measured to study the effect of TEOS on the viscosity average molecular weight of PVDF.

The viscosity average molar mass of all types of PVDF was determined by using Mark-Houwink equation. The Mark Houwink constant values for HMWHP-PVDF and LMWHP-PVDF were obtained from the work of Florian *et al.* [20] in order to calculate the average viscosity molecular weight. The study of Maohua *et al.* served as the source for the Mark Houwink constant values employed

to determine the average viscosity molecular weight of LMWCP-PVDF and HMWCP-PVDF [21]. Table 2 contains information on the intrinsic viscosities and average molecular weights of LMWHP-PVDF, HMWHP-PVDF, LMWCP-PVDF, and HMWCP-PVDF. The LMWCP-PVDF had the lowest average molecular weight of 28,2756 g/mol, while the HMWHP-PVDF had the greatest average molecular weight of 668,991 g/mol.

$$[\eta] = KM^a \quad (7)$$

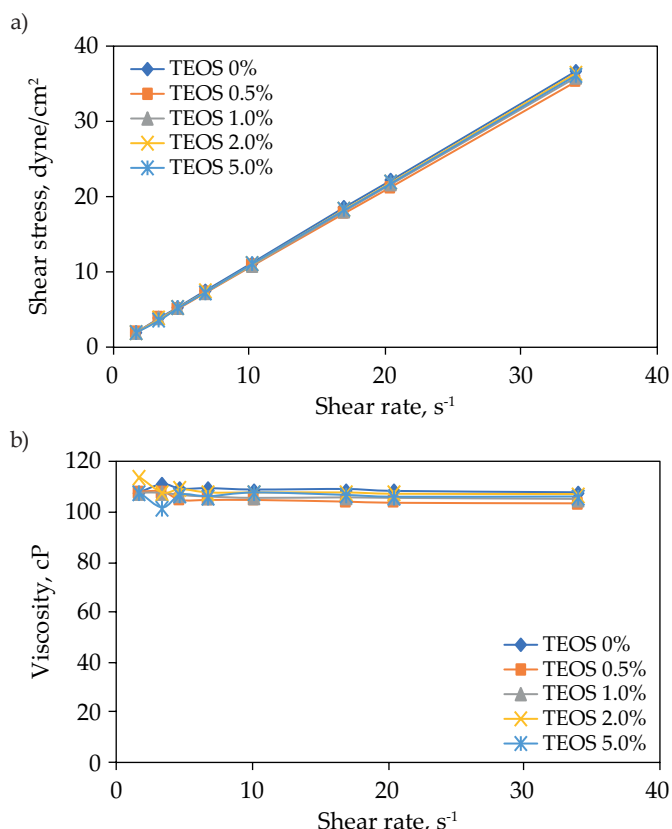

**Fig. 3.** Effect of TEOS on the  $M_w$ : a) LMWHP-PVDF, b) HMWHP-PVDF, c) LMWCP-PVDF, d) HMWCP-PVDF

**T a b l e 3.** Consistency indices ( $k$ ) and flow behavior indices ( $n$ ) of various dope solutions of LMWHP-PVDF

| TEOS wt% | $n$    | $k$    | $R^2$ |
|----------|--------|--------|-------|
| 0        | 0.9968 | 1.0981 | 1     |
| 0.5      | 0.9855 | 1.0871 | 1     |
| 1        | 0.9914 | 1.0866 | 1     |
| 2        | 0.985  | 1.1255 | 1     |
| 5        | 1.0038 | 1.0578 | 0.999 |

**T a b l e 4** Consistency indices ( $k$ ) and flow behavior indices ( $n$ ) of various dope solutions of HMWHP-PVDF

| TEOS wt% | $n$    | $k$    | $R^2$ |
|----------|--------|--------|-------|
| 0        | 0.9942 | 10.589 | 1     |
| 0.5      | 0.9959 | 10.917 | 1     |
| 1        | 0.9887 | 10.014 | 1     |
| 2        | 1.0011 | 10.568 | 1     |
| 5        | 0.9893 | 10.809 | 1     |



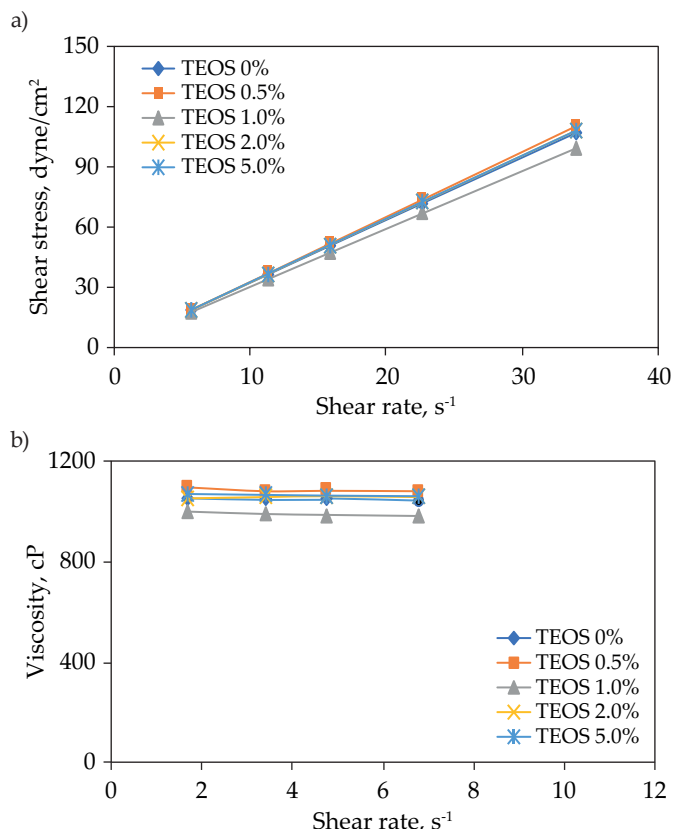
**Fig. 4.** Rheological properties of LMWHP-PVDF: a) shear stress, b) apparent viscosity

Intrinsic viscosity –  $\eta$ , molecular weight –  $M$ ,  $K$ , and  $a$  are empirically derived parameters for a given polymer solvent temperature system. Equation 8 was derived from equation 7, and it was used to calculate the average molecular weight from viscosity.

$$M_w = e^{\frac{\ln \eta - \ln k}{a}} \quad (8)$$

### The effect of TEOS on the average viscosity molecular weight of PVDF based polymers

Figure 3 shows the effect of TEOS on the average viscosity and molecular weight of PVDF-based polymers. For LMWHP-PVDF, addition of TEOS decrease the average molecular weight, with exception of 2 wt% TEOS (Fig. 3a). This indicates, that TEOS does not assist the polymer chains in creation of bonds between them. It is believed that TEOS is causing the chains to spread,



**Fig. 5.** Rheological properties of HMWHP-PVDF: a) shear stress, b) apparent viscosity

which lowers the molecular weight. For HMWHP-PVDF addition of TEOS does not affect the average viscosity molecular weight. This may indicate lack of interaction between TEOS and HMWHP-PVDF. The addition of TEOS (0.5 wt%) to LMWCP-PVDF initially causes an increase in molecular weight, but it decreases when further added. Initial increase of  $M_w$  may be attributed to extending of polymer chains. For HMWCP-PVDF, addition of 0.5 and 2 wt% of TEOS cause increase in molecular weight, when different 1 and 5 wt% is lowering  $M_w$ . Lower TEOS content led to extension of polymer chains or creation of additional bonds between them when the higher content results in spreading of chains.

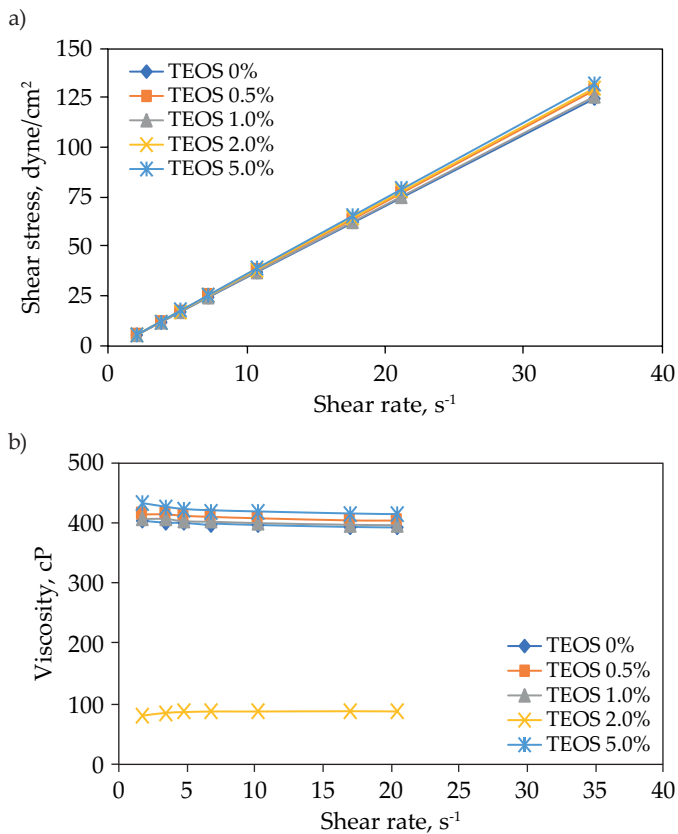
### The influence of TEOS on the viscosity of LMWHP-PVDF

LMWHP-PVDF exhibited pseudoplastic behaviour, yet the amount of pseudoplastic behaviour increased with



**Table 5. Consistency indices ( $k$ ) and flow behavior indices ( $n$ ) of various dope solutions of LMWCP-PVDF**

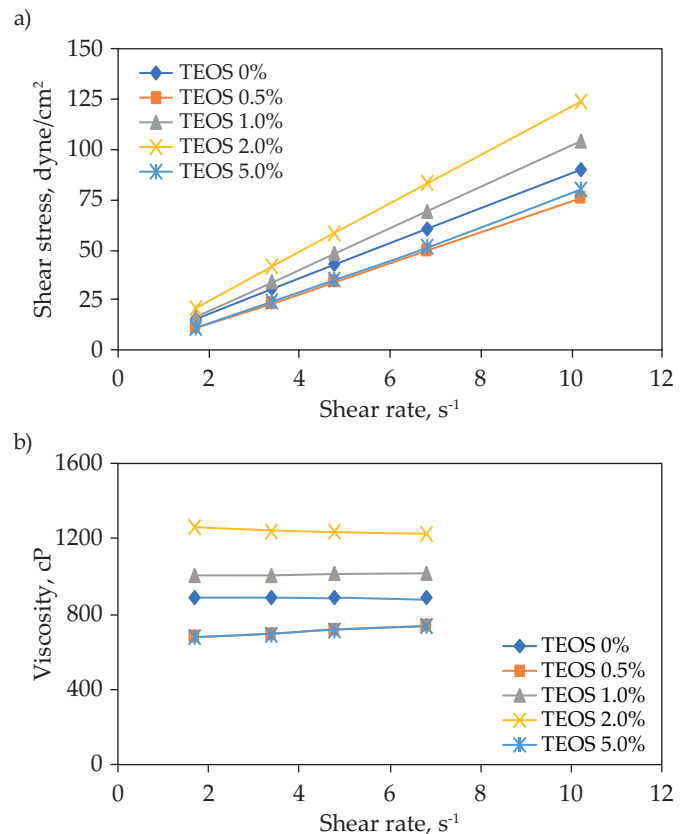
| TEOS wt% | $n$    | $k$    | $R^2$ |
|----------|--------|--------|-------|
| 0        | 1.0148 | 0.8514 | 0.999 |
| 0.5      | 1.0084 | 0.9861 | 1     |
| 1        | 1.0203 | 0.8522 | 0.999 |
| 2        | 1.0295 | 0.8021 | 0.999 |
| 5        | 1.0324 | 0.7994 | 0.999 |


**Fig. 6. Rheological properties of LMWCP-PVDF: a) shear stress, b) apparent viscosity**

the addition of TEOS. However, the behavior towards dilatant has been led by 5 wt% TEOS, the behavior of the dope solution is represented by the flow index value ( $n$ ), and the thickness of the dope solution is indicated by the consistency index value ( $k$ ), as shown in Figure 4. The power law was used to determine the values of  $n$  and  $k$ . Table 3 shows the values of  $n$  and  $k$  for LMWHP-PVDF and LMWHP-PVDF-TEOS. Furthermore, TEOS is showing a significant influence on LMWHP-PVDF thickness. Because of the thickness increase caused by the 2 wt% TEOS, the solution's viscosity has also increased. This could be as a result of the increasing chain lengths and decreasing chain mobility. While 5 wt% TEOS has significantly reduced LMWHP-PVDF's thickness, indicating that it must have aided in the chain's mobility in LMWHP-PVDF and lowered the viscosity value, 0.5 wt% and 1 wt% TEOS have also had an impact on LMWHP-PVDF's viscosity by reducing the thickness of the dope solutions.

**Table 6. Consistency indices ( $k$ ) and flow behavior indices ( $n$ ) of various dope solutions of HMWCP-PVDF**

| TEOS wt% | $n$    | $k$    | $R^2$  |
|----------|--------|--------|--------|
| 0        | 0.9916 | 9.0072 | 1      |
| 0.5      | 1.0544 | 6.5586 | 0.9999 |
| 1        | 1.008  | 10.022 | 1      |
| 2        | 0.976  | 12.817 | 1      |
| 5        | 1.0784 | 6.5293 | 0.9999 |


**Fig. 7. Rheological properties of HMWCP-PVDF: a) shear stress, b) apparent viscosity**

### The influence of TEOS on the viscosity of HMWHP-PVDF

In Fig. 5 the flow curves in terms of shear stress/apparent viscosity-shear rate connections for HMWHP-PVDF homopolymer PVDF are shown. The dope solutions displayed pseudoplastic behavior with or without the addition of TEOS, as indicated by their flow index values of  $n$  in table 4. Bair *et al.* studied the effect of concentration and found that the existence of Newtonian behavior in solutions at concentrations lower than 7% by weight. Higher concentrations result in solutions exhibiting pseudoplastic fluid properties [22]. Moreover, In HMWHP-PVDF, the thickness values of  $K$  are significantly higher as compared to LMWHP-PVDF. The viscosity has increased dramatically with the 0.5 wt% TEOS, suggesting that it may have increased chain entanglements and impeded chain mobility. Although 1 wt% TEOS has sharply reduced the viscosity, this might be because the TEOS has caused the chains to shorten or there are fewer

**Table 7. Effect of temperature on the viscosity**

| Temperature<br>°C | Viscosity, cP  |                |                |
|-------------------|----------------|----------------|----------------|
|                   | LMWHP-<br>PVDF | LMWCP-<br>PVDF | HMWCP-<br>PVDF |
| 20                | 1385           | 1285           | 1408           |
| 30                | 1106           | 993            | 1107           |
| 40                | 981            | 833            | 906            |
| 50                | 942            | 689            | 750            |

entanglements. Also, it is likely that the TEOS has assisted in spreading the chains, which has resulted in the viscosity lowering. Dobos *et al.* studied rheological behavior of cellulose acetate (CA) with TEOS blends in tetrahydrofuran (THF) and found that the addition of TEOS decreased the viscosity with increasing shear rate [23].

### The influence of TEOS on the viscosity of LMWCP-PVDF

In Figure 6, the flow curves for LMWCP-PVDF are depicted in terms of shear stress and apparent viscosity-shear rate relationships. In Table 5 the dope solutions' rheological behavior was non-Newtonian, and the flow index values were  $n > 1$ , which express the behavior of dilatant fluids with and without the addition of TEOS. The rheological properties of LMWCP-PVDF are distinguished from those of LMWHP-PVDF and HMWHP-PVDF by the presence of 0.5 wt% TEOS, which significantly enhances the viscosity, where addition of 2 and 5 wt% TEOS have reduced it. 0.5 wt% TEOS may act as a promoter for the formation of aggregates or clusters in the LMWCP-PVDF solution. These aggregates hinder the flow of the polymer chains and cause an increase in viscosity as the shear rate is increased, or TEOS may enhance the entanglement of the LMWCP-PVDF polymer chains. As the shear rate increases, the chains become more entangled, leading to higher resistance to flow and increased viscosity. While 2 wt% and 5 wt% TEOS may increase the flexibility of LMWCP-PVDF chains, which can lead to increased molecular mobility by making it easier for the chains to slide past each other under shear stress.

### The influence of TEOS on the viscosity of HMWCP-PVDF

Fig. 7 shows the flow curves for HMWCP-PVDF in terms of shear stress/apparent viscosity-shear rate relationships, respectively. The HMWCP-PVDF dope solution had pseudoplastic behavior at first, but after addition of TEOS caused behavior shift to dilatant. Only exception was 2 wt% TEOS where behavior reverted to pseudoplastic. When comparing the effects of TEOS between HMWCP-PVDF and HMWHP-PVDF, it is noticed, that 0.5 wt% of TEOS increased thickness in HMWHP-PVDF but decreased it in HMWCP-PVDF. The addition of 1 and

**Table 8. Effect of 5 wt% TEOS on activation energy**

| Temperature<br>°C | Activation energy, J/mol |                |                |
|-------------------|--------------------------|----------------|----------------|
|                   | LMWHP-<br>PVDF           | LMWCP-<br>PVDF | HMWCP-<br>PVDF |
| 30                | 110                      | 126            | 117            |
| 40                | 124                      | 183            | 208            |
| 50                | 67                       | 315            | 314            |

2 wt% TEOS resulted in negligible thickness change in HMWHP-PVDF, but 0.5 and 5 wt% TEOS decreased the viscosity in HMWCP-PVDF. It further indicates that the 0.5 and 5 wt% TEOS may have assisted in spreading the chains to shorten the chain length and lower viscosity. Table 6 shows the values of  $n$  and  $k$  at different concentrations of TEOS.

### Effect of temperature on the viscosity

The effect of temperature on the viscosity was observed in four polymer dope solutions containing 10 wt% of LMWHP-PVDF, HMWHP-PVDF, LMWCP-PVDF and HMWCP-PVDF, respectively, with 5 wt% TEOS and 85 wt% of DMF. It was observed that the temperature has inverse relation to the viscosity of the polymer dope solutions. This may be due to molecules that are usually attached by intermolecular forces. As the temperature increases, the molecules gain more energy, which causes the intermolecular forces to weaken, causing the viscosity to decrease. Bair *et al.* used the rheometric method to examine the rheological characteristics of PVDF solutions in *N*-methylpyrrolidone. It was found that as the temperature increases, the viscosity of polymer solutions decreases non-linearly [22]. Byoung and Kim [24] discovered that raising the temperature gradually reduces the viscosity of the polymer solutions after studying the rheological characteristics of PVDF in dimethyl acetamide (DMAc). The viscosities of polymer dope solutions were recorded at 20, 30, 40 and 50°C. Gradual decrease in viscosity values is presented in the Table 7.

### Activation energy

Table 8 shows relationship between TEOS and activation energy. It is concluded, that the higher the temperature, the more molecules possess energies equal to or greater than the activation energy. At higher temperatures, a larger fraction of molecules can surmount the energy barrier and participate in the reaction. This results in a faster reaction rate. It is found that chain flexibility rises with temperature. Mobility is improved by 5 wt% TEOS, a plasticizer used in LMWHP-PVDF. It decreases the activation energy barrier, allowing the surrounding polymer's segments to relax more readily. By extending the matrix free volume, 5 wt% TEOS in LMWHP PVDF also aids in reducing the relaxation time. It was also found that HMWHP-PVDF and HMWCP-PVDF

had higher activation energy at higher temperature. Moreover, LMWHP-PVDF shows the highest chemical reactivity.

## CONCLUSIONS

The viscosity changes of the tested PVDF solutions can be explained using the Ostwald-de Waele model. Pseudoplastic behavior was confirmed for LMWHP-PVDF and HMWHP-PVDF. The exception is LMWCP-PVDF with the addition of 5 wt% and 2 wt% TEOS, which shows dilatation behavior. HMWCP also has dilatation properties. The exception is HMWCP containing 2 wt% TEOS. The flow curves show how significantly the addition of TEOS affects the viscosity of the PVDF solution. The PVDF concentration is effectively diluted by the addition of TEOS, increasing the total volume of the solution. Because there are fewer PVDF polymer chains per unit volume and fewer intermolecular interactions and entanglements, this dilution can help reduce viscosity. In the case of PVDF, TEOS can also be used as a plasticizer. By increasing the mobility of the chain, it increases flexibility and processability. TEOS affects the PVDF chains, which reduces intermolecular forces and increases the chains mobility. Viscosity may be reduced due to increased chain mobility. It was also found that as the intrinsic viscosity increases, the average molecular weight also increases. Moreover, LMWHP-PVDF showed the highest chemical reactivity at 50°C.

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## REFERENCES

- [1] Li M., Katsouras I., Piliago C. *et al.*: *Journal of Materials Chemistry C* **2013**, 1, 7695.  
<https://doi.org/10.1039/C3TC31774A>
- [2] Omar A. Goma I., Mohamed O.A. *et al.*: *Optical and Quantum Electronics* **2023**, 55, 381.  
<https://doi.org/10.1007/s11082-023-04663-6>
- [3] Otsuka T., Chujo Y.: *Polymer* **2009**, 50(14), 3174.  
<https://doi.org/10.1016/j.polymer.2009.05.018>
- [4] Yuennan J., Sukwisute P., Muensit N.: *Materials Research Express* **2018**, 5(5), 055702.  
<https://doi.org/10.1088/2053-1591/aabf4d>
- [5] Kozhevnikov I.V., Chibiryaev A.M., Martyanov O.: *Chemical Engineering Journal* **2021**, 426, 131871.  
<https://doi.org/10.1016/j.cej.2021.131871>
- [6] Chen W., Su Y., Zhang L. *et al.*: *Journal of Membrane Science* **2010**, 348(1–2), 75.  
<https://doi.org/10.1016/j.memsci.2009.10.042>
- [7] Castricum H.L., Kreiter R., van Veen H.M. *et al.* : *Journal of Membrane Science* **2008**, 324(1–2), 111.  
<https://doi.org/10.1016/j.memsci.2008.07.014>
- [8] van Veen H.M., Rieterk M.D.A., Shanahan D.P. *et al.*: *Journal of Membrane Science* **2011**, 380(1–2), 124.  
<https://doi.org/10.1016/j.memsci.2011.06.040>
- [9] Van Krevelen D.W., Te Nijenhuis K.: “Properties of Polymers”, Elsevier Science, Amsterdam 2009.
- [10] Norzita Y., Norhashidah T., Maznah M. *et al.*: *Journal of Nuclear and Related Technologies* **2013**, 10(1), 40.
- [11] Francis P.S., Cooke Jr. R.C., Elliott J.H.: *Journal of Polymer Science* **1958**, 31(123), 453.  
<https://doi.org/10.1002/pol.1958.1203112323>
- [12] Budtova T., Navard P.: *Nordic Pulp and Paper Research Journal* **2015**, 30(1), 99.  
<https://doi.org/10.3183/npprj-2015-30-01-p099-104>
- [13] Vinogradov G.V., Malkin A.Y.: “Rheology of Polymers”, Springer, Berlin 1980.
- [14] Fernández I., Bickelhaupt F.M.: *Chemical Society Reviews* **2014**, 43(14), 4953.  
<https://doi.org/10.1039/C4CS00055B>
- [15] Gillespie D.T.: *Journal of Computational Physics* **1976**, 22(4), 403.  
[https://doi.org/10.1016/0021-9991\(76\)90041-3](https://doi.org/10.1016/0021-9991(76)90041-3)
- [16] Hellmann R., Gaviglio P., Renders P.J.N. *et al.*: “Experimental pressure solution compaction of chalk in aqueous solutions. Part 1. Deformation behavior and chemistry” in “Water-Rock Interactions, Ore Deposits, and Environmental Geochemistry: A tribute to David A. Crerar”, Geochemical Society, St. Louis 2002. p. 153.
- [17] Yu L.-Y., Xu Z.-L., Shen H.-M. *et al.*: *Journal of Membrane Science* **2009**, 337(1–2), 257.  
<https://doi.org/10.1016/j.memsci.2009.03.054>
- [18] Ribeiro C., Costa C.M., Correia D.M. *et al.*: *Nature Protocols* **2018**, 13(4), 681.  
<https://doi.org/10.1038/nprot.2017.157>
- [19] Briscoe B., Luckham P., Zhu S.: *Journal of Applied Polymer Science* **1998**, 70(3), 419.  
[https://doi.org/10.1002/\(SICI\)1097-4628\(19981017\)70:3<419::AID-APP1>3.0.CO;2-Q](https://doi.org/10.1002/(SICI)1097-4628(19981017)70:3<419::AID-APP1>3.0.CO;2-Q)
- [20] Brandl F., Drache M., Beuermann S.: *Polymers* **2018**, 10(9), 1008.  
<https://doi.org/10.3390/polym10091008>
- [21] Quan M., Yang B., Wang J. *et al.*: *ACS Applied Materials and Interfaces* **2018**, 10(4), 4243.  
<https://doi.org/10.1021/acsami.7b17230>
- [22] Damdinov B.B., Danilova V.A., Minakov A.V. *et al.*: *Journal of Siberian Federal University. Mathematics and Physics* **2021**, 14(3), 265.  
<https://doi.org/10.17516/1997-1397-2021-14-3-265-272>
- [23] Dobos A.M., Filimon A., Bargan A. *et al.*: *Journal of Molecular Liquids* **2020**, 309, 113129.  
<https://doi.org/10.1016/j.molliq.2020.113129>
- [24] Lee K.H., Song I.K., Kim B.C.: *Korea Australia Rheology Journal* **2008**, 20(4), 213.

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