

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of Glass Fiber Surface

SEM micrographs (Figure 4.1) show that as-received glass fiber had a smooth surface with small islands of sizing spread over its surface, whereas the untreated glass fiber showed a clean, smooth surface. This indicates that the sizing had been completely removed from the as-received fibers.

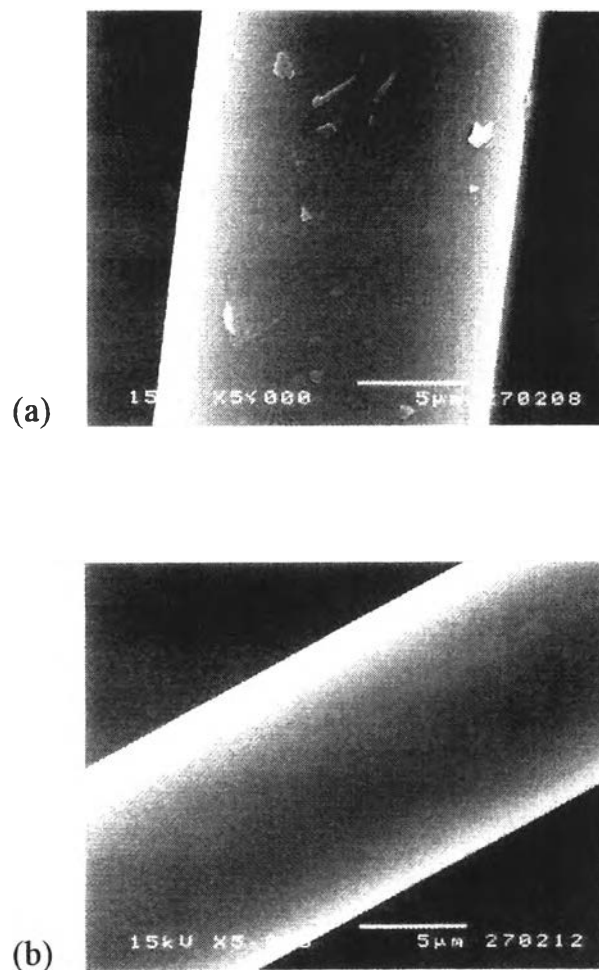


Figure 4.1 SEM micrographs of (a) as-received glass fiber and (b) untreated glass fiber.

4.2 Admicelle Formation of SDS onto Glass Fiber Surfaces

The concentration of the SDS surfactant was maintained at or below its critical micelle concentration (cmc) to prevent micelle formation in the aqueous supernatant and, consequently, to avoid any emulsion polymerization from taking places in solution (Sakhalkar *et. al.*, 1995). The aim was to restrict the polymerization reaction within the surfactant bilayers assemblies on the glass fiber surfaces. The cmc of SDS in water medium is given in Table 4.1 (Rosen, 1989).

Table 4.1 Critical micelle concentration of sodium dodecyl sulfate in water at 25°C.

Surfactant	Solvent	cmc (M)
SDS	H ₂ O	8.2×10^{-3}

Moreover, to obtain admicelle formation, the most critical parameter to be manipulated is the solution pH such that the surface exhibits a net surface charge of zero (referred to as the point of zero charge or PZC). In this study, glass fibers were used, which typically have a PZC in the acidic range (Sakhalkar *et. al.*, 1995). Since an anionic surfactant (SDS) was used to form surfactant bilayers, the pH of surfactant solution was adjusted to a low level of 4 (Grady *et. al.*, 1998). This acidity level should assure that the glass fiber surfaces become protonated, i.e. become more positively charged, without destroying the glass fibers. Admicelle formation could then proceed by adsorption of surfactant molecules onto the glass fiber surfaces.

4.3 Pressure Drop of Ethylene during the Adsolubilization and Polymerization Processes.

Before determining the pressure drop for the adsolubilization process the amount of ethylene dissolved in water was first determined by means of a “blank” in order to find out the exact amount of ethylene solubilized into the surfactant bilayers. Figure 4.2 shows the relationship between the pressure drop of ethylene gas for both the adsolubilization and the admicellar polymerization steps with time of a blank system (absent of surfactant and initiator).

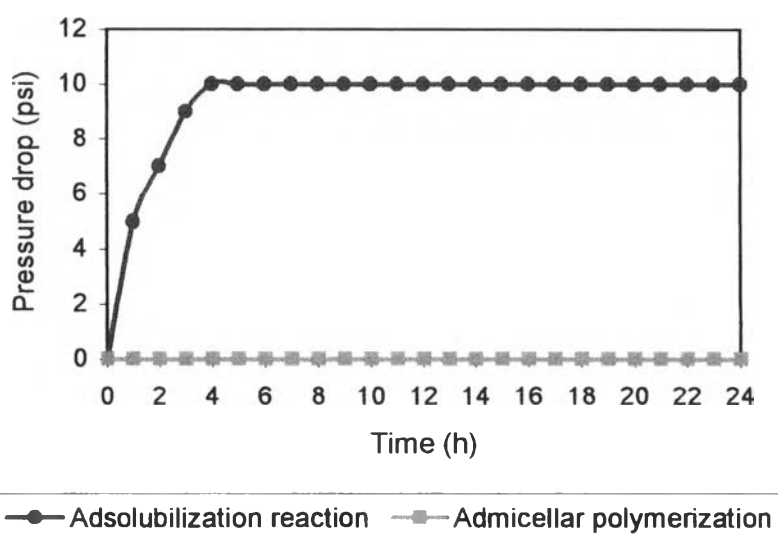


Figure 4.2 Dissolution of ethylene into water for adsolubilization and admicellar polymerization steps.

Table 4.2 Summary of ethylene pressure drop for adsolubilization and admicellar polymerization steps of the blank system.

Step	Total ethylene pressure drop (psi)
Adsolubilization	10.00
Admicellar polymerization	0.00

It was found that there was some solubility of ethylene gas in water for the adsolubilization step, as shown in Table 4.2. Ten psi of ethylene pressure drop was observed with no further pressure drop occurring when the temperature was raised from 25°C to 70°C (corresponding to admicellar polymerization conditions). The zero pressure drop for the polymerization reaction conditions (70°C) indicates that no further dissolution of ethylene occurred in the aqueous medium.

Figure 4.3 and Table 4.3 indicate that some ethylene had been adsolubilized in the SDS bilayers on the glass fiber surface. The reaction curve of ethylene pressure drop for the adsolubilization step with 1:1 initiator to surfactant ratio system differed from that of the blank system. The former shows a lower slope, i.e. equilibrium pressure was attained at a slower rate. A possible explanation is that when glass fiber is present in the system there are two equilibrium conditions in the reaction mixture. One equilibrium is that of ethylene solubilized in water and the other is the equilibrium of ethylene solubilized inside the admicelles. At a 1:1 initiator to surfactant ratio the time to reach a balance point of these two equilibrium systems is extended. The ethylene in the water gradually solubilizes into the surfactant bilayers on the glass surface resulting in a lower slope. On the other hand, ethylene solubilized into only water was possibly easier and faster.

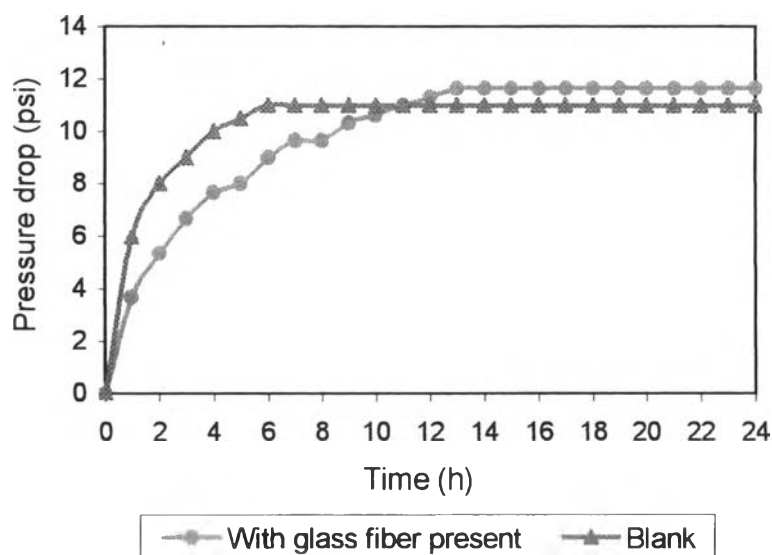


Figure 4.3 Pressure drop of ethylene (psi) in the adsolubilization step of initiator:surfactant = 1:1 system.

Table 4.3 Summary of ethylene pressure drop for the blank system and glass fiber/adsolubilization system (initiator:surfactant = 1:1).

Condition	Total ethylene pressure drop (psi)
Blank (without glass fiber)	11.00
System with glass fiber	11.67
ΔP	0.67

Table 4.4 shows that, as for the 1:1 initiator to surfactant ratio system, the 2:1 initiator to surfactant ratio system also had a net ethylene pressure drop of 0.67 psi for the adsolubilization process. However, the slopes of the reaction curves for both with and without glass fiber present at initiator to surfactant ratio of 2:1 were almost the same (Figure 4.4).

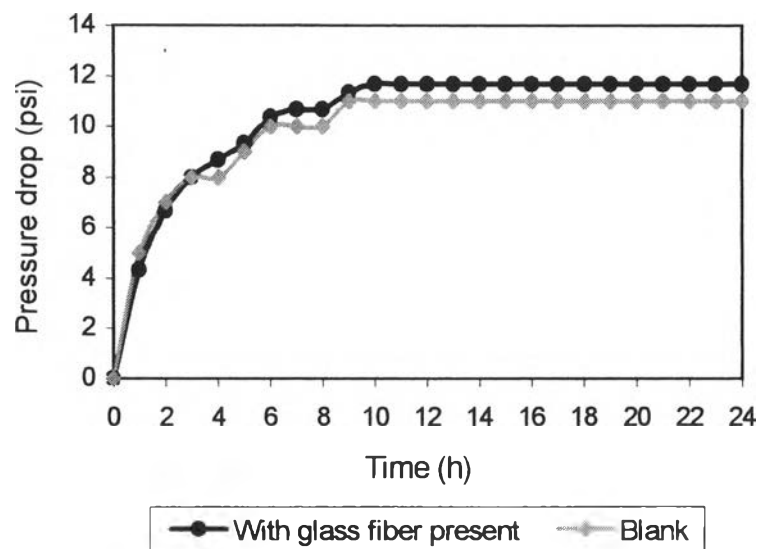


Figure 4.4 Pressure drop of ethylene (psi) in the adsolubilization step of initiator:surfactant = 2:1 system.

Table 4.4 Summary of ethylene pressure drop for the blank system and glass fiber/adsolubilization system (initiator:surfactant = 2:1).

Condition	Total ethylene pressure drop (psi)
Blank (without glass fiber)	11.00
System with glass fiber	11.67
ΔP	0.67

When the initiator to surfactant ratio was increased to 3:1, a net pressure drop of ethylene for the adsolubilization process was still 0.67 psi as illustrated in Figure 4.5 and Table 4.5. The results indicate that the amount of initiator does not affect the amount of ethylene pressure drop for the adsolubilization process.

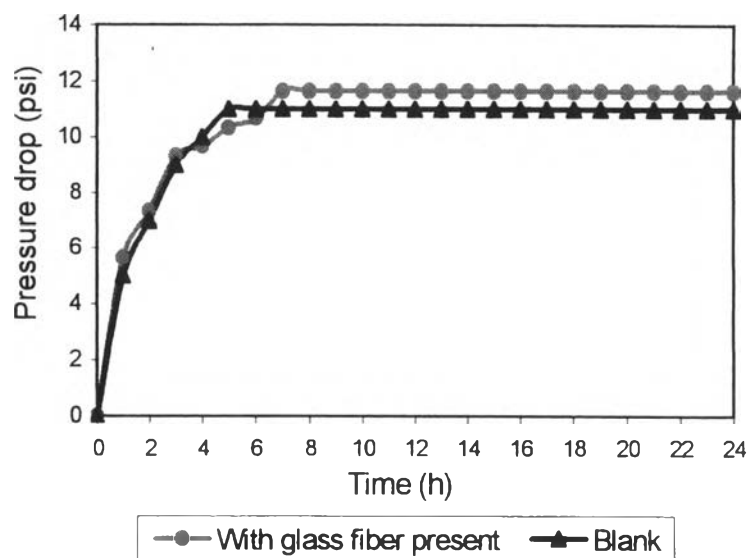


Figure 4.5 Pressure drop of ethylene (psi) in the adsolubilization step of initiator:surfactant = 3:1 system.

Table 4.5 Summary of ethylene pressure drop for the blank system and glass fiber/adsolubilization system (initiator:surfactant = 3:1).

Condition	Total ethylene pressure drop (psi)
Blank (without glass fiber)	11.00
System with glass fiber	11.67
ΔP	0.67

4.4 Effect of Initiator on the Adsolubilization Process

Although the amount of ethylene solubilized into the surfactant bilayers were the same i.e. corresponding to a pressure drop of 0.67 psi for different initiator to surfactant ratio systems, the initiator had an effect on the rate of adsolubilization. Figure 4.6 compares the adsolubilization curves of systems at different initiator to surfactant ratios.

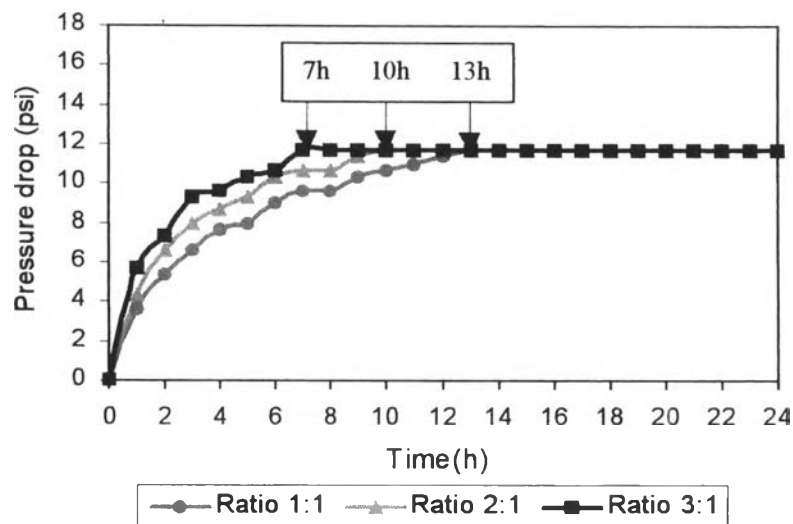


Figure 4.6 Comparison of time to reach equilibrium for different ratios of initiator:surfactant (1:1, 2:1, and 3:1).

Higher ratios of initiator to surfactant resulted in higher rates of adsolubilization as can be seen from the curves in Figure 4.6. The times to reach equilibrium for the three systems are shown by the values (inset), i.e. thirteen hours for the 1:1 ratio, ten hours for the 2:1 ratio and seven hours for the 3:1 ratio.

A possible explanation for this result could be the decrease in repulsion between the similarly charged head groups of SDS (anionic surfactant). An increasing amount of initiator will lead to higher amounts of Na^+ which will cause a decrease in the repulsion between the negative charges of the surfactant head groups in the admicelles, thereby increasing the aggregation number (the number of surfactant molecules in the admicelles) and the volume of the admicelles (Rosen, 1989).

An increase in the aggregation number of the admicelles will presumably result in an increase in hydrocarbon (ethylene monomers) solubilization inside the admicelles. Therefore, for the same ethylene solubilized into the admicelles (pressure drop 0.67 psi), a higher amount of initiator will give a higher solubilization rate.

4.5 Pressure Drop of Ethylene during the Admicellar Polymerization Process

The • line of Figure 4.7 displays the pressure drop of ethylene for the system without glass fiber (blank) at reaction temperature of 70°C while the ■ line shows the pressure drop of ethylene for the system with glass fiber present during admicellar polymerization at 70°C. The ethylene pressure drop of 10.50 psi, as shown in Table 4.6, represents the consumption of ethylene in the absence of glass fiber in the system. It was first presumed that some polymerization might have taken place in the aqueous solution. One hypothesis is that when the temperature was raised from 25°C to 70°C the sodium persulfate initiator thermally decomposed into persulfate radicals which initiated polymerization of the ethylene dissolved in the water. However, it was found that the supernatant liquid of the blank system did not show any signs of ethylene polymerization, i.e. the reaction mixture remained clear. This seems to indicate that polymerization did not occur in aqueous solution although an ethylene pressure drop was observed.

Nevertheless, this situation is similar to the work of Lai *et. al.*, (1995) who found that in the admicellar polymerization of tetrafluoroethylene at an initiator concentration of 2.5 wt% there was considerable polymerization of tetrafluoroethylene (gas phase) in the bulk solution even though the concentration of sodium perfluororheptanoate surfactant was below its cmc (a murky solution being observed in the supernatant), but this did not happen at a lower initiator concentration of 0.25 wt% (a clear solution remained in the supernatant). However, they concluded that a small degree of polymerization in the bulk solution seems not unreasonable.

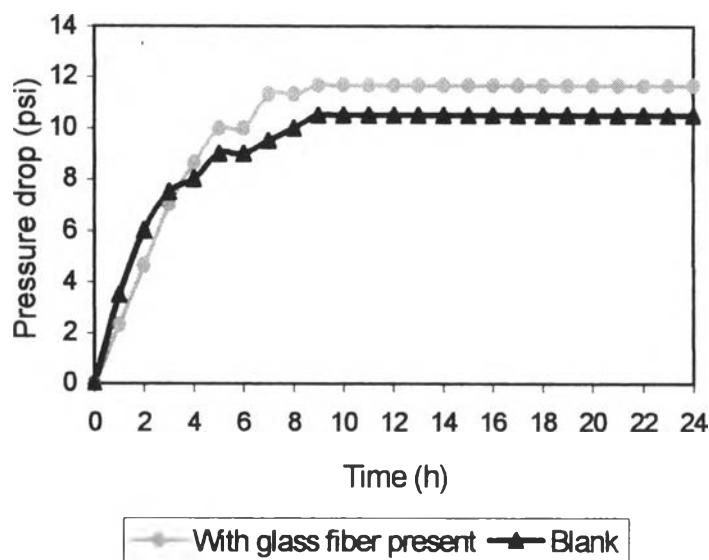


Figure 4.7 Pressure drop of ethylene (psi) for the admicellar polymerization of initiator:surfactant = 1:1 system at the reaction temperature of 70°C.

Table 4.6 Summary of ethylene pressure drop for the blank system and glass fiber/admicellar polymerization system (initiator:surfactant = 1:1) at the reaction temperature of 70°C.

Condition	Total ethylene pressure drop (psi)
Blank (without glass fiber)	10.50
System with glass fiber	11.67
ΔP	1.17

With glass fiber present in the system, the ethylene pressure drop was found to increase from 10.50 to 11.67 psi as shown in Table 4.6. The result was taken to indicate that the pressure difference of 1.17 psi represents ethylene consumption for the admicellar polymerization process.

When the initiator to surfactant ratio was increased to 2:1, the ethylene pressure drop in both the systems with and without glass fiber was found to increase (Figure 4.8). The amount of ethylene pressure drop in the admicellar polymerization in this case was 1.67 psi as shown in Table 4.7.

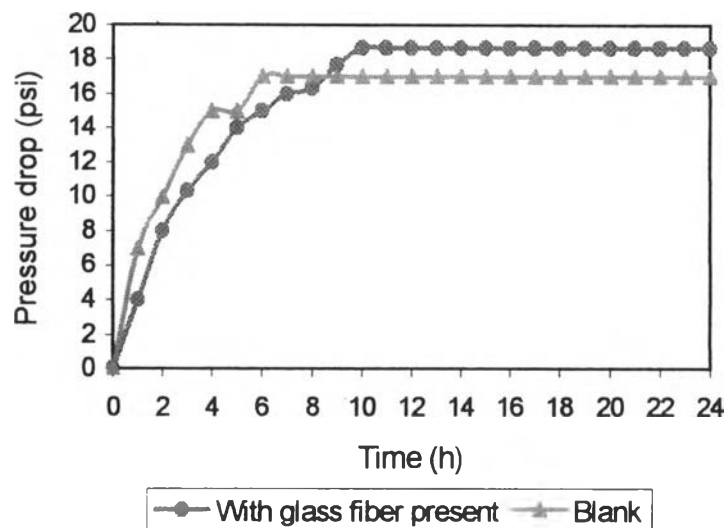


Figure 4.8 Pressure drop of ethylene (psi) for the admicellar polymerization of initiator:surfactant = 2:1 system at the reaction temperature of 70°C.

Table 4.7 Summary of ethylene pressure drop for the blank system and glass fiber/admicellar polymerization system (initiator:surfactant = 2:1) at the reaction temperature of 70°C.

Condition	Total ethylene pressure drop (psi)
Blank (without glass fiber)	17.00
System with glass fiber	18.67
ΔP	1.67

For the case of 3:1 initiator to surfactant ratio, there was a marked increase in the pressure drop for both the blank and with glass fiber systems compared with lower initiator to surfactant ratio systems (Figure 4.9). A net pressure drop of 2.67 psi, as shown in Table 4.8, represents a relatively high ethylene consumption for the admicellar polymerization at 3:1 initiator to surfactant ratio. The results indicate that introducing glass fiber into the system allows the formation of SDS bilayers which can adsorb monomer from

the aqueous solution. Polymerization of the adsorbed monomer results in a pressure drop of the system.

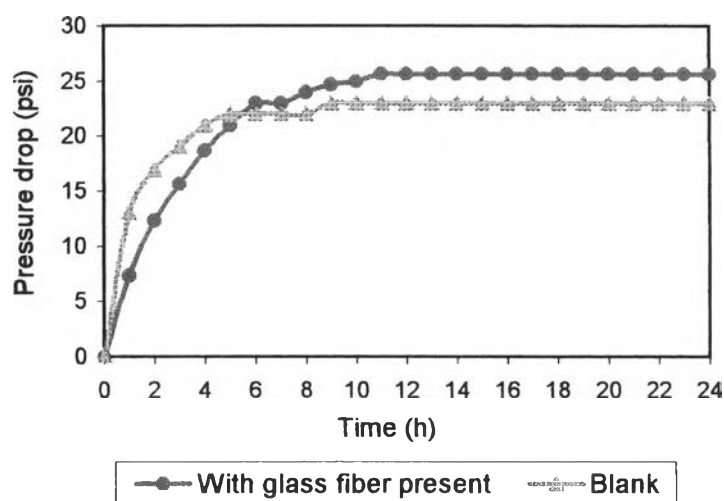


Figure 4.9 Pressure drop of ethylene (psi) for the admicellar polymerization of initiator:surfactant = 3:1 system at the reaction temperature of 70°C.

Table 4.8 Summary of ethylene pressure drop for the blank system and glass fiber/admicellar polymerization system (initiator:surfactant = 3:1) at the reaction temperature of 70°C.

Condition	Total ethylene pressure drop (psi)
Blank (without glass fiber)	23.00
System with glass fiber	25.67
ΔP	2.67

Figure 4.10 compares the pressure drop of ethylene at three different initiator to surfactant ratios for the admicellar polymerization. It can be seen that higher initiator to surfactant ratios give higher rates of polymerization. Furthermore, the net pressure drop increased with increasing initiator to surfactant ratio, i.e. 1.17, 1.67, and 2.67 psi for initiator to surfactant ratios 1:1, 2:1, and 3:1 respectively (Table 4.9).

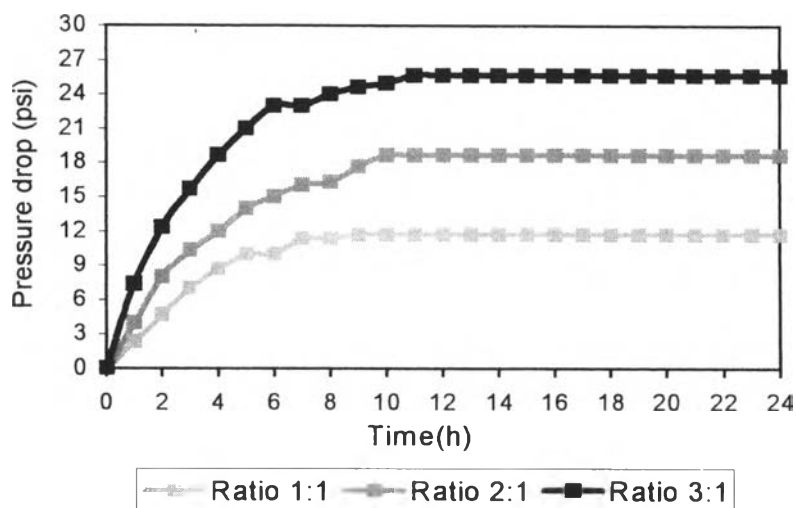


Figure 4.10 Comparison of ethylene pressure drop (psi) for different ratios of initiator:surfactant (1:1, 2:1, 3:1).

Table 4.9 Summary of ethylene pressure drop for different ratios of initiator:surfactant (1:1, 2:1 and 3:1) in the admicellar polymerization reaction.

Initiator:surfactant (molar ratio)	Net ethylene pressure drop* (psi)
1:1	1.17
2:1	1.67
3:1	2.67

*Net ethylene pressure drop is the difference between the ethylene pressure drop with glass fiber present system and that without glass fiber present.

Table 4.10 summarizes the net pressure drop of ethylene for both the adsolubilization process and the admicellar polymerization reaction. It can be concluded that the initiator did not affect the amount of ethylene consumed in the adsolubilization process, but an increase in the amount of initiator brought about an increase in pressure drop for the admicellar polymerization process. As mentioned in section 4.4, increasing the amount of initiator will lead to an increase in the aggregation number and therefore the volume of the admicelles. Thus, there will be more spaces inside the admicelles to undergo

polymerization of ethylene when the initiator to surfactant ratio is increased. Consequently, the ethylene pressure drop for the admicellar polymerization process was enhanced.

Table 4.10 Summary of total ethylene pressure drop in the adsolubilization and the admicellar polymerization steps.

Initiator:Surfactant (molar ratio)	Adsolubilization process (psi)	Admicellar polymerization (psi)	Total ethylene pressure drop (psi)
1:1	0.67	1.17	1.84
2:1	0.67	1.67	2.34
3:1	0.67	2.67	3.34

4.6 Gravimetric Analysis (Percentage Weight Loss)

Table 4.11 summarizes the percentage weight loss of the various types of surface modified glass fiber. It was found that the percentage weight loss increases with increasing initiator to surfactant ratio.

Table 4.11 Summary of percentage weight loss for the different types of surface modified glass fiber.

Type of surface modified glass fiber	Weight loss (%) [*]
Untreated glass fiber	0.01049
As-received glass fiber	0.04497
Admicellar glass fiber (initiator:surfactant = 1:1)	0.19550
Admicellar glass fiber (initiator:surfactant = 2:1)	0.24772
Admicellar glass fiber (initiator:surfactant = 3:1)	0.37832

^{*}Based on 5.0 g samples of glass fiber.

The percentage weight loss of the glass fiber is shown graphically in Figure 4.12. This clearly shows that the admicellar-treated glass fibers had significantly greater weight loss compared with the untreated and as-received glass fibers. Furthermore, the weight loss increased with increasing initiator to surfactant ratio. This indicated that at higher initiator ratio there was more coating on the surface of the glass fiber.

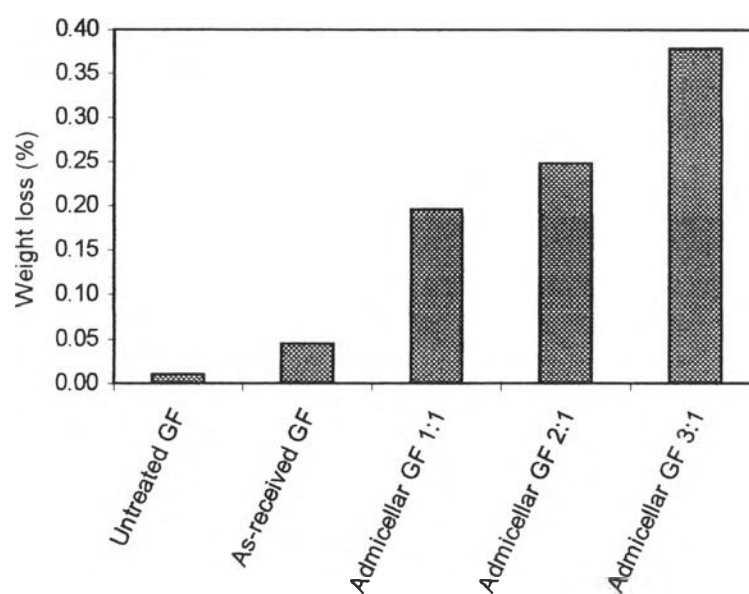


Figure 4.11 Relationship between the different types of surface modified glass fiber and percentage weight loss.

4.7 Surface Characterization on Modified Glass Fiber

As is clearly seen in Figure 4.12, when the initiator to surfactant ratio was increased there was more coating on the surface of the glass fiber and the coating tended to be thicker and also more uniform. The observations corresponded well with the amount of ethylene consumed during polymerization as well as the percentage weight loss measurements. This is

strong evidence to suggest that an increase in the amount of initiator leads to a greater amount of admicellar polymerization.

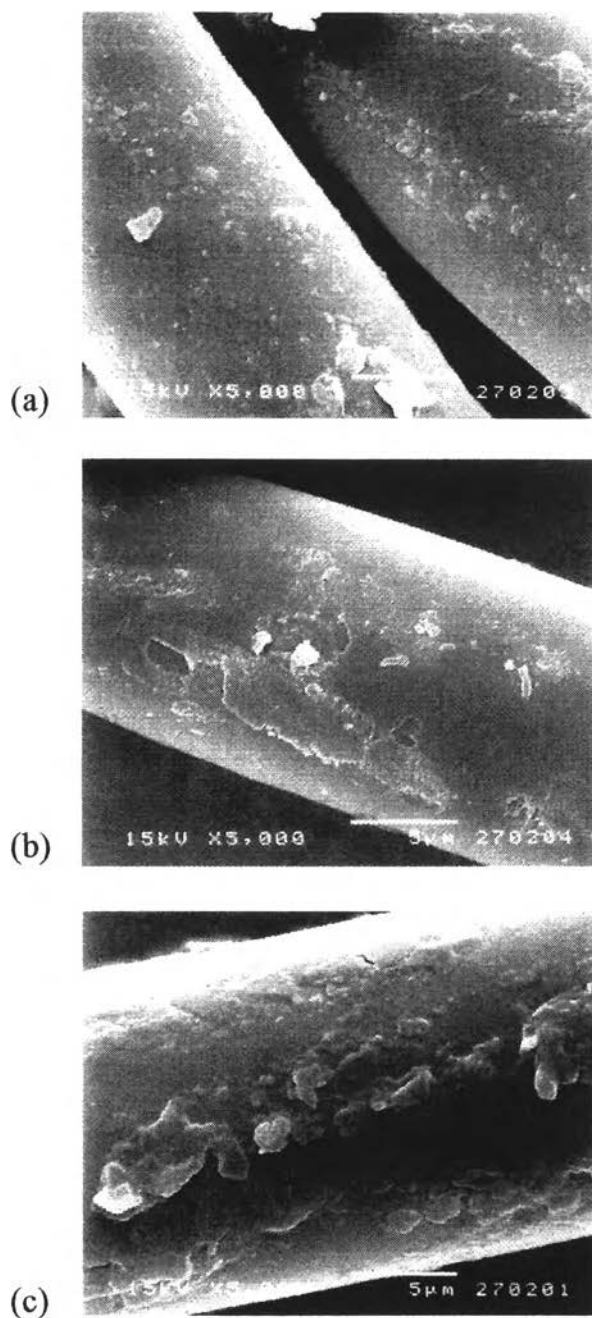


Figure 4.12 SEM micrographs of (a) admicellar-treated glass fiber with initiator to surfactant ratio 1:1 (b) admicellar-treated glass fiber with initiator to surfactant ratio 2:1 and (c) admicellar-treated glass fiber with initiator to surfactant ratio 3:1.

4.8 Mechanical Properties of Glass Fiber Reinforced HDPE Composites

The glass fiber contents of most commercial glass fiber reinforced thermoplastics range from 20 to 40%. The optimum content is based on a trade-off between desired strength levels, strength increments with added glass, overall cost, and ease of processing (Shibley, 1982). So, in this preliminary study about adhesion improvement in glass fiber/HDPE composites, 20 %wt of glass fiber content was selected for all composite materials in order to economize on the amount of glass fiber used.

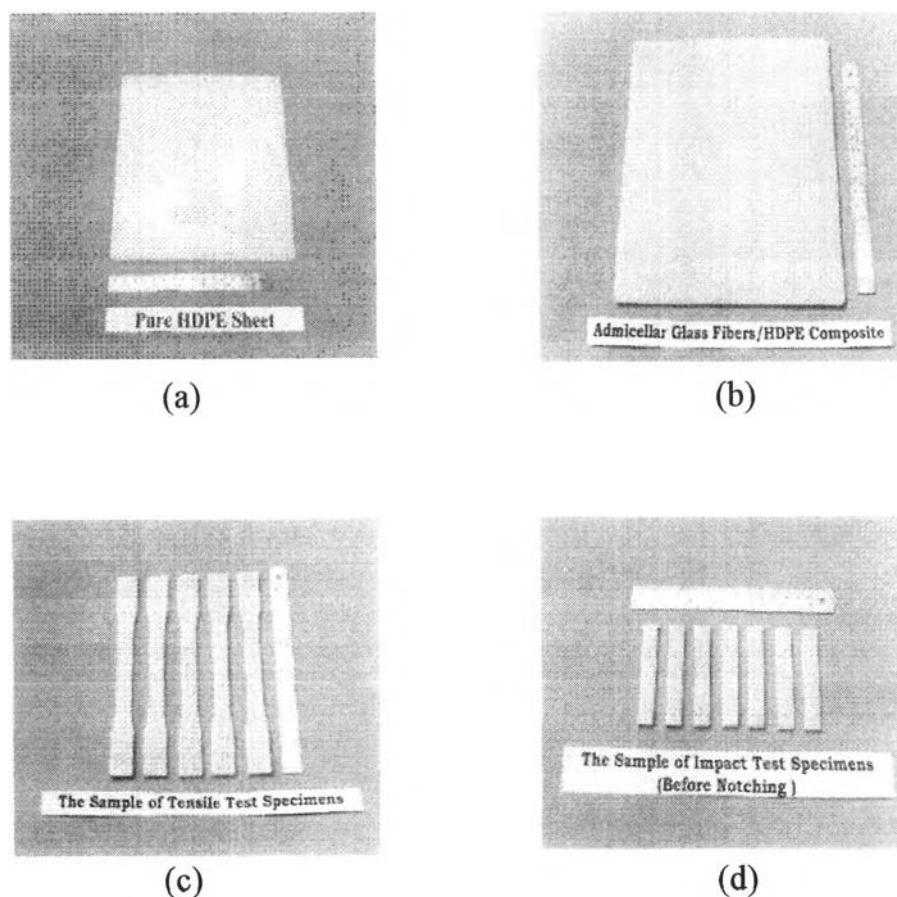


Figure 4.13 Examples of (a) pure HDPE (b) admicellar-treated glass fiber/HDPE sheet (c) tensile test specimens and (d) impact test specimens (before notching).

4.9.1 Tensile Strength

The tensile strength results for composites made from the three types of glass fibers with HDPE are shown in Table 4.12.

Table 4.12 Summary of the tensile strengths of various types of surface modified glass fiber reinforced HDPE composites.

Type of glass fiber used in composite	Tensile strength (MPa)
Untreated glass fiber	22.7 ± 0.5
As-received glass fiber	22.5 ± 0.5
Admicellar-treated glass fiber (initiator:surfactant = 1:1)	22.4 ± 0.7
Admicellar-treated glass fiber (initiator:surfactant = 2:1)	23.5 ± 0.7
Admicellar-treated glass fiber (initiator:surfactant = 3:1)	26.1 ± 0.6

The tensile strength results show that an increase in initiator to surfactant ratio brought about an increase in tensile strength for the composites made from admicellar-treated glass fiber. This trend is clearly shown in Figure 4.14, which also highlights the significant improvement in tensile strength of the higher initiator to surfactant ratio system compared with untreated and silane-treated glass fiber.

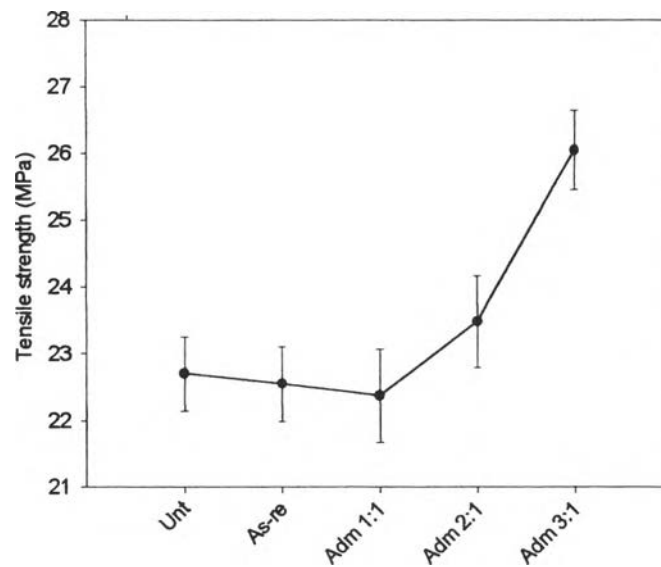


Figure 4.14 Tensile strength values for the different types of glass fiber/HDPE composites.

These results were taken to indicate that the more and thicker coating of polyethylene onto the glass fiber surface leads to a greater improvement in adhesion between glass fiber and HDPE matrix. Tensile strength is an important mechanical characteristic because it indicates the maximum load that a composite can sustain without experiencing plastic destruction or unrecoverable deformation. And the tensile strength is largely due to the fact that as a load is applied to the composite, the interfacial adhesion between fiber and matrix will limit the load-transfer process. If composites have higher fiber-matrix adhesion, the applied stress will be higher before debonding occurs and vice versa.

4.9.2 Flexural Strength

Table 4.13 illustrates the flexural results for composites made from the three types of glass fibers with HDPE. All admicellar-treated glass fiber reinforced HDPE composites had higher flexural strengths than composites made from untreated and as-received glass fiber (Figure 4.15).

For the admicellar-treated glass fiber/HDPE composites, the flexural strength increased with increasing initiator to surfactant ratio.

Table 4.13 Summary of the flexural strengths of various types of surface modified glass fiber reinforced HDPE composites.

Type of glass fiber used in composite	Flexural strength (MPa)
Untreated glass fiber	24.0 ± 1.2
As-received glass fiber	23.9 ± 0.6
Admicellar-treated glass fiber (initiator:surfactant = 1:1)	25.0 ± 0.5
Admicellar-treated glass fiber (initiator:surfactant = 2:1)	26.6 ± 0.7
Admicellar-treated glass fiber (initiator:surfactant = 3:1)	27.0 ± 1.1

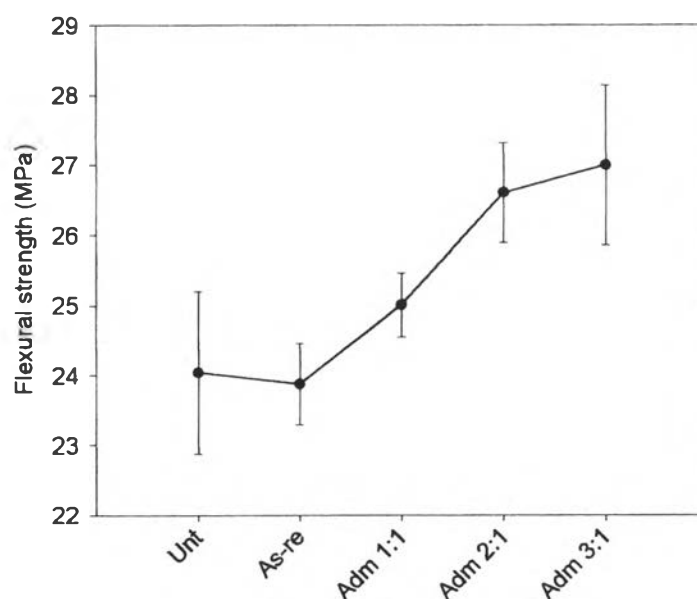


Figure 4.15 Flexural strength values for the different types of glass fiber/HDPE composites.

This result corresponded well with the tensile strength results, i.e. the more and thicker coating of polyethylene on the glass fiber surface leads to a greater improvement in adhesion between the glass fiber and HDPE matrix.

4.9.3 Impact Strength

Impact strength may be defined as toughness or the ability of a rigid material to withstand a sharp blow, such as that from a hammer (Seymour, 1993). Notched Izod impact strength results of the various types of surface modified glass fiber reinforced HDPE composites prepared are shown in Table 4.14.

Table 4.14 Summary of the Impact strengths of various types of surface modified glass fiber reinforced HDPE composites.

Type of glass fiber used in composite	Impact strength (KJ/m ²)
Untreated glass fiber	7.7 ± 0.3
As-received glass fiber	8.3 ± 0.3
Admicellar-treated glass fiber (initiator : surfactant = 1:1)	6.4 ± 0.3
Admicellar-treated glass fiber (initiator : surfactant = 2:1)	6.0 ± 0.1
Admicellar-treated glass fiber (initiator : surfactant = 3:1)	5.9 ± 0.1

As is graphically seen in Figure 4.16, when the initiator to surfactant ratio was increased, the impact strength tended to decrease. This result corresponded with the findings of Yue and Cheung (1992). They stated that the nature of the interface also has a large influence on the mode of failure and the toughness of the composites. Theoretical analysis based on the strain energy release rate of the propagation of a penny-shaped crack in a composite

has been conducted. Such an analysis showed that a strong interface would promote crack propagation across the fibers, whilst a weak interface would promote failure by fiber debonding and pull-out.

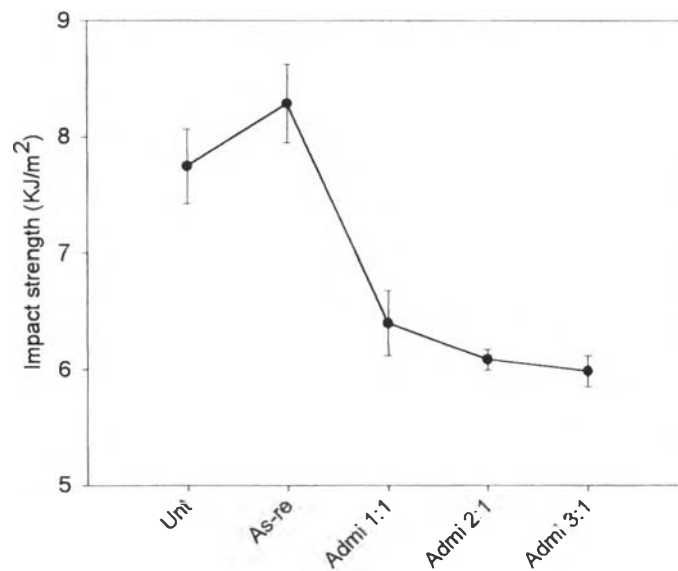


Figure 4.16 Impact strength values for the different types of glass fiber/HDPE composites.

The low impact strength values of admicellar-treated glass fiber reinforced HDPE composites indicate that the interfacial adhesion between glass fiber and HDPE matrix is perhaps rigid because a rigid, or brittle interface would promote crack propagation across the fiber.