CHAPTER IV

RESULTS AND DISCUSSION

In general, to minimize the formation of micelles in the aqueous supernatant and at the same time maximizing the amount of polymer formed in the admicelles, the desired surfactant concentration for admicellar polymerization should be maintained at or below its critical micelle concentration (CMC) (Grady *et. al.*, 1998). This limits, as much as possible, the chance of polymerization in the bulk solution. The CMC of the 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^{0}C.

Surfactant	Solvent	CMC (M)
SDS	H_2O	8.2 x 10^{-3}

However, to obtain admicelle formation, the most critical parameter to control is the solution pH. A study of PZC for the substrate provides information on the pH range to use. Glass fibers, which were used in this study, typically have PZC values in the acidic range (Sakhalkar *et. al.*, 1995). The pH of the solution was, therefore, adjusted to a low level of 4 in order to adsorb the surfactant bilayer molecules onto the glass fiber surface with their negatively charged hydrophilic head groups oriented toward the positively charged surface (because of electrostatic attraction).

4.1 Pressure Drop of Ethylene Gas.

In order to find out the exact amount of ethylene gas solubilized into the surfactant bilayers it was first necessary to determine the amount of ethylene dissolved in the water. The amount of ethylene is referred to as “the blank” (absence of surfactant and initiator).

Table 4.2 shows that the amount of ethylene of 10 psi was dissolved in the water at 25^{0}C. However, there was no ethylene pressure drop in the second step, so it was assumed that no further dissolution of ethylene in water had occurred.

Table 4.2 Summary of ethylene pressure drop for the first and second steps for the blank system.

Conditon	Ethylene pressure drop (psi)	
	First step (25^0C)	Second step (70^0C)
Blank	10.00	0.00

As can be clearly seen in Figure 4.1, the gas pressure decreased with time in the first step until it reached an equilibrium value after four hours. Then, even at the higher temperature of 70^0C, no change in pressure took place.

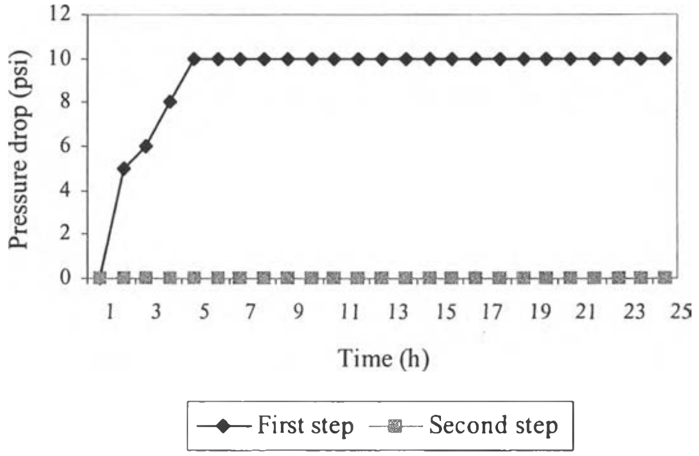


Figure 4.1 Dissolution of ethylene into water for the first and second steps of the admicellar polmerization process.

4.2 Effect of Varying the Initiator to Surfactant Ratio

Comparing the ethylene pressure drops of the two systems with and without surfactant (Table 4.3), both of which were at 8.2 mM surfactant concentration and 3:1 initiator to surfactant ratio, the difference in the ethylene pressure drops for adsolubilization was 0.67 psi. It appeared that some ethylene had dissolved in the admicelles formed on the glass fiber surface. For the admicellar polymerization step, the pressure drop difference was 2.33 psi, indicating that some polymerization had taken place in the admicelles.

Table 4.3 Summary of ethylene pressure drops for the adsolubilization and admicellar polymerization steps of the systems with and without surfactant at 8.2 mM surfactant concentration and 3:1 initiator to surfactant ratio.

Condition	Ethylene pressure drop (psi)	
	Adsolubilization	Admicellar Polymerization
Glass fiber, initiator and surfactant	10.67	26.33
Glass fiber and initiator only	10.00	24.00
ΔP	0.67	2.33

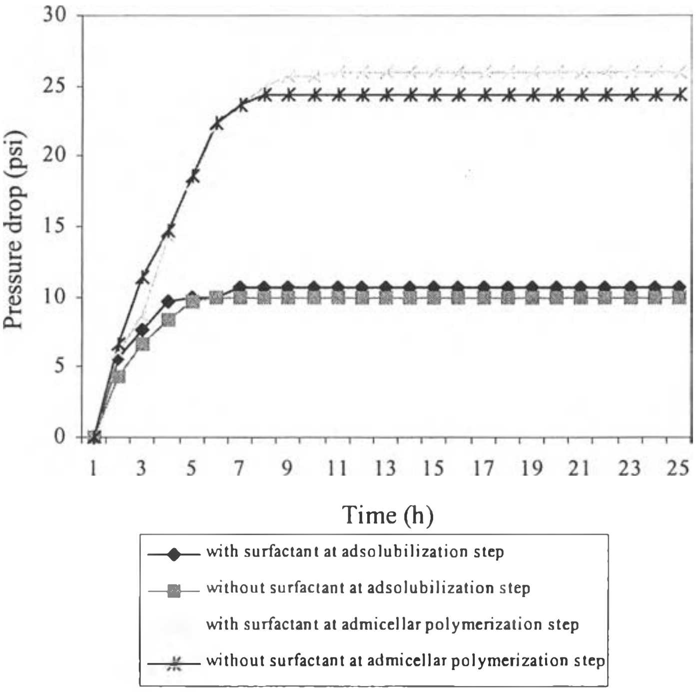


Figure 4.2 Ethylene pressure drops for the adsolubilization and admicellar polymerization steps of the systems with and without surfactant at 8.2 mM surfactant concentration and 3:1 initiator to surfactant ratio.

However, there was also some ethylene consumption in the system without surfactant in the polymerization step. This suggests that some polymerization also occurred in the aqueous medium, hereafter called 'solution polymerization'. Therefore, both solution and admicellar polymerizations appeared to take place in the system containing surfactant.

The pressure drop trends for both systems (with and without surfactant) were almost the same (Figure 4.2). This means that the rate of decrease in gas pressure was the same for each system. The system with surfactant, however, had a slightly lower equilibrium point in both adsolubilization and admicellar polymerization steps which were at 6 and 10 hours respectively. For the system without surfactant, the times to reach equilibrium were 5 and 7 hours during the adsolubilization and admicellar polymerization steps respectively. A possible explanation for this is that in the presence of surfactant in the solution, two equilibrium conditions were set up in the reaction mixture. One equilibrium is that of ethylene solubilized in the water and the other is the equilibrium of ethylene solubilized inside the admicelles. The ethylene inside admicelle came from ethylene in the water which gradually solubilized into the surfactant bilayers (admicelles) on the glass fiber surface until ethylene saturated both the water and admicelles. Moreover, it was probably easier and faster to solubilize ethylene monomer into the water.

The ethylene pressure drops during the adsolubilization step, as shown in Table 4.4, for the systems with and without surfactant, 8.2 mM surfactant concentration, and 6:1 initiator to surfactant ratio, was exactly the same as for the previous systems (with and without surfactant), viz. 8.2 mM surfactant concentration and 3:1 initiator to surfactant ratio (Table 4.3). This indicates that the amount of initiator did not affect the amount of ethylene pressure drop for the adsolubilization step. The results for the polymerization step indicate that more ethylene was polymerized when using higher amounts of initiator because an increase in free radical concentration will produce small-sized polymer molecules, but more polyethylene is formed. However, the difference in the pressure drops between the systems with and without surfactant during the admicellar polymerization step was about the same as the system with 3:1 initiator to surfactant ratio indicating that polymerization in the admicelles did not increase with an increase in initiator concentration.

Table 4.4 Summary of ethylene pressure drops for adsolubilization and admicellar polymerization steps for systems with and without surfactant at 8.2 mM surfactant concentration and 6:1 initiator to surfactant ratio.

Condition	Ethylene pressure drop (psi)	
	Adsolubilization	Admicellar Polymerization
Glass fiber, initiator and surfactant	10.67	43.67
Glass fiber and initiator only	10.00	41.67
ΔP	0.67	2.00

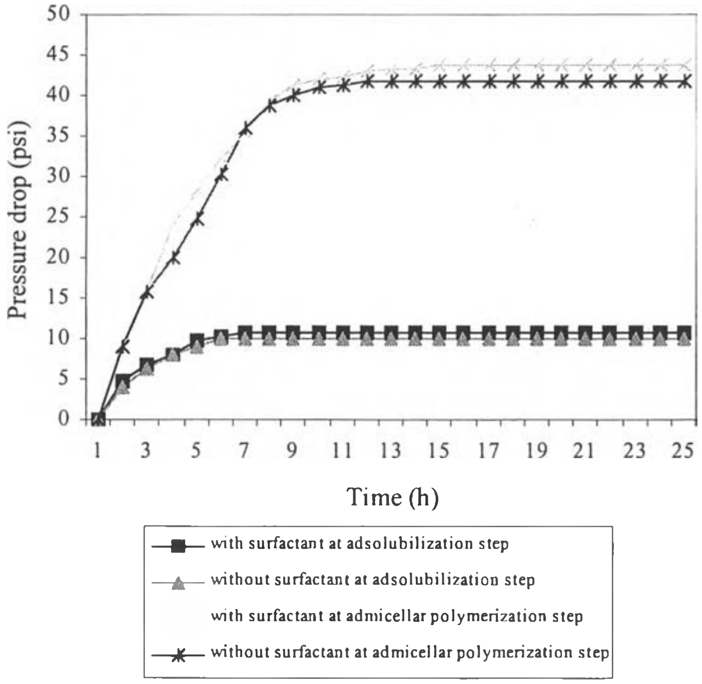


Figure 4.3 Ethylene pressure drops for the adsolubilization and admicellar polymerization steps of the systems with and without surfactant at 8.2 mM surfactant concentration and 6:1 initiator to surfactant ratio.

As for the two previous systems, the rate of adsolubilization and polymerization of ethylene monomer for these two systems with and without surfactant (8.2 mM surfactant concentration and 6:1 admicellar polymerization) was very similar, as seen in Figure 4.3. The times to reach equilibrium in the adsolubilization step for the systems with and without surfactant were also the same as the two previous systems with 8.2 mM surfactant concentration and 3:1 initiator to surfactant ratio. On the other hand, the equilibrium points of the two systems with and without surfactant in the admicellar polymerization step were 11 and 14 psi respectively. The system with surfactant reached equilibrium at a slower rate for the same reasons given for the first two systems (8.2 mM surfactant concentration and 3:1 initiator to surfactant ratio).

4.3 Effect of Varying the Amount of Surfactant Used

It was observed that for both steps – adsolubilization and admicellar polymerization – polyethylene was coated on the glass fiber surface by admicellar polymerization but to a far less extent than for polymer formed in solution, as observed from the amount of ethylene pressure drop between two systems with and without surfactant. Therefore, the effect of increasing the surfactant concentration was investigated. The surfactant concentration was increased from 8.2 mM to 15 mM. Even though the surfactant concentration was now higher than its CMC, it was expected that more polyethylene would be coated onto the glass fiber surface by admicellar polymerization.

Table 4.5 Summary of ethylene pressure drops for adsolubilization and admicellar polymerization steps for systems with and without surfactant at 15 mM surfactant concentration and 3:1 initiator to surfactant ratio.

Condition	Ethylene pressure drop (psi)	
	Adsolubilization	Admicellar polymerization
Glass fiber, initiator and surfactant	11.67	38.33
Glass fiber and initiator only	10.00	35.33
ΔP	1.67	3.00

It can be seen (Table 4.5) that there was a slight increase in the difference in ethylene pressure drops during the adsolubilization and admicellar polymerization steps indicating that an increase in the amount of surfactant led to a small increase in ethylene pressure drop in the admicellar polymerization step. In the case of 15 mM surfactant concentration, there was an increase in ethylene pressure drop in the polymerization step when compared to the reaction with 8.2 mM surfactant concentration. This suggests that micelles might have occurred in solution (emulsion polymerization) since the surfactant concentration used was well above its CMC. Therefore, the solubility of ethylene monomer in the medium was enhanced due to the solubilization of ethylene in micelles in the aqueous phase. This, in turn, means that the presence of micelles promotes the solubility of the monomer in the solution and increases the rate of solubilization of the monomer in the micelles. Therefore, there appeared to be three types of polymerization occurring in this system, viz. emulsion, admicellar and solution polymerizations.

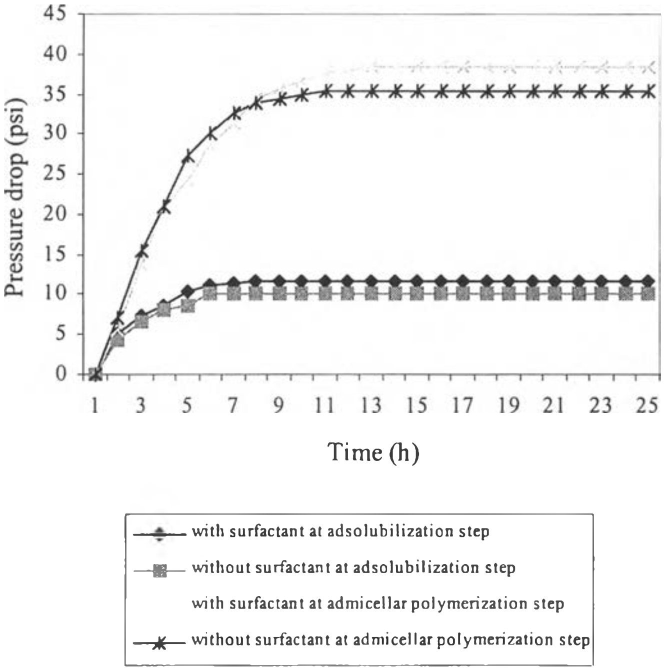


Figure 4.4 Ethylene pressure drop for the adsolubilization and admicellar polymerization steps of the systems with and without surfactant at 15 mM surfactant concentration and 3:1 initiator to surfactant ratio.

Figure 4.4 shows that the time to reach equilibrium for both adsolubilization and admicellar polymerization with surfactant present was still lower than the system without surfactant. Moreover, there was the extra emulsion polymerization process present, so the time to reach equilibrium (7 hours) in the adsolubilization step was lower than for the two previous systems with surfactant present (8.2 mM surfactant concentration and 3:1 and 6:1 initiator to surfactant ratio).

It can be seen in Figure 4.5 that for the adsolubilization step for the three systems with surfactant, the rate of attainment of equilibrium pressure drops were almost the same. On the other hand, when higher amounts of initiator were used, the equilibrium point for the admicellar polymerization step was reached much slower; 10 hours and 14 hours for the two systems with 8.2 mM surfactant concentration and 3:1 and 6:1 initiator to surfactant ratio respectively, and 12 hours for the 15 mM surfactant concentration and 3:1 initiator to surfactant ratio system. The reason for the longer reaction times to reach equilibrium was that more ethylene could be polymerized in the system.

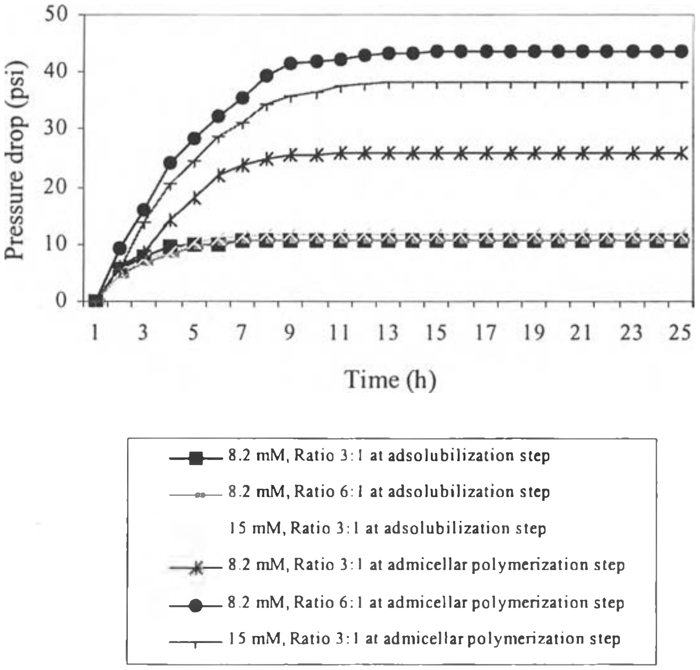


Figure 4.5 Ehylene pressure drops for various system conditions containing surfactant.

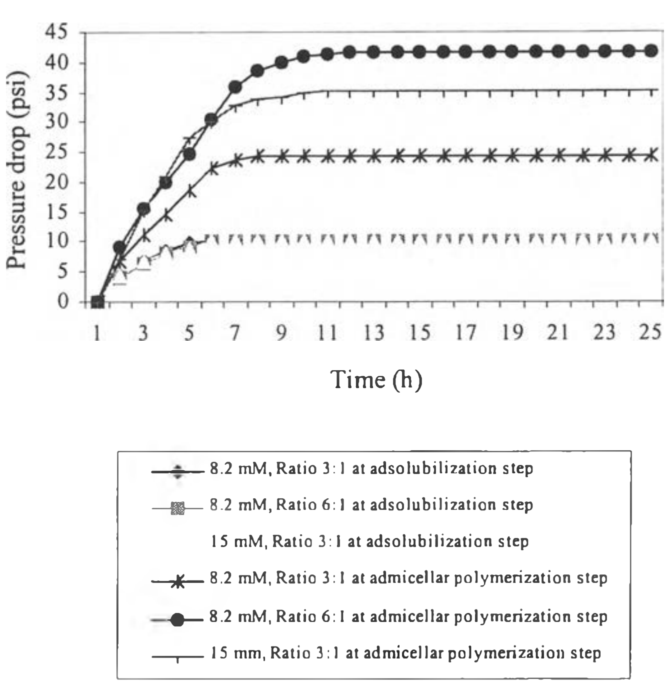


Figure 4.6 Ethylene pressure drops for various conditions of the systems in absence of surfactant.

For the systems containing surfactant, the same trends were observed as for the systems without surfactant (Figure 4.6). That is, the equilibrium times were the same for each system for the adsolubilization step. Furthermore, the times to reach equilibrium in the admicellar polymerization steps decreased with increasing amount of initiator; 7 hours and 11 hours for the two systems with 8.2 mM surfactant concentration and 3:1 and 6:1 initiator to surfactant ratio respectively, and 12 hours for the 15 mM surfactant concentration and 3:1 initiator to surfactant ratio system.

Table 4.6 Summary of ethylene pressure drops for adsolubilization and admicellar polymerization steps for all systems with and without surfactant at various surfactant concentrations and initiator to surfactant ratios.

Surfactant concentration (mM)	Initiator to surfactant ratio	Condition	Ethylene pressure drop (psi)	
			Adsolubilization	Admicellar Polymerization
8.2	3:1	Glass fiber, initiator and surfactant	10.67	26.33
8.2	3:1	Glass fiber and initiator only	10.00	24.00
8.2	6:1	Glass fiber, initiator and surfactant	10.67	43.67
8.2	6:1	Glass fiber and initiator only	10.00	41.67
15.0	3:1	Glass fiber, initiator and surfactant	11.67	38.33
15.0	3:1	Glass fiber and initiator only	10.00	35.33

Table 4.6 summarizes all the systems studied. The data indicates that polymerization occurred not only in the admicelles but also in the supernatant. With increasing initiator to surfactant ratio, more polyethylene occurred in both the aqueous solution and in the admicelles. In other words, increasing the surfactant concentration generated micelles in the solution, i.e. emulsion polymerization occurred.

4.4 Gravimetric Analysis (Percentage Weight Loss)

Table 4.7 shows the weight loss of polyethylene for various system conditions.

Table 4.7 Summary of percentage weight loss for different types of surface modified glass fibers.

Surfactant concentration (mM)	Initiator to surfactant ratio	Condition	Weight loss (%)
-	-	As-received glass fiber	0.0672
-	-	Untreated glass fiber	0.0300
8.2	3:1	Admicellar and solution-treated glass fiber	0.1636
8.2	3:1	Solution-treated glass fiber	0.1552
8.2	6:1	Admicellar and solution-treated glass fiber	0.2003
8.2	6:1	Solution-treated glass fiber	0.1970
15.0	3:1	Micelle, admicellar and solution-treated glass fiber	0.1719
15.0	3:1	Solution-treated glass fiber	0.1702

It can be seen from Table 4.7 that untreated glass fibers had the lowest weight loss. This was expected because the glass fibers were unmodified. The highest weight loss recorded was for the system with 6:1 initiator to surfactant ratio and 8.2 mM surfactant concentration. This system contained the highest amount of initiator, so more ethylene monomer could have been polymerized on the fiber surface. These results correlate well with the amount of ethylene consumed, as determined by the relative gas pressure drops of the different systems.

In addition, there was a weight loss of polyethylene for the system without surfactant. This suggests that after ethylene had been polymerized in the aqueous solution, it was deposited on the glass fiber surface. Compared to the systems in which glass fibers were modified by admicellar polymerization, the percentage weight loss of the system without surfactant was less because the system without surfactant was composed of only one kind of polymerization, i.e. solution polymerization (Figure 4.7). The results correlate well with the increase in ethylene pressure drop in the presence of surfactant then confirming that both admicellar and solution polymerization took place in the system with surfactant.

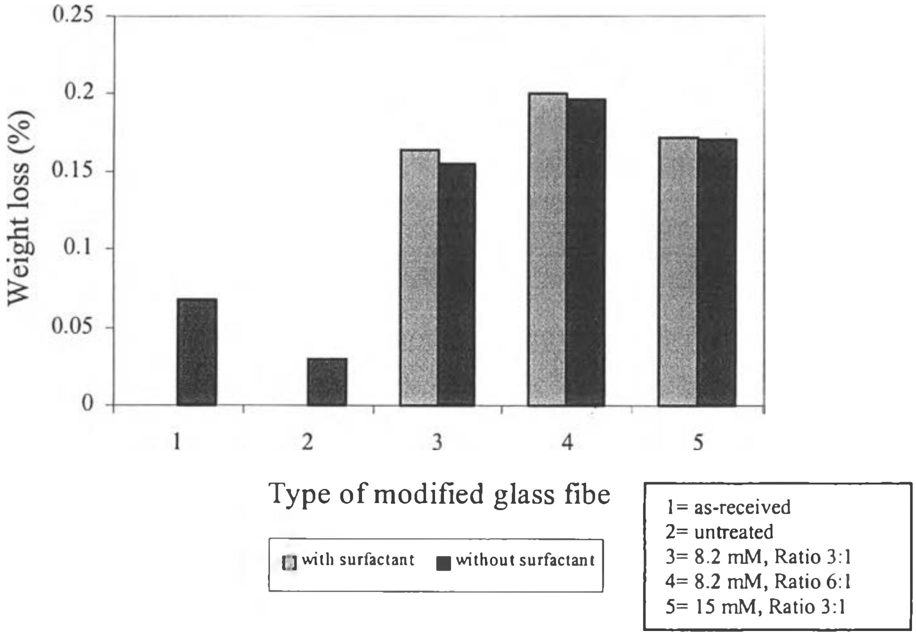
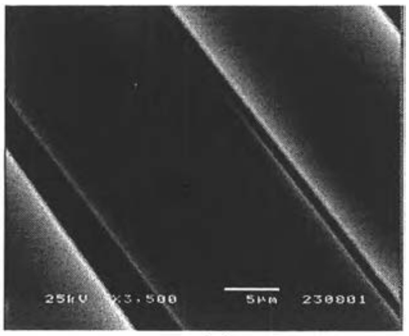


Figure 4.7 Relationship between the various types of surface modified glass fiber and percentage weight loss.

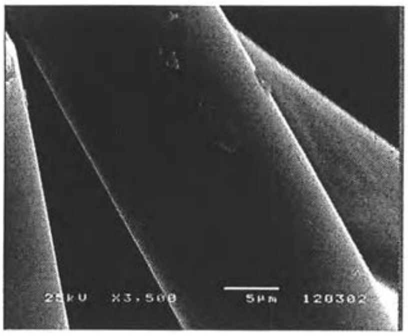
For the same initiator to surfactant ratio of 3:1 the percentage weight loss of polyethylene for the system with 15 mM surfactant concentration was higher than the percentage weight loss of polyethylene for the system having 8.2 mM surfactant concentration because in addition to there being three types of polymerization taking place, there was also a higher amount of initiator present.

4.5 Surface Characterization of Modified Glass Fiber

Scanning electron microscopy was used to observe the nature of the polymer – fiber interface. Glass fibers themselves and the interfaces between glass fiber and polyethylene were observed to check for the presence of a polymer film. Firstly, the surfaces of untreated and as-received glass fibers were studied.



(a)



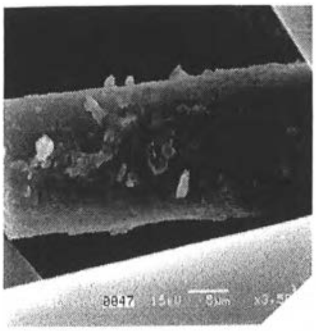
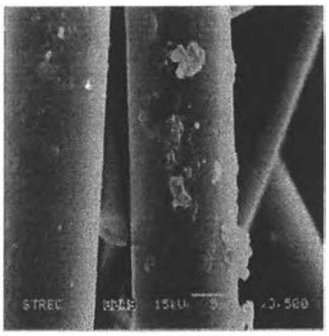
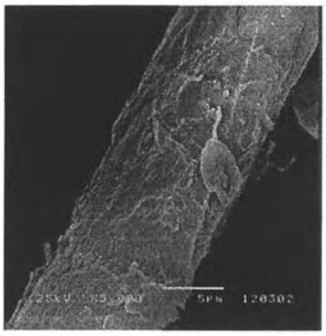
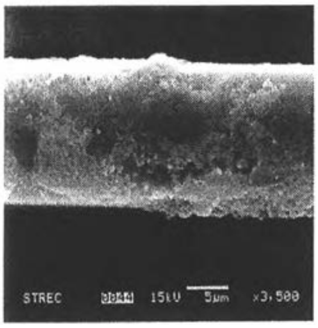
(b)

Figure 4.8 SEM micrographs of (a) untreated glass fiber and (b) as-received glass fiber.

SEM micrographs (Figure 4.8) show that as-received glass fiber (b) had a smooth surface with small islands of sizing spread over its surface, whereas the untreated glass fiber (a) showed a clean, smooth surface. This indicates that the sizing had been completely removed from the as-received glass fibers.

Then, the various kinds of modified glass fiber surface were studied. The micrographs shown in Figure 4.9 represent the two systems having 8.2 mM surfactant concentration, i.e. the 3:1 and 6:1 initiator to surfactant ratio systems.

Figure 4.9 SEM micrographs of polyethylene coated onto glass fiber surfaces at 8.2 mM surfactant concentration and varying initiator to surfactant ratios.

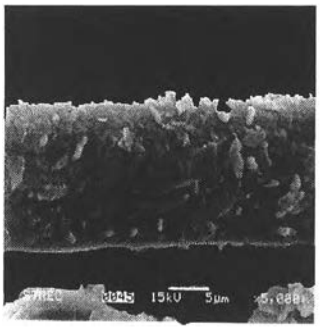
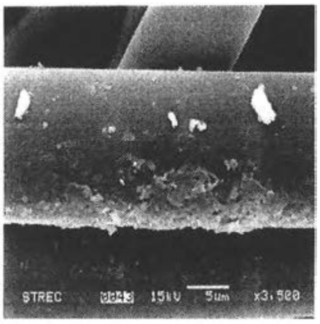
Initiator to surfactant ratio	Surface treated glass fiber	
	Admicellar and solution-treated glass fiber	Solution-treated glass fiber
3:1		
6:1		

The micrographs of treated glass fibers (Figure 4.9) showed nonuniform coatings of polymer on the glass fiber surfaces. Sakhalkar *et al.* (1995) proposed that this nonuniform coating using admicellar polymerization could be due to the unequal distribution of charges on the surface of the glass fibers. They stated that it is known that glass is composed of silica and alumina as its major constituents along with other metal oxides. Hence, the glass fibers will have both silica and alumina molecule present on the surface in large proportions. Pure silica and alumina have points of zero charge at pH values of approximately 3 and 10, respectively. Therefore, at a pH of 4, the positive charge on those parts of the glass fibers having silica on its surface may not be large enough to maintain a strong electrostatic attraction between anionic surfactant molecules and the glass fiber surface. On the other hand, those portions with alumina on the surface are able to attract enough surfactant molecules to form admicelles. However, similar island formation has been reported on surfaces of pure quartz. This suggests that, in addition to this charge effect, there could be other effects such as surface roughness or cleanliness that could effect the coverage for certain types of cooperative interaction.

On the other hand, for fibers coated by solution polymerization only, the micrographs indicate the presence of globules of polymer on the glass fiber surface. This demonstrates that there was indeed polymerization occurring in the supernatant and that polymer, after being formed, was deposited onto the glass fiber surface. However, there were two kinds of polymerization in the systems containing surfactant, i.e. admicellar and solution polymerizations. Thus, both film formation and polyethylene formed in solution appear to have coated the glass fiber surface. Thus, more polyethylene covered the surface of glass fiber in systems containing surfactant compared with systems without surfactant.

For both systems with and without surfactant, it was found that an increase in the amount of initiator caused more polyethylene to be deposited onto the glass fiber surface.

Figure 4.10 SEM micrographs of polyethylene coated onto glass fiber surfaces at 15 mM surfactant concentration and 3:1 initiator to surfactant ratio.

Surface treated glass fiber	
Micelle, admicellar and solution-treated glass fiber	Solution-treated glass fiber
	

It can be seen in Figure 4.10 that at high surfactant concentrations there are several types of polymerization reactions taking place. Therefore, polyethylene film was deposited on the fibers via admicellar polymerization together with polyethylene formed in solution (by emulsion and solution polymerization). However, the layer of polyethylene that formed in the system having a surfactant concentration of 15 mM and 3:1 initiator to surfactant ratio was thicker than for the system with surfactant concentration of 8.2 mM and both 3:1 initiator to surfactant ratios.

4.6 Mechanical Properties of Glass Fiber Reinforced HDPE Composites

In this preliminary study of 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. The optimum fiber content is based on a trade-off between desired strength levels, strength increments with added glass, overall cost, and ease of processing (Shibley, 1982).

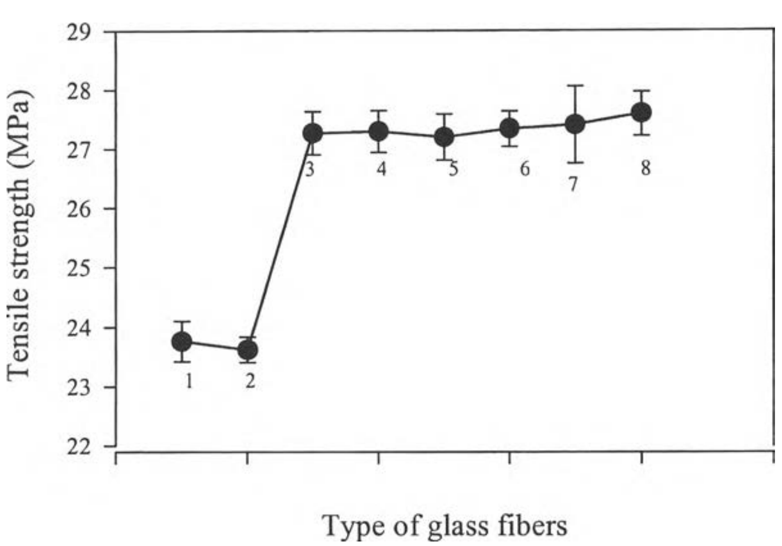
4.6.1 Tensile Strength

Table 4.8 shows the tensile results of various types of glass fiber reinforced HDPE composites. As-received and untreated glass fiber reinforced HDPE had low tensile strengths compared with the composites made with modified glass fiber. Hence, the interaction between polyethylene and pure glass fiber was very poor. Surprisingly, the as-receive glass fiber did not improve the adhesion between fiber and matrix even though the use of adhesion promoters (such as silanes), to improve the properties of the interface between a polymer and an inorganic phase, is well known. A possible reason is that polyethylene is a chemically inert material and will act as a barrier for any interactions, so that the interaction between an organofunctional silane and polyethylene is weak.

Table 4.8 Summary of tensile strengths of various types of surface modified glass fiber reinforced HDPE composites.

Type of glass fiber used in composite			Tensile strength (MPa)
Surfactant concentration (mM)	Initiator to surfactant ratio	Condition	
-	-	As-received glass fiber	23.761±0.34
-	-	Untreated glass fiber	23.615±0.21
8.2	3:1	Admicellar and solution-treated glass fiber	27.269±0.36
8.2	3:1	Solution-treated glass fiber	27.296±0.35
8.2	6:1	Admicellar and solution-treated glass fiber	27.201±0.39
8.2	6:1	Solution-treated glass fiber	27.341±0.30
15.0	3:1	Micelle, admicellar and solution-treated glass fiber	27.408±0.65
15.0	3:1	Solution-treated glass fiber	27.882±0.35

Furthermore, tensile strength increased when the glass fibers were modified, as clearly seen in Figure 4.11. An increase in tensile strength accompanied an increase in stiffness but a reduction in toughness. Thus, it can be concluded that admicellar polymerization increases the interfacial bond strength because if the interface is well bonded, the stress can transfer across the fiber-matrix interface several times, hence the high strength composite. Nevertheless, the absence of surfactant also improved the adhesion between the glass fiber and matrix. The results show that polyethylene deposited on the glass fiber surface due to solution polymerization is as effective in improving adhesion in the composite as the polymer obtained from admicellar and solution polymerization.



1= as-received
2= untreated
3= admicellar and solution-treated at 8.2 mM, initiator surfactant ratio at 3:1
4= solution-treated at 8.2 mM, initiator to surfactant ratio at 3:1
5= admicellar and solution-treated at 8.2 mM, initiator to surfactant ratio at 6:1
6= solution-treated at 8.2 mM, initiator to surfactant ratio at 6:1
7= micelle, admicelle and solution-treated at 15 mM , initiator to surfactant ratio at 3:1
8= solution-treated at 15 mM, initiator to surfactant ratio at 3:1

Figure 4.11 Tensile strengths of different types of glass fiber/HDPE composites.

4.6.2 Flexural Strength

The results of flexural strength values for both unmodified and modified glass fibers are given in Table 4.9.

Composites made with modified glass fibers had high flexural strength compared with composites made with untreated and as-received glass fibers, as seen in Figure 4.12. These results correlate well with the tensile results (Figure 4.11). This demonstrates that the adhesion between the glass fibers and HDPE matrix was improved when all kinds of polymerization methods were used to coat the glass fiber surfaces.

Table 4.9 Summary of flexural strengths of various of surface modified glass fibers reinforced HDPE composites.

Type of glass fiber used in composite			Flexural strength (MPa)
Surfactant concentration (mM)	Initiator to surfactant ratio	Condition	
-	-	As-received glass fiber	33.081±0.29
-	-	Untreated glass fiber	33.003±0.34
8.2	3:1	Admicellar and solution-treated glass fiber	34.866±0.61
8.2	3:1	Solution-treated glass fiber	35.878±0.64
8.2	6:1	Admicellar and solution-treated glass fiber	35.607±0.62
8.2	6:1	Solution-treated glass fiber	34.794±0.40
15.0	3:1	Micelle, admicellar and solution-treated glass fiber	35.647±0.72
15.0	3:1	Solution-treated glass fiber	35.211±0.54

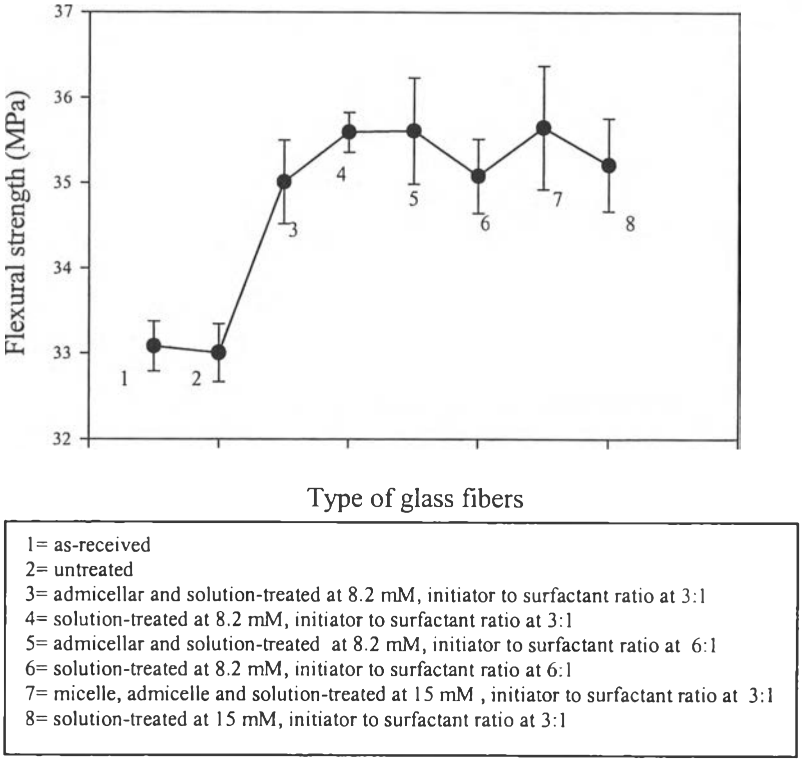


Figure 4.12 Flexural strengths of different types of glass fiber/HDPE composites.

4.6.3 Impact Strength

Conventional Izod impact tests measure the energy required to break a notched specimen. The toughness of polymers can be quantified by their impact strength.

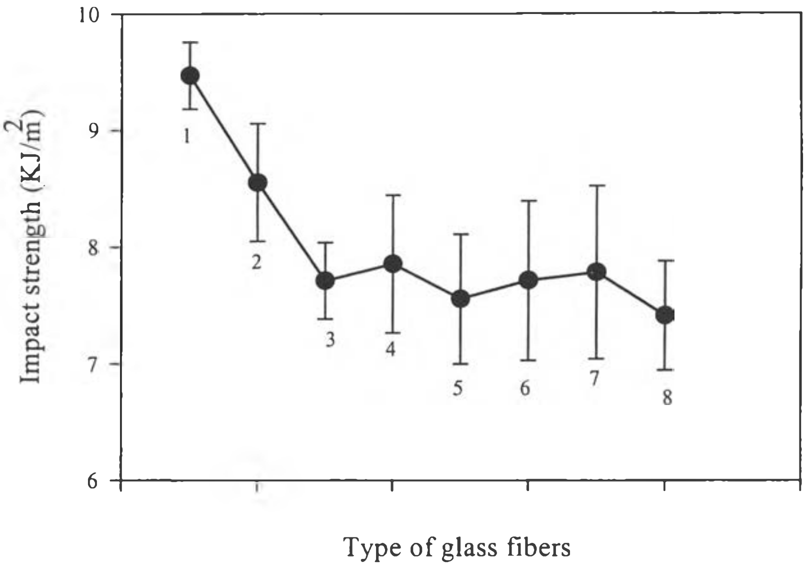
Table 4.10 gives a summary of the impact strengths of various types of surface-modified glass fiber reinforced HDPE composites. The results show that the impact strength of modified glass fiber composites were slightly lower than for composites made from using unmodified glass fibers.

Table 4.10 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)
Surfactant concentration (mM)	Initiator to surfactant ratio	Condition	
-	-	As-received glass fiber	9.50±0.29
-	-	Untreated glass fiber	8.55±0.50
8.2	3:1	Admicellar and solution-treated glass fiber	7.71±0.33
8.2	3:1	Solution-treated glass fiber	7.86±0.59
8.2	6:1	Admicellar and solution-treated glass fiber	7.56±0.56
8.2	6:1	Solution-treated glass fiber	7.71±0.68
15.0	3:1	Micelle, admicellar and solution-treated glass fiber	7.78±0.74
15.0	3:1	Solution-treated glass fiber	7.27±0.57

Figure 4.13 clearly shows that composites made from as-received glass fiber had the highest impact strength. This is probably due to a weak fiber – matrix interface because a weak interface would promote failure at the fiber – matrix interface. The second toughest material was the untreated glass fiber composite.

Moreover, all modified glass fiber composites had relatively low impact strengths and had similar values. Low impact strength may indicate that the interface has a propensity to undergo brittle fracture. This type of failure could occur if the interfacial adhesion between the glass fiber and HDPE matrix is very rigid because a rigid, or brittle interface would promote crack propagation across the fiber.



1= as-received
2= untreated
3= admicellar and solution-treated at 8.2 mM, initiator to surfactant ratio at 3:1
4= solution-treated at 8.2 mM, initiator to surfactant ratio at 3:1
5= admicellar and solution-treated at 8.2 mM, initiator to surfactant ratio at 6:1
6= solution-treated at 8.2 mM, initiator to surfactant ratio at 6:1
7= micelle, admicelle and solution-treated at 15 mM , initiator to surfactant ratio at 3:1
8= solution-treated at 15 mM, initiator to surfactant ratio at 3:1

Figure 4.13 Impact strengths of the different types of glass fiber/HDPE composites.