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Lignin Graft Copolymer as a Drilling Mud Thinner for High Temperature Well

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Abstract: A study was conducted on graft copolymerization of Kraft lignin with 2-propenamide (acrylamide). The copolymerization process was carried out via a free radical reaction using methanol as the reaction medium, ferrous ion as the catalyst and benzoyl peroxide as the initiator. The formulation of lignin-acrylamide graft copolymer (PLA) was verified by infrared (IR) spectroscopy and Differential Scanning Calorimetry (DSC) analyses. Thermogram observations showed that there were two T_g values indicating that the yield was a copolymer. Then, the performance of the PLA as a polymeric thinning agent for aqueous bentonite mud was evaluated. The rheological performances of the copolymer were compared with that of a commercial thinner (lignosulfonate). At the optimum dosage of 0.3% of total mud volume, the PLA acted more effectively as a thinner and also as an agent for controlling filtration loss than did the lignosulfonate. Unlike the commercial lignosulfonate, the newly formulated thinner (PLA) showed better thinning performance at a high temperature of 190°C. Furthermore, the PLA was more tolerant than lignosulfonate towards salt contamination.

Key words: Kraft lignin, free radical reaction, lignin-acrylamide graft copolymer, rheological performances

INTRODUCTION

Formulation of drilling mud is one of the most important aspects in drilling engineering. This is because as drilling progresses, the mud would become more viscous and thus reduce the optimum speed of the drill bits. Therefore, the right formulation of drilling mud is needed to ease drilling operation. This is achieved by using mud additives that act as an agent to disperse colloidal suspensions responsible for mud viscosity. The problem with the current drilling mud system is that some of the additives are toxic such FeCr-lignosulfonate. Drilling workers are probably the most at risk while handling drilling operations. These operations may also cause the toxic drilling mud to migrate and contaminate drinking water resources.

On the other hand, the increasing amount of waste from the oil palm industry is another environmental concern in Malaysia that necessitates the need for better waste management. There are 2.5 million ha of oil palm estates and over 300 palm oil processing plants all over the country (<http://www.sabutek.com.my>). The demand for oil palm is once again on the rise regardless of competition from other vegetable oils. This could be due

to the low cholesterol content in palm oil as well as its rich vitamin E content. Nevertheless, palm oil processing plants are facing challenges to eliminate the empty fruit bunch (EFB) from their compounds. Despite of these challenges, an environmentally friendly drilling mud thinner known as Fe-tannin-lignin (FTL) has been successfully formulated from this oil palm lignocellulosic waste (Muhamad Ibrahim *et al.*, 2003).

The present study is to address the problem of thermal decomposition of lignin based mud additives above 121°C (Meister *et al.*, 1985). In order to increase its thermal stability, the lignin has been copolymerized with acrylamide to produce poly-lignin acrylamide or better known as PLA.

MATERIALS AND METHODS

The raw material used in this study was oil palm empty bunch (EFB) long fiber supplied by Sabutek (M) Sdn. Bhd., Teluk Intan, Malaysia, a local company specializing in recycling oil palm lignocellulosic wastes. This study was conducted from July 2004 until January 2005 at School of Chemical Sciences, Universiti Sains Malaysia.

The EFB fiber was pulped in a 20 L stainless steel rotary digester unit together with 25% NaOH (cooking liquor) for 3 h at a maximum cooking temperature of 170°C.

The mixture of cooking liquor to the EFB fiber was in the ratio of 10:1. Prior to the pulping process, the fiber was soaked in water for two days to remove dirt.

During the pulping process, the pH of black liquor was measured as 12.45 and its density was determined to be 0.987 g mL⁻¹. The soda lignin was precipitated from the concentrated black liquor by acidifying it to pH 2 using 20% sulfuric acid. The precipitate was filtered and washed with pH 2 water, which was prepared utilizing the same acid as in the earlier step. The soda lignin was then dried in an oven at 55°C for 24 h prior to further analysis.

The lignosulfonate (LS), a commercial thinner and bentonite clay used in this study were supplied by Kota Mineral (Malaysia) Sdn. Bhd. The rest of the chemicals including 2-propenamide (acrylamide), ferrous ammonium sulphate, benzoyl peroxide, methanol and acetone were purchased from local chemical agents and the chemicals used were of analytical grade.

A reaction solution was prepared by mixing 0.5 g lignin, 0.02 g ferrous ammonium sulphate and 50 mL of methanol in a three-neck flask until complete dissolution. The mixture was saturated with nitrogen for 10 min before 0.02 g of benzoyl peroxide was added into the mixture. After being saturated with nitrogen for 20 min 2.5 g of acrylamide was added to the mixture, which was further saturated with nitrogen for another 10 min. This reaction process continued for about two hours before it was terminated using 0.5 mL of 1% of hydroquinone as a retardant. The prepared poly-lignin acrylamide graft copolymer (PLA) consisted of a fine dark brown powder.

Mud properties test: Three sets of experiments were performed in this study. These mud property tests were performed according to the American Petroleum Institute (API) specifications (Roland and Rejmann, 2000; Zhang and Yin, 1999 and American Petroleum Institute, 1997). Each of base mud used in each experiment was prepared by adding 80 g of bentonite and 4 g of sodium carbonate into 1000 mL of water before aging it for more than 24 h (Roland and Rejmann, 2000; Zhang and Yin, 1999; American Petroleum Institute, 1997; American Petroleum Institute, 1986; Bourgoyne *et al.*, 1991; Mohamad *et al.*, 2003; Van Olphen, 1963).

For each of the experiment, a Fann model 286 viscometer was used at two rotating rates of 300 rpm (θ_{300}) and 600 rpm (θ_{600}), respectively. Then apparent viscosity (μ_a), plastic viscosity (μ_p) and yield point (τ_y) were calculated as follows American Petroleum Institute, (1986).

$$\mu_a = \theta_{600} / 2 \quad (1)$$

$$\mu_p = \theta_{600} - \theta_{300} \quad (2)$$

$$\tau_y = 0.511 (\theta_{300} - \mu_p) \quad (3)$$

In Experiment I, the effect of different dosages of each thinner used at room temperature and under strong agitation (90°C) was studied. Three dosage levels of PLA were tested which were 0.3, 0.5 and 0.7. This experiment was designed to highlight the importance of using correct dosage of treatment to ensure optimum performance of thinner as well as to reduce unnecessary cost. Besides, the use of excessive or insufficient dosage might bring negative impact to the mud properties (Mohamad Ibrahim *et al.*, 2003).

For Experiments II and III, the base mud samples were added either with 0.3% of PLA or 0.3% LS (commercial thinner). 0.3% was chosen since PLA acts optimally as a thinner at this level (based on Experiment I results). Experiment II was performed to evaluate thinning performance at different aging temperatures for 16 h. This experiment was designed to observe the influence of temperature on the performance of each thinner. This is because the drilling process normally will take place at high temperature, which is usually greater than 60°C. At higher temperatures, the electrochemical charge of hydrate dispersion bentonite becomes unstable and tends to flocculate or thicken.

Experiment III was designed to evaluate the performance of the additives in relation to salt contamination before and after the mud samples were heated in the Fann Roller Oven Series 2500 at 160°C for 16 h. These laboratory conditions were used to simulate the actual drilling process. This experiment is important because salt (NaCl) contamination is commonly encountered in drilling and such contamination is sometimes also found in make-up water. When make-up water is very salty, bentonite will neither hydrate nor disperse (Roland and Rejmann, 2000) As a result, the undispersed or the unhydrated bentonite particles will tend to flocculate which will result in an increase in yield points and apparent viscosity values.

To complement Experiments II and III, the API filtrate volume data was presented in order to evaluate the performance of the additives as a fluid reducer. The Fann Filter Press model Series 300 was used to measure the API filtrate volume. Filtered volume is the amount of fluid that can be delivered through a permeable filter medium after it has been subjected to a set of differential pressure for a specified period of time.

RESULTS AND DISCUSSION

Graft copolymerization is the process of adding a polymeric side chain [poly (1-amidoethylene)] to an

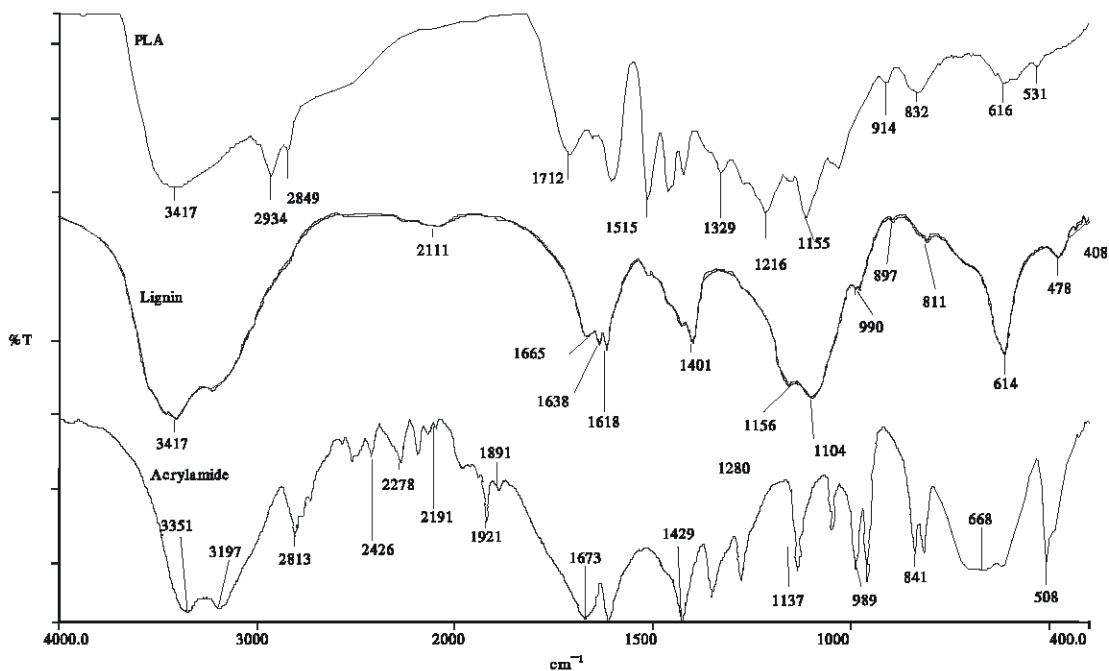


Fig. 1: IR spectra of lignin, acrylamide and PLA

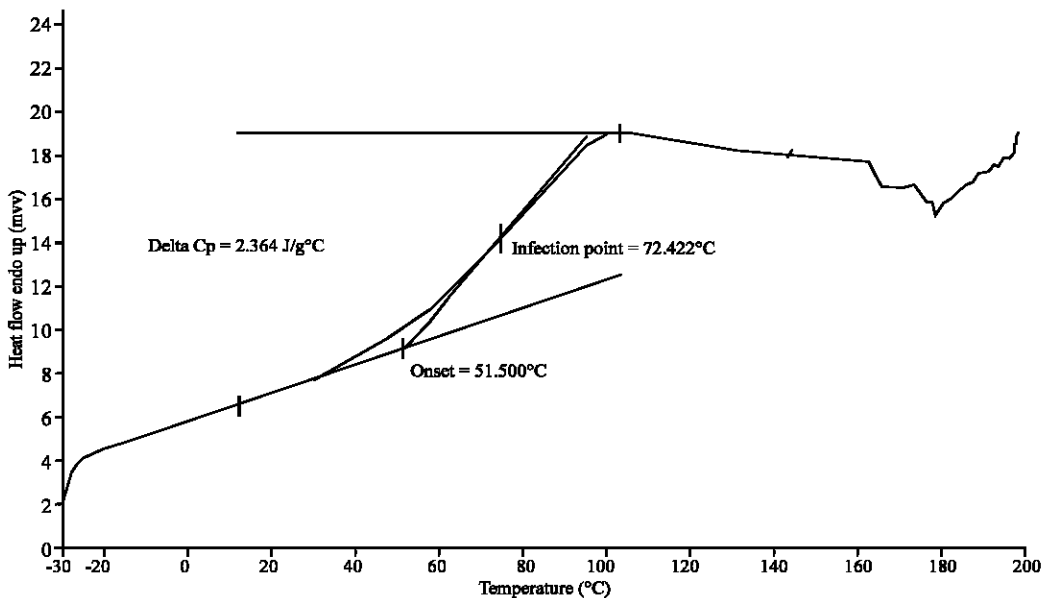


Fig. 2: DSC thermogram for lignin

existing polymer (lignin) to produce a two-part molecule. The two parts of the molecule are of different chemical composition or structure. In this case, the graft copolymer which formed, was trivially named poly-lignin acrylamide, PLA (Meister *et al.*, 1985).

Figure 1 depicts the infrared (IR) spectra of the PLA, lignin and acrylamide samples. The IR spectrum of lignin shows absorption at 3417 cm^{-1} for the phenolic or hydroxyl group. Absorption at 1638 cm^{-1} is attributed to the aromatic ring while absorption at 1462 cm^{-1} is

assigned to either CH stretching of methyl or CH stretching of methylene group. The 3351 and 3197 cm^{-1} bands in the spectrum of acrylamide depict the stretching vibration for the primary amide (NH_2) group. The carbonyl ($\text{C}=\text{O}$) group can be seen at 1673 cm^{-1} , while the C-N stretch can be seen at 1429 cm^{-1} . In contrast to the lignin and acrylamide spectra, the PLA shows four different bands from lignin which are 1712 cm^{-1} for carbonyl group ($\text{C}=\text{O}$), 1515 cm^{-1} for aromatic C=C stretch, 1216 cm^{-1} and 1329 cm^{-1} which cannot be seen also in the

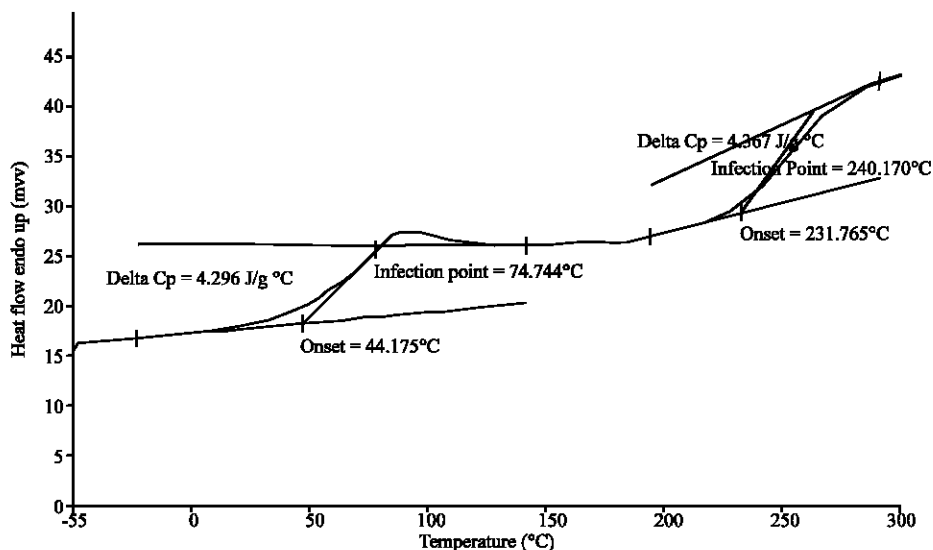


Fig. 3: DSC thermogram for PLA

acrylamide spectrum. The PLA spectrum displays no distinct peak for the amide group (NH_2). The shift of bands and the existence of new peaks suggest that chemical reactions had taken place.

Lignin as an amorphous compound does not have any melting point peak as shown in Fig. 2. After the lignin had been copolymerized, there were two glass transition point T_g values observed in PLA thermogram as clearly shown in Fig. 3. The second T_g value was more than three times that of the first value. This could be due to the presence of macromolecule PLA that was produced at the end of copolymerization process. This macromolecule apparently caused a steric hindrance, which increased the T_g values. Besides T_g values were also influenced by the polymer structure either in its cis or trans form. The amide polar group ($-\text{CONH}-$) in acrylamide contributed to the high T_g value due to hydrogen bonding in the product and restrictions in polymer chain movement.

Table 1 depicts the optimum dosage of PLA at 0.3%. This table shows that 0.3% PLA generated the lowest yield point compared to other dosages at both temperatures of 27 and 90°C. These temperature values were used to confirm that the performance of PLA would be consistent at both room temperature and at high temperature. Yield point represents the degree of electrostatic interaction between clay platelets. As yield point values increase, friction between the drill string and mud increases proportionately.

Experiment II was conducted at a high temperature of 190°C to simulate the deep well drilling process. Observations of the mud samples were done before and after hot rolling. PLA displayed the best μ_a , μ_p , and τ_y values compared to other formulations at high temperature especially after hot rolling. Besides, PLA also

showed good API filtrate volume at a high temperature. These findings seem to suggest that PLA with its high molecular weight and high decomposition temperature could act quite well in the very high temperature condition of 190°C. This is important for the deep well drilling process which commonly encounters high temperature and high-pressure conditions. For instance, a temperature of 190°C represents drilling at about 10,000 m underground (Table 2).

Results from the third experiment (Experiment III) suggested that the newly formulated poly-lignin acrylamide (PLA) exhibited good qualities as a thinning agent even in the presence of salt contamination especially after hot rolling at 160°C. μ_a and τ_y values for mud samples treated with PLA after hot rolling were the lowest (Table 3). μ_p values, however, showed small improvement because the effect of reduction in viscosities was smaller compared to the increased in solids concentrations in the mud as more solids (NaCl and LS or PLA) being added to the mud. This experiment is important because the common contaminant encountered in drilling is salt (NaCl), which is sometimes also found in make-up water (Table 3). When make up water is very salty, bentonite will neither hydrate nor disperse (Roland and Rejmann, 2000) and as a result the bentonite particles tend to flocculate thus increasing yield point and the apparent viscosity values (Table 3).

Experiment II and III show that lignin-based drilling mud thinner (lignin PLA) can also act as good fluid reducers. The fluid loss control during drilling process is important to make sure that drilling left-over is efficiently transmitted from the bottom hole to the surface (hole cleaning process). If the mud viscosity is too high due to the fluid lost to the formation, the drilling process will be

Table 1: Basic mud rheological properties under different PLA dosages

Mud formulation	T (°C)	μ_a (mPa.S)	μ_p (mPa.S)	τ_y (Pa)
Base mud + 0.3% PLA	27	23.17	12.66	10.74
Base mud + 0.5% PLA		24.50	13.67	11.07
Base mud + 0.7% PLA		26.17	15.00	11.41
Base mud + 0.3% PLA	90	18.34	6.00	12.61
Base mud + 0.5% PLA		18.17	5.33	13.46
Base mud + 0.7% PLA		19.67	5.00	14.99

All test data were measured at 27±1°C

Table 2: Basic mud rheological properties after aging at high temperature (before and after rolling at 190°C for 16 h)

Mud formulation	μ_a (mPa.S)		μ_p (mPa.S)		τ_y (Pa)		API filtrate (mL)	
	Before	After	Before	After	Before	After	Before	After
Base mud	30.00	58.00	16.00	30.00	14.31	33.00	14.00	20.00
Base mud + 0.3% LS	20.00	52.67	14.00	39.00	6.13	13.97	13.50	16.20
Base mud + 0.3% PLA	18.00	35.17	9.33	21.33	8.86	14.14	12.60	14.00

All test data were measured at 27±1°C

Table 3: Basic mud rheological properties at different salinity (before and after hot rolling at 160°C)

Mud formulation	μ_a (mPa.S)		μ_p (mPa.S)		τ_y (Pa)		API filtrate (mL)	
	Before	After	Before	After	Before	After	Before	After
Base mud + 0.7% NaCl	29.17	70.83	8.66	15.34	20.96	56.71	15.2	23.6
Base mud + 0.7% NaCl + 0.3% LS	30.67	85.83	21.33	18.67	9.54	68.64	12.8	22.6
Base mud + 0.7% NaCl + 0.3% PLA	33.34	59.65	10.34	23.97	23.50	36.48	12.0	15.2

All test data were measured at 27±1°C

more difficult due to pipe sticking phenomenon. In other words, the mud sample with small filtrate volume indicates that the mud is capable to hold fluid from losing to the formation. The results of the experiment are to confirm that the formulated thinner, especially lignin PLA is not only functioning as a good drilling mud thinner but also at the same time acts as good fluid reducer.

In conclusion, the polymerization of lignin PLA has been successfully formulated by cross-linking the lignin with acrylamide in the presence of benzoyl peroxide under nitrogen atmosphere. The comparison studies between lignin PLA and LS suggested that the thinning abilities of the lignin PLA show better tolerance at high temperature of 190°C. Beyond this temperature value however, the performance of this newly formulated lignin based thinner has not been tested. This is due to, as stated earlier, a temperature of 190°C represents drilling at about 10,000 m underground, which is already falls into a deep well category. Therefore, the polymerization of lignin PLA is inevitably provides a better alternative to hydrocarbon drilling industry as a drilling fluid thinner especially for high temperature.

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