



## PRODUCTION OF CHEMICALLY MODIFIED SHEAR THICKENING FLUIDS AND INVESTIGATION OF THEIR RHEOLOGICAL PROPERTIES

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**Abstract:** In this study, the rheological properties of shear thickening fluid, which are generally used as single solid phase in the literature, were investigated by chemical material reinforcement. Considering that the unique shear thickening effect of STF is used in many areas such as increasing the impact resistance of fabrics and energy dissipation, this study aims to provide guidance for investigating what STFs can do with chemical bonds as well as physical bonding. Methylene diphenyl diisocyanate (MDI) was used in varying proportions for chemical reinforcement. When the rheological properties of the suspensions reinforced with MDI as a chemical additive were evaluated, the initial viscosity values increased as the MDI ratio increased, while the solidification behavior under shear was observed significantly in the sample with 2.5% MDI ratio with increasing shear ratio.

**Keywords:** Shear-thickening fluid, Chemical reaction, Rheology

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### 1. Introduction

High performance fabrics have been used extensively to provide protection without restricting the movement of personnel. In recent years, shear thickening fluids (STF) have been investigated to increase the energy absorbing capacity of these systems. Shear Thickening Fluids are non-Newtonian suspensions that exhibit a sudden increase in viscosity with increasing shear rate. This property of STFs is reversible. Thus, when the stress that increased the viscosity is removed, the liquids return to their initial state. Many studies have been conducted to understand the rheological properties of these fluids and to use them in engineering applications. (Hoffman, 1972; Hoffman, 1974; Bossis and Brady, 1989; Boersma et al., 1992). The rheological properties of STFs mainly depend on parameters such as the solid medium (shape, size, proportion, hardness, additional particles), the liquid medium (type, density) and the physical conditions of the suspension. It was observed that the viscosity of the suspension increased with increasing molecular weight of polyethylene glycol (PEG) used as a liquid medium (Baharvandi et al., 2016). In the study by Qin et al., three different PEGs with mole weights of 200, 400 and 600 were added at a ratio of 45% to STF produced using PS microspheres and PEG. PEG 600 was reported to be more effective in the solidification behavior of the added sample (Qin et al., 2017). The addition of additional

particles to the suspension in the production of STF significantly changes the rheological properties. In the study by Sha et al., CNT and GNP were added as additional particles to CACS produced using 650 nm diameter spherical silica and PEG 200 (Sha et al., 2013). Hasanzadeh et al. investigated the effect of multi-walled carbon nanotube (CNT) reinforced STF on the puncture resistance performance of high modulus polypropylene (HMPP) fabrics (Hasanzadeh et al., 2016). Li et al. investigated the energy dissipation mechanisms of clean and STF impregnated UHMWPE fabrics in dynamic impact tests with knife and nail tip (Li et al., 2016). Tan et al. investigated the effects of graphene nanoplate (GNP) reinforcement on the rheological properties of STF (Tan et al., 2018). Wang et al. investigated the rheological properties and inter-yarn friction properties of STF at temperatures between -15 °C and 35 °C to examine their properties in different climatic conditions (Wang et al., 2019).

In the literature review, there are many studies in which the rheological properties of single and multi solid phase shear thickening fluids are determined and their effect on the energy absorbing performance of high performance fabrics is examined. When the FTIR analysis of the STFs' produced in previous studies was examined, it was determined that no chemical bond was formed between the silica and PEG forming the suspension content



(Yanen et al., 2020). In the literature review, no study was found in which chemically bonded STF's were produced. Within the scope of this study, chemically modified shear thickening fluid (CSTF) was first produced and rheological properties were investigated.

**2. Materials and Methods**

The silica particles were oven dried at 150 °C for about 12 hours to remove moisture absorbed on the surface. To prepare the STF samples, polyethylene glycol and silica particles were mixed at 6000 rpm using a high speed mechanical mixer. During the mixing process, silica particles were gradually added to prevent agglomeration as suggested in previous studies (Zhang et al., 2008; Gürgen and Kuşhan, 2017; Wang et al., 2017). Stirring was continued until the mixture became homogeneous. The stirring was carried out in a temperature adjustable water bath to keep the suspension temperature constant (Figure 1). The same method was used in the production of nanoparticle reinforced STF. In the production of STF's

developed by chemical modification, PEG 400 and Aerosil 150 were first homogenized with a high speed mechanical mixer (Table 1). Diphenylmethane diisocyanate (MDI) at the rate of 5% by mass was added to the resulting mixture and stirred at room temperature for 1 hour.

The rheological properties of CSTFs were determined using Anton Paar MCR 102 voltage-controlled rheometer, pictured in Figure 2, as in previous studies (Yanen et al., 2020; Yanen et al., 2021). The tests were performed using a 25 mm diameter parallel plate apparatus. During the testing process, liquids were placed in the inner region between the upper and lower measuring plates. The gap between the plates was kept constant at 0.3 mm and all tests were performed at 25 °C. Rheological measurements were performed in the shear rate range of 0-1000 s<sup>-1</sup>. FTIR analysis was performed using Shimadzu S11025C (QATR-S) instrument to study the bond formation in the suspensions produced to obtain CSTF.

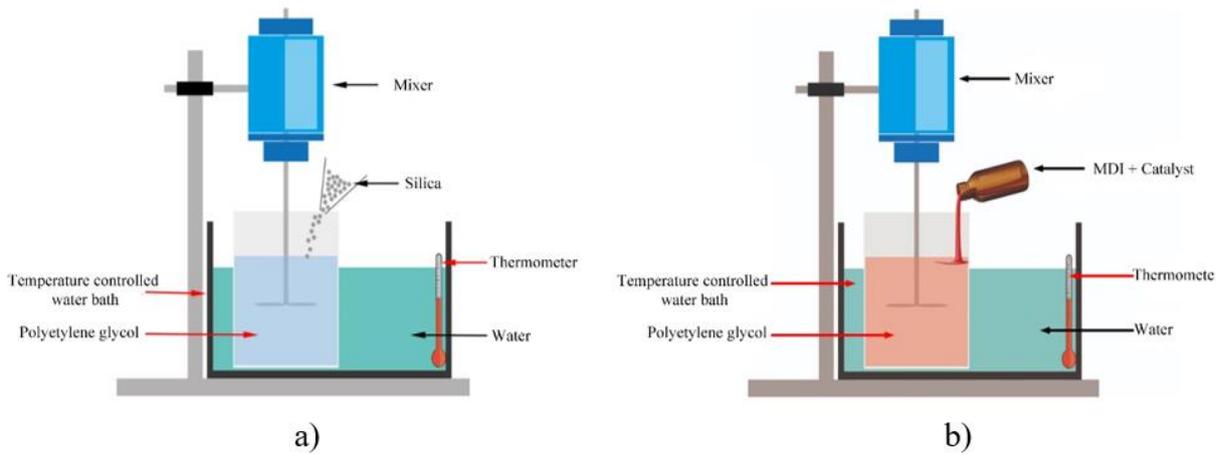


Figure 1. a) STF production b) CSTF production using STF.



Figure 2. Anton Paar MCR 102 Rheometer.

Table 1. Specimen nomenclature and properties used in the experiments

Specimen No	Factor investigated	STF	Silica Ratio	Chemical Ratio
1				0
2	Chemical Ratio	Aerosil 150 + PEG 400	25%	2.50%
3				5%
4				7.50%

### 3. Results and Discussion

Figure 3 shows the rheological properties of the suspensions reinforced with MDI as a chemical additive. All MDI reinforced samples exhibit non-Newtonian behavior. When pure STF and MDI reinforced samples were compared, it was observed that MDI additive reduced the critical shear rate. If the results are evaluated, while the initial viscosity values increase as the MDI ratio increases, the solidification behavior under shear is clearly observed in the sample with 2.5% MDI ratio with increasing shear rate. There is no significant difference between the critical shear rates with increasing MDI ratio. The final viscosity values change inversely proportional to the MDI ratio.

#### 3.1. Chemical Reaction in the Production of CSTF

It is necessary to study the chemical reaction between polyethylene glycol and methylene diphenyl isocyanate (MDI) in the production of CSTF. Other components provide physical interactions among themselves. For example, aerosil, polyethylene glycol, fabric and nanoparticles do not make chemical bonds with each other. The chemical reaction described below shows that a chemical reaction takes place between the functional hydroxyl (-OH) groups in ethylene glycol and the cyanate

groups (-N=C=O) in methylene diphenyl isocyanate (Figure 4).

#### 3.2. Fourier Transform Infrared Spectrophotometer (FTIR) Results

In the FTIR spectra, stress vibrations of hydroxyl bonds in polyethylene glycol are observed in the wavelength range of 3400-3550  $\text{cm}^{-1}$  (Figure 5). In the wavelength range 2850-3000  $\text{cm}^{-1}$ , stress vibrations of CH groups occur. Since methylene diphenyl diisocyanate gives chemical bonds with hydroxyl bonds in polyethylene glycol, it was determined that hydroxyl bonds decreased as the MDI ratio increased. However, free isocyanates that cannot undergo chemical reaction are seen at a wavelength of approximately 2225  $\text{cm}^{-1}$ . In this study, polyethylene glycol reacts chemically at an optimum rate with about 2.5% MDI. The use of higher proportions of MDI indicates an increase in free isocyanates in the wavelength range 2215-2235  $\text{cm}^{-1}$ . The highest rheological performance in the obtained CSTF samples was observed in 2.5% MDI reinforced samples. The use of high percentage of MDI decreases the rheological performance of the CSTF samples since it is present in the mixture without chemical reaction.

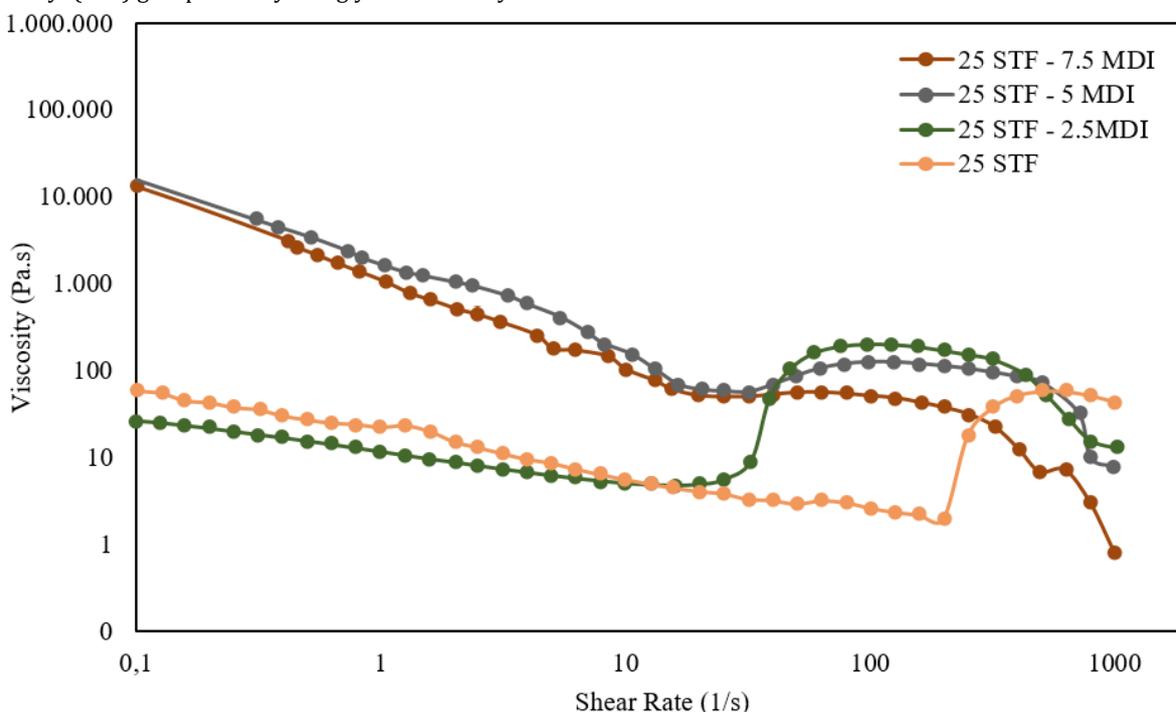


Figure 3. Effect of MDI ratios on rheological properties.

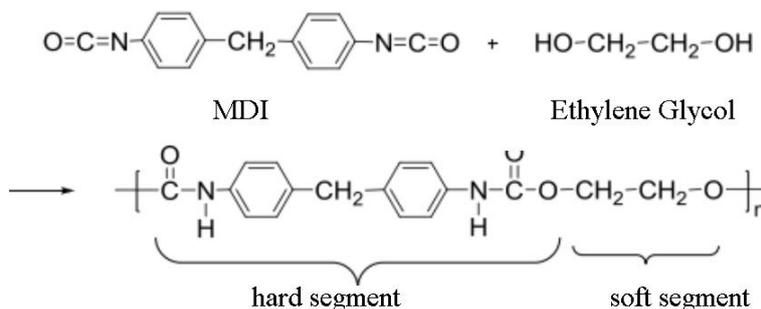


Figure 4. Chemical reaction between MDI and polyethylene glycol.

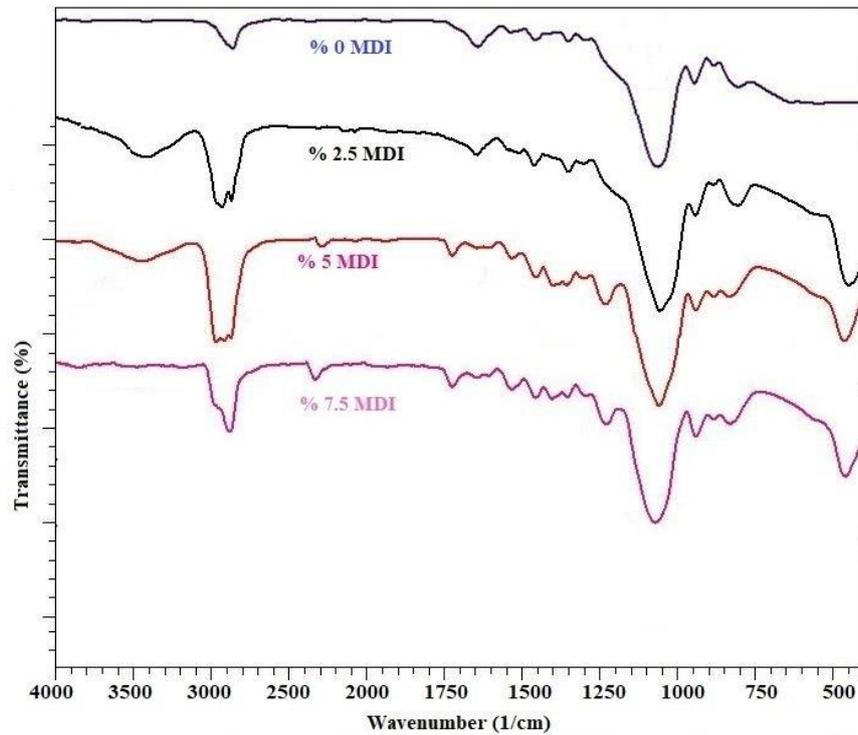


Figure 5. FTIR spectra of CSTF samples produced with different MDI ratios by mass.

#### 4. Conclusion

In the suspensions produced within the scope of this study, solidification behavior under shear was observed and it was determined that properties such as critical shear rate and viscosity profile can be controlled by properties such as the ratio of reinforcement material. In the study, CSTF were impregnated into two different Twaron para-aramid fabrics. The effects of impregnating these high-performance fabrics with CSTF on their energy absorption capacities and low-speed impact tests were investigated. The information obtained as a result of the study can be summarized as follows;

- When the rheological properties of the suspensions reinforced with MDI as a chemical additive were evaluated, the initial viscosity values increased with increasing MDI ratio, while the solidification behavior under shear was observed significantly in the sample with 2.5% MDI ratio with increasing shear ratio. No significant difference was detected between the critical shear rates with increasing MDI ratio. The final viscosity values change inversely proportional to the MDI ratio.
- When FTIR peaks have been examined in this study, it is determined that the isocyanates in MDI are consumed. However, the use of high amounts of MDI indicates that free isocyanates are present in the mixture despite the chemical reaction taking place. It can be seen in the FTIR peaks that the hydroxyl bonds in PEG have decreased. When optimum 2.5 % MDI is used, peaks of free isocyanates are not observed in the wavelength range of 2215-2235 cm<sup>-1</sup>. As a result, it has been determined that the chemically reacting components are consumed at

this optimum rate.

- All of the nanoparticle reinforced specimens exhibited solidification behavior under shear. As in the case of CSTF, the system consists of three stages: shear thinning, solidification under shear and the formation of a relative plateau.
- It is thought that the addition of MDI to the liquids solidified under shear creates a chemical reaction and may strengthen the connection between the fabric and the suspension in future studies.

#### Author Contributions

The percentage of the author(s) contributions is presented below. All authors reviewed and approved the final version of the manuscript.

	M.Y.S.	C.Y.	C.K.	E.A.
C	30	25	20	25
D	20	30	30	20
S	40	20	20	20
DCP	20	30	30	20
DAI	20	30	20	30
L	20	30	30	20
W	20	30	30	20
CR	20	30	20	30
SR	20	30	30	20
PM	30	20	30	20

C=Concept, D= design, S= supervision, DCP= data collection and/or processing, DAI= data analysis and/or interpretation, L= literature search, W= writing, CR= critical review, SR= submission and revision, PM= project management.

**Conflict of Interest**

The authors declared that there is no conflict of interest.

**Ethical Consideration**

Ethics committee approval was not required for this study because of there was no study on animals or humans.

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