CHAPTER IV
RESULTS AND DISCUSSION

4.1 Properties of Cellulose Fibers-g-TDI/18OH (Modified Cellulose Fibers)

4.1.1 Characterizations of Surface Modified Fibers

The thermogravimetric curves of unmodified and modified fibers were studied by TGA. In all cellulose fiber samples, there is an initial weight loss, around 5%, between 50 and 100°C which is attributed to the elimination of the humidity or water retained in the samples (Khullar R. *et al.* 2008). The onset of thermal degradation can be identified by a dramatic decrease in sample weight and increase in the temperature difference due to the exothermic combustion reactions taking place (Beckermann G.W. *et al.* 2008).

The thermogravimetric results of polypropylene (PP) and cellulose fiber (CMF) show distinct processes of weight loss occurring at different temperatures, Figure 4.1. For PP, there is only one weight loss process, while the CMF curve shows evidence of two weight loss processes. From the TGA curve, it is possible to observe the starting of CMF weight loss at 313°C. The first process of weight loss of CMF is attributed to the thermal degradation of pectine, lignin and hemicellulose that is contained in the fiber (Tomezak F. *et al.* 2007). The next weight loss is associated with the decomposition of cellulose within the fiber. The TGA curve of PP shows the starting of volatiles emission at 424°C and 442°C (for CMF and CF samples, respectively).

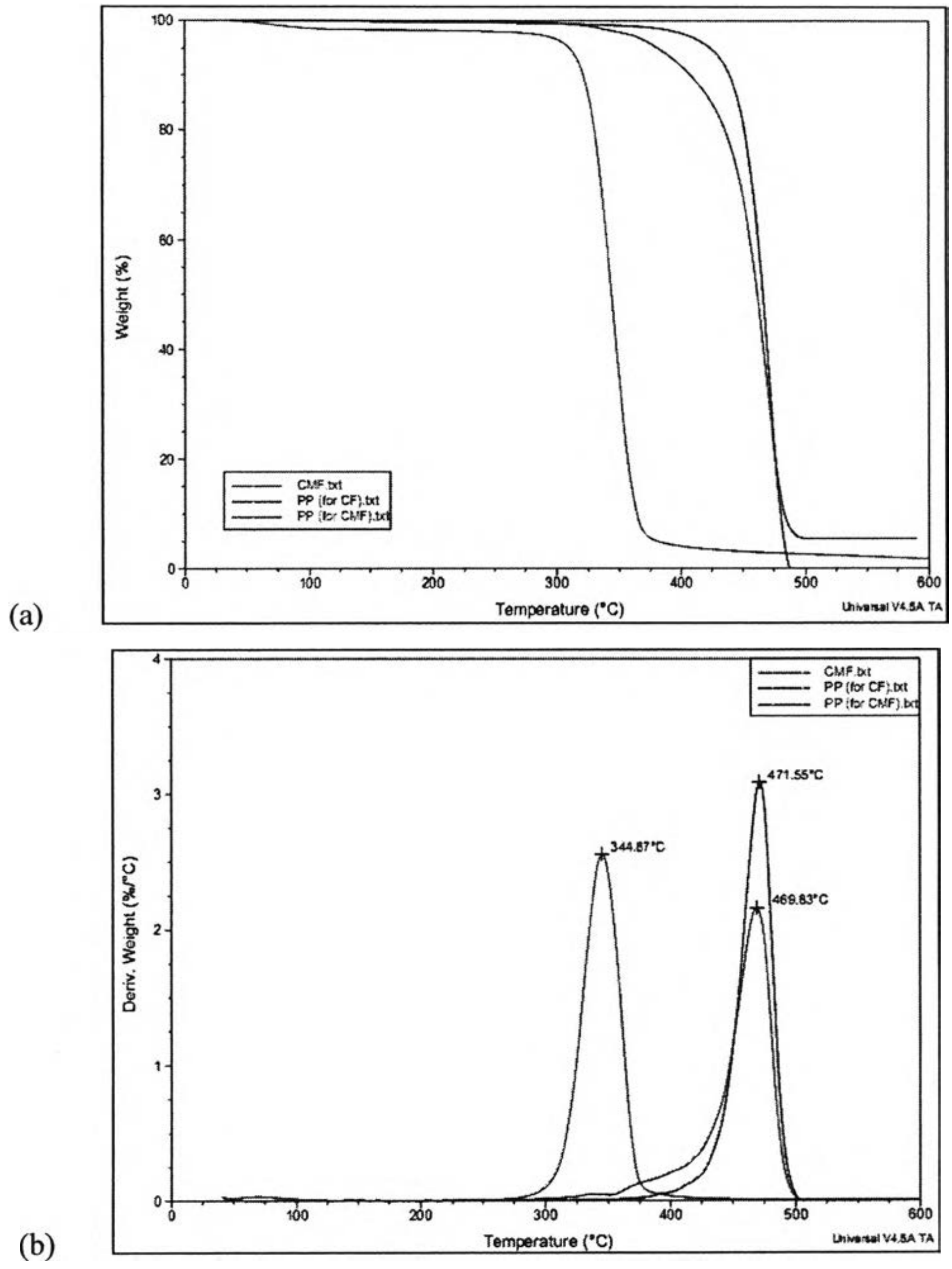


Figure 4.1 (a) TGA and (b) DTA curves of pure PP and CMF.

The thermal degradation of CF, Figure 4.2, begins at 333°C, while the thermal degradation of CF-g-TDI/18OH starts at 339°C. This result indicated that grafting with

TDI/18OH modifier reduces the overall thermal stability of CF because the modified surface decomposes at a lower temperature than the unmodified CF.

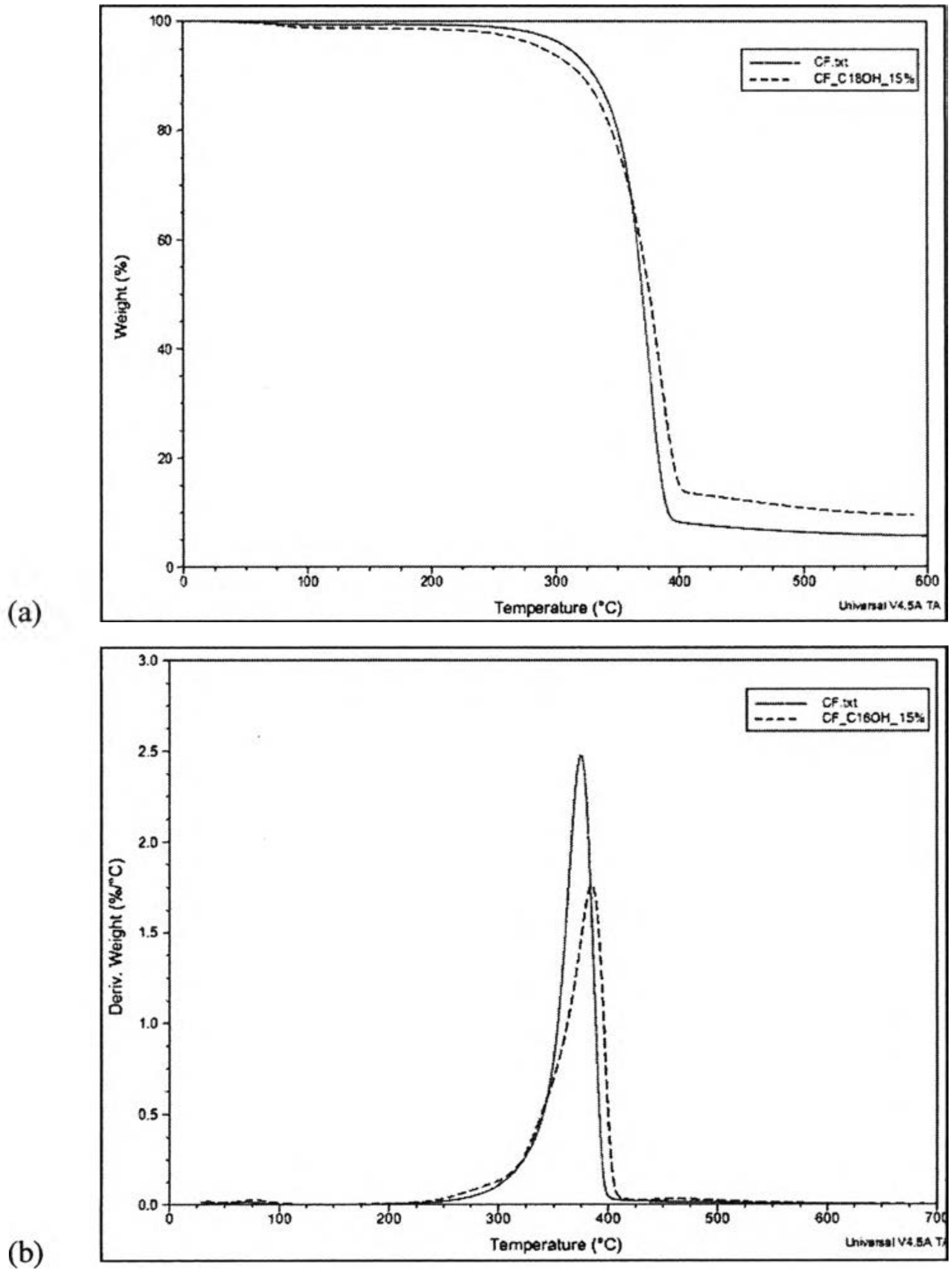


Figure 4.2 (a) TGA and (b) DTA curves of CF and CF-g-TDI/18OH.

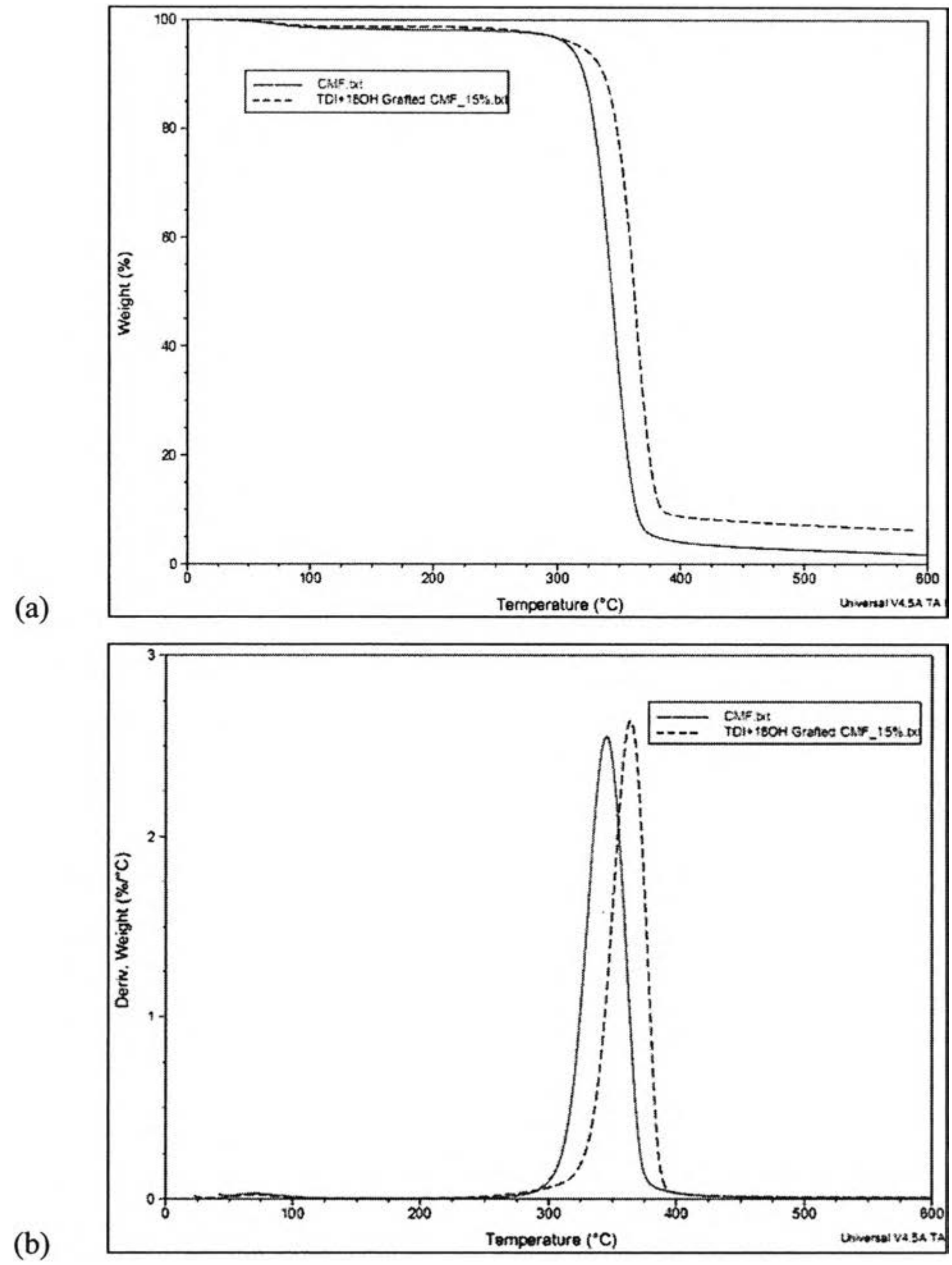


Figure 4.3 (a) TGA and (b) DTA curves of CMF and CMF-g-TDI/18OH.

On the other hand, the onset temperature of the decomposition for TDI/18OH modified CMF is 339°C compared to 324°C for unmodified CMF, Figure 4.3. The percent weight loss of CMF-g-TDI/18OH shows two degradation steps at 339°C and 378°C which correspond to the decomposition of the surface modifier and cellulose fiber, respectively.

The TGA confirms the successful grafting of the TDI/18OH coupling agent on CMF (Lu J. *et al.* 2008). The thermal analysis of different fiber types was also reported by Mohanty (Mohanty A.K. *et al.* 2000). Moreover, the grafting yield and efficiencies were calculated and shown in Table 4.1.

Table 4.1 The grafting yield and efficiency of modified cellulose fibers

Sample	Grafting Efficiency (%)	Grafting Yield (%)
CF-g-TDI/18OH	5.84	4.38
CMF-g-TDI/18OH	7.73	5.79

The unmodified and modified cellulose fibers were characterized by FTIR spectroscopy, Figure 4.4. The broad absorption band between 3000 and 3650 cm^{-1}, which corresponds to the hydroxyl groups stretching vibrations of anhydroglucose units in cellulose fibers (Qingxiu L. *et al.* 2003; Vaibhav J. *et al.* 2007; LORI ′A–BASTARRACHEA M.I. *et al.* 2002), is detected in both spectra. The widening of this band is caused by intermolecular hydrogen bonds among the hydroxyl groups (H–O–H) (CANCHE ′–ESCAMILLA G. *et al.* 1997). Additional characteristic bands at 2887, 1366 and 1326 cm^{-1} appeared due to the stretching of methyl and methylene (CH_3 and CH_2) linkages. A slight increase in the intensity of these stretching vibrations is observed due to the presence of TDI/18OH grafted on the CMF surface. The isocyanates coupling 1–Octadecanol and grafted cellulose fibers displayed the appearance of a very strong absorption band of amide functional groups at 1637 cm^{-1}, which belongs to the grafted fibers. This is related to the presence of these bonds in the chemical structure of TDI/18OH that has reacted with CMF. The weak band at 1055 cm^{-1} is attributed to the skeletal vibration involving C–O stretching of the cellulose backbone (LORI ′A–

BASTARRACHEA M.I. *et al.* 2002). In the CMF-g-TDI/18OH spectra, the presence of a band at 898 cm^{-1} associated with the presence of the di–substitute aromatic ring confirmed the occurrence of chemical bonds between cellulose fibers and the modifier agent studied (TDI/18OH) (Ly B. *et al.* 2008).

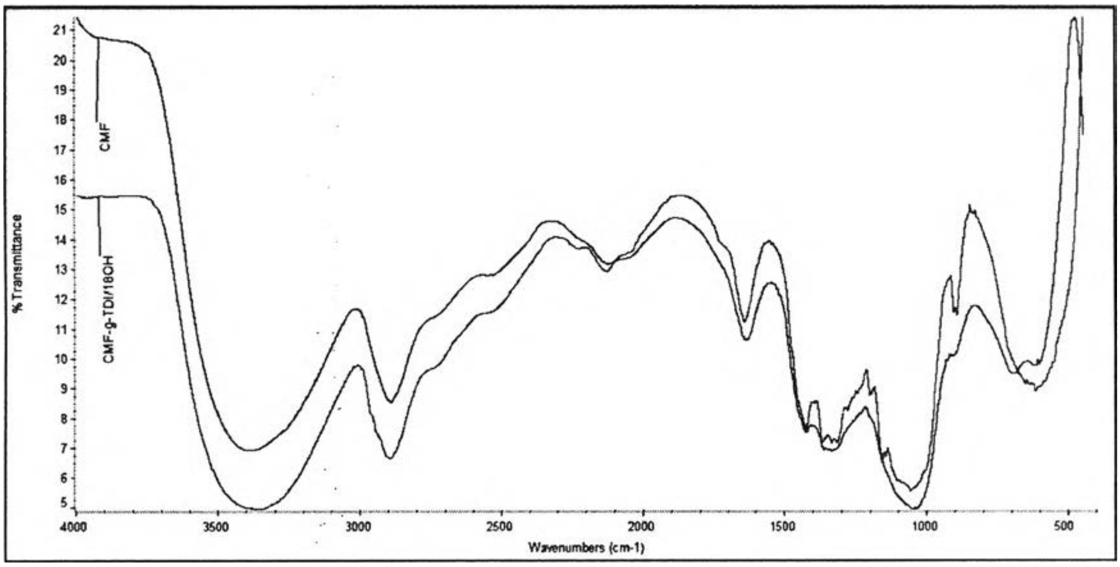


Figure 4.4 FTIR spectra of CMF and CMF-g-TDI/18OH.

4.1.2 Surface Wettability

The results from the static contact angle measurement, Figure 4.5, show that a water droplet was absorbed instantly at the dropping on the surface of unmodified CF and CMF. While a water droplet can stand on the surface of CF-g-TDI/18OH and CMF-g-TDI/18OH grafted products at 136.8° and 111.0°, respectively. The increasing of the contact angle on grafted samples demonstrated an enhancement of the hydrophobic character of the cellulose fibers (Mohanty A.K. *et al.* 2000) and a lower value for the polar component of the surface energy (Carvalho A.J.F. *et al.* 2005).

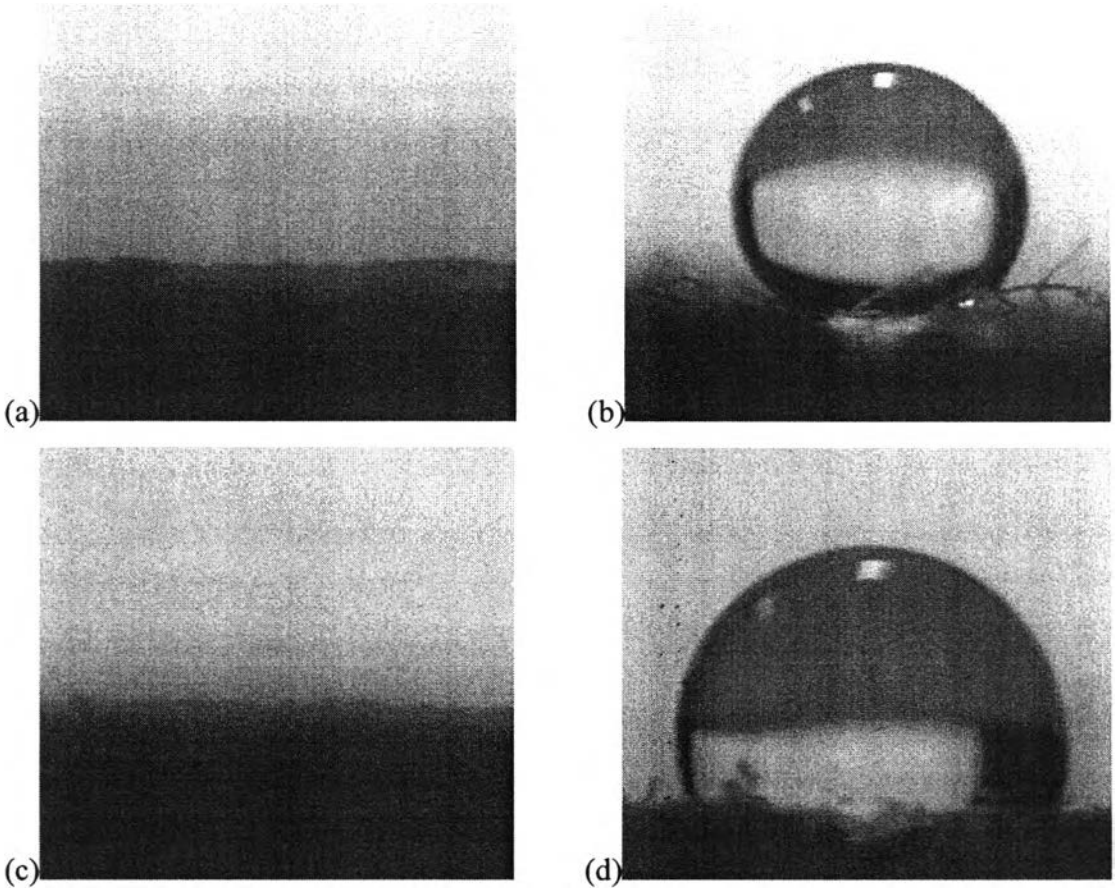


Figure 4.5 Contact angle images of (a) CF (b) CF-g-TDI/18OH, 136.8° (c) CMF and (d) CMF-g-TDI/18OH, 111.0°.

4.2 Properties of PP/Cellulose Fibers-g-TDI/18OH Composites

4.2.1 Mechanical Properties of PP–reinforced Modified Cellulose Fiber Composites

The influence of TDI/18OH on the mechanical properties of PP/CMF materials are shown in Table 4.2. The modified–fibers reinforced PP effectively increased mechanical properties compared with the neat PP. Tensile strength represented an increase of 68.9% from 23.1 to 39.02 MPa, flexural strength exhibited an increase of 77.4% from 29.2 to 51.81 MPa, and flexural modulus showed an improvement of 50.8% from 1.3 to 1.96 GPa. These results provided clear evidence that TDI/18OH was an effective interfacial coupling agent for PP/CMF composites. Similar observations were reported by Karmarkar A. *et al.* (2007) in wood–fiber reinforced PP composite systems.

Thus, addition of TDI/18OH can significantly improve the tensile and flexural properties of PP–based composites. These results are attributed to achieve the high strength of modulus cellulose fibers and to improve the interface interaction and adhesion between fibers and PP matrix. The pendent isocyanate group (–NCO) presented in TDI/18OH not only covalently bond with hydroxyl groups but also interact with cellulose fiber surfaces (Karmarkar A. *et al.* 2007).

Table 4.2 The mechanical properties of PP–reinforced modified cellulose fibers composites

Sample	Tensile Strength (MPa)	Flexural Modulus (GPa)	Flexural Strength (MPa)
PP*	23.10	1.30	29.20
PP/CMF-g-TDI/18OH	39.02	1.96	51.81
PP/CF-g-TDI/18OH	30.07	2.41	45.37

* C.G. Guo and Q.W. Wang, Journal of Applied Polymer Science, **109**, 3080–3086 (2008)

4.2.2 Surface Morphology

Scanning electron microscopy (SEM) was used to monitor the fracture surface of the composites after quenching the samples in liquid nitrogen. The fracture surfaces of the composites with 40% cellulosic fibers with coupling agent are shown in Figure 4.6.

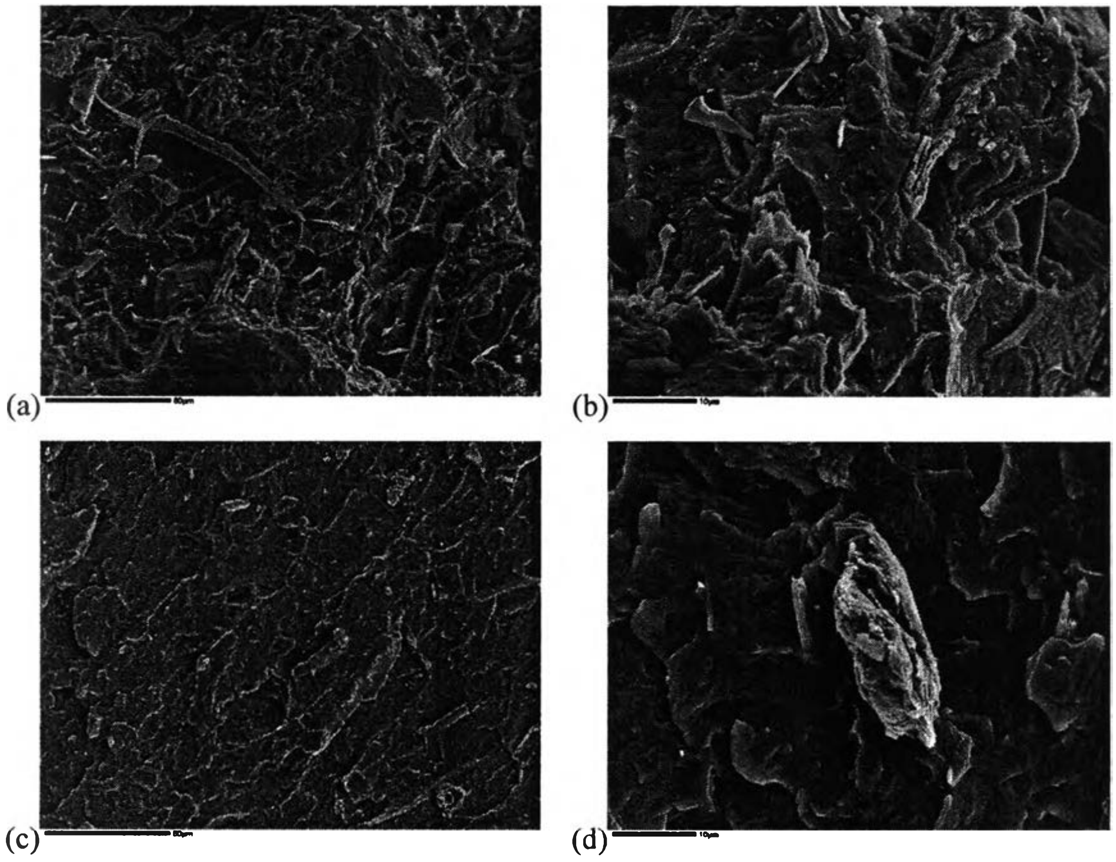


Figure 4.6 Scanning Electron Microscope at different magnifications of (a) and (b) PP/CF-g-TDI/18OH; (c) and (d) PP/CMF-g-TDI/18OH.

As is visible in the overview micrograph of the composite with TDI and 1–octadecanol coupling agent shown above. The figures of CF-g-TDI/18OH, Figure 4.6 (a) and (b), showed signs of fiber pulled–out since most of the fibers were fractured. At higher magnification, Figure 4.6 (b), it was also possible to observe the distinct gaps between CF-g-TDI/18OH and the matrix indicating poor adhesion. Moreover, the fracture surface of composites showed some gaps between modified cellulose fiber and the polypropylene matrix. This modification did not help the interfacial adhesion between the cellulose fibers and the polypropylene matrix.

On the other hand, the interfacial bonding between CMF-g-TDI/18OH and the polypropylene matrix was improved. The overview surface is quite smooth compared to the CF-g-TDI/18OH one. The smoother surface of the grafted fibers might be cause by the decreasing of the interfacial adhesion between 1–Octadecanol and cellulose fibers (Qui, W. *et al.*, 2006). It was difficult to make certain conclusions regarding the dispersion of fibers in the matrix from the SEM micrographs. However, there was no strong evidence of agglomerates of fibers on the studied surfaces. The improved interfacial adhesion is in agreement with the enhanced tensile strength as shown in Table 4.2.

4.2.3 Thermogravimetric Analysis

The thermogravimetric curves of PP and its composites are shown in Figure 4.7. It can be observed from these curves that the thermal degradation of neat PP and PP/CF-g-TDI/18OH occurs through a two–stage process, while PP/CMF-g-TDI/18OH shows a single–stage process. This indicated that the modified PP–based composites give a higher degradation temperature than that of the neat PP resulting in the improvement of the thermal stability of the PP–based composites (Beckermann G.W. *et al.* 2008).

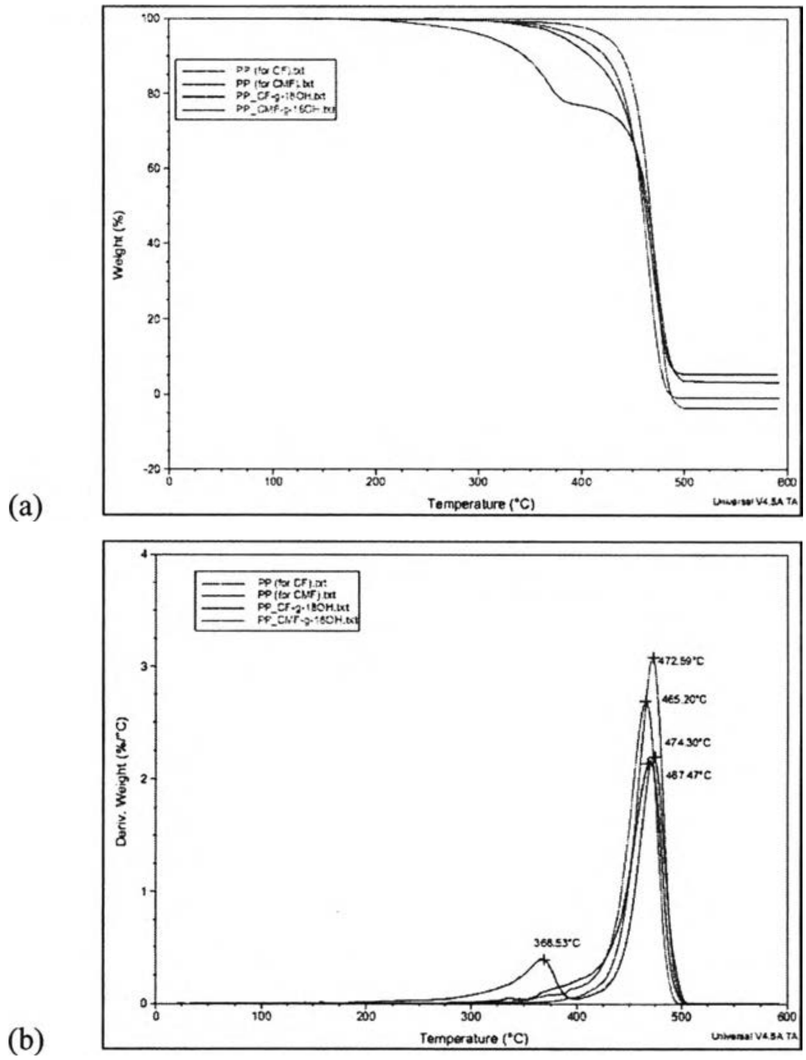


Figure 4.7 (a) TGA and (b) DTA curves of PP and its composites.

4.2.4 Thermal Analysis of PP–based Biocomposites

The melting behavior of pure PP and its composites are shown as the DSC curves in Figure 4.8 and Table 4.3. The melting behavior of a polymer determines not only the processing conditions and the application areas, but also the properties of the materials.

Table 4.3 The melting temperature of PP and its composites

Sample	**T_m (°C)**
PP for CF	162.13
PP/CF-g-TDI/18OH	162.98
PP for CMF	163.69
PP/CMF-g-TDI/18OH	166.55

The PP reveals a main melting peak as well as a shoulder. When the modified–cellulose fibers were blended with PP, composites were obtained, and the melting peak moved to a higher temperature showing that the perfect crystals was formed.

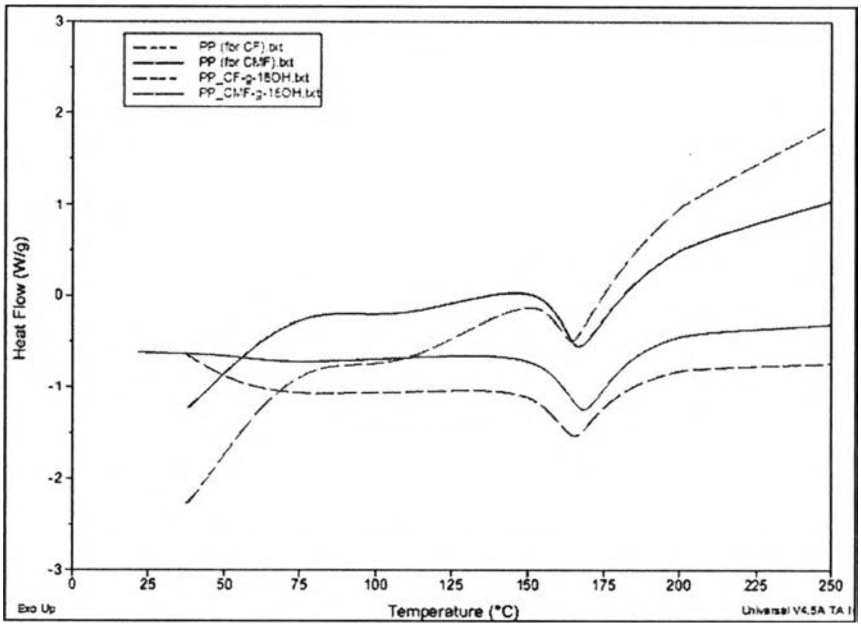


Figure 4.8 DSC curves of PP/CF-g-TDI/18OH and PP/CMF-g-TDI/18OH composites.

4.3 The Effect of Alcohol Types

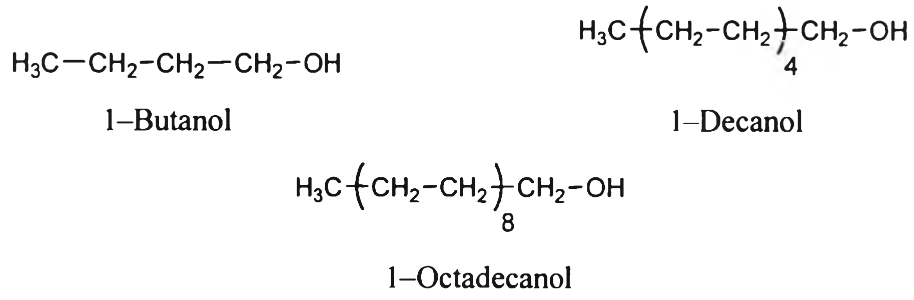
The short and long chain alcohols, Figure 4.9 and Table 4.4, were used to graft with the TDI coupling agent in order to optimize the grafting reaction.

Table 4.4 The properties of different alcohol used in the grafting reaction

Alcohol	Molecular Formula	Molecular Weight	Density (g/cm^3)	Boiling Point (°C)
1–Butanol	$C_4H_{10}O$	74.12	0.8098	117.73
1–Decanol	$C_{10}H_{22}O$	158.28	0.8297	231.00
1–Octadecanol	$C_{18}H_{38}O$	270.49	0.8120	210.00

The isocyanate group (–NCO) is very active with the hydroxyl group (either from alcohols or cellulose fibers), the active participation of the functional group of isocyanate forms a covalent bond with –OH surface groups of the fiber (Nourbakhsh A. et al. 2008). Therefore, grafting of different types of alcohol via the TDI coupling agent tends to degrade the bonding between the cellulose fiber and the matrix but an addition functional group –NCO still leads to an interfacial adhesion improvement. Because of the highly reactive of the –NCO group from the TDI coupling agent to the –OH group from alcohols and cellulose fiber, thus alcohols/TDI modifier is chemically linked to the cellulose matrix through strong covalent bonds.

The quantitative comparison of various alcohols via the TDI coupling agent is characterized by the TGA, Figure 4.10. Also the grafting efficiency and grafting yield are calculated and shown in Table 4.5.



$H_3C-CH_2-CH_2-CH_2-OH$

1–Butanol

$H_3C\left(CH_2-CH_2\right)_4CH_2-OH$

1–Decanol

$H_3C\left(CH_2-CH_2\right)_8CH_2-OH$

1–Octadecanol

Figure 4.9 The structure of different alcohols.

Theoretically, 1–Butanol (4OH) should give the highest in both grafting efficiency and grafting yield due to its short chain alcohol which can go through the TDI molecule easier than the other two. In this case, CMF-g-TDI/18OH shows 7.73 and 5.79% (the highest values) of grafting efficiency and grafting yield, respectively. Since 1–Octadecanol (18OH) is a long fatty alcohol chain and insoluble in water, an adequate chain length of 1–Octadecanol can improve the thermal stability of the modified–fibers molecule which is consistent with the degradation temperature as shown in Table 4.6.

Table 4.5 The grafting efficiency and grafting yield of CMF grafted with various alcohol

Sample	Grafting Efficiency (%)	Grafting Yield (%)
CMF-g-TDI/4OH	3.17	4.36
CMF-g-TDI/10OH	1.62	4.76
CMF-g-TDI/18OH	7.73	5.79

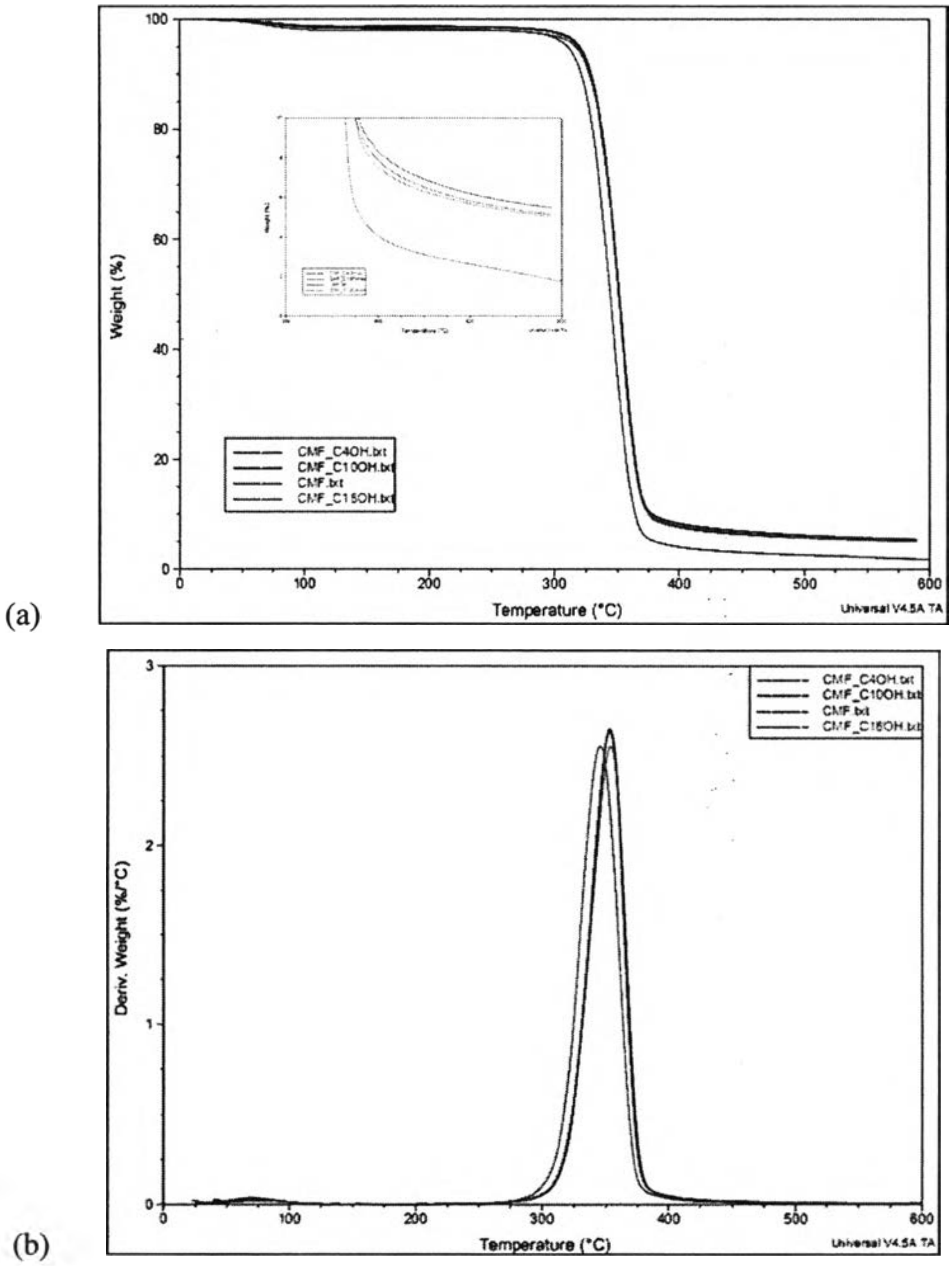


Figure 4.10 (a) TGA and (b) DTA curves of CMF grafted with different alcohols.

The stability property of CMF-g-TDI/18OH shows the highest degradation temperature, 342°C, which is a 6% increased from untreated CMF. However, the grafting with all three alcohols can enhance the stability of the modified–fibers due to the deposition of alcohols on cellulose fiber surfaces.

Table 4.6 The degradation temperature of CMF grafted various alcohols

Sample	Degradation Temperature (°C)
CMF	322
CMF-g-TDI/4OH	330
CMF-g-TDI/10OH	331
CMF-g-TDI/18OH	342

4.4 The Effect of the Amount of Alcohol (Modifier Amount)

The results in Figure 4.11 and Table 4.7 reveal that a higher amount of modifier (TDI/18OH) gives a lower grafting efficiency. The 5% 18OH shows the highest grafting yield (5.98%).

Table 4.7 The grafting efficiency and grafting yield of CMF-g-TDI/18OH at different ratios

The Amount of 18OH	Grafting Efficiency (%)	Grafting Yield (%)
1%	96.14	4.81
5%	23.93	5.98
10%	9.25	4.63
15%	7.73	5.79
100%	0.71	3.57

On the other hand, 1% 18OH presents the highest grafting efficiency (96.14%) due to the adsorption of TDI/18OH on the fiber surface which is not chemically bond.

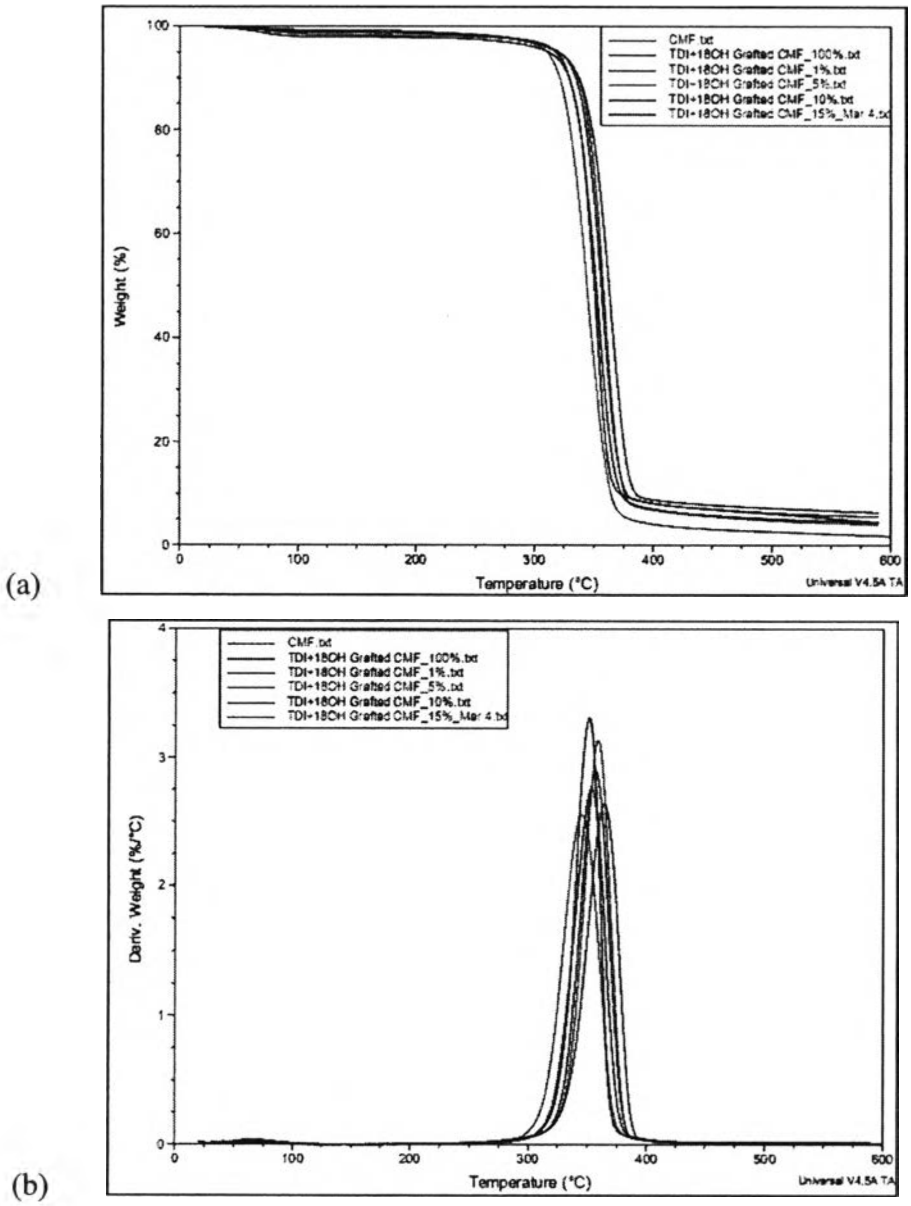


Figure 4.11 (a) TGA and (b) DTA curves of CMF-g-TDI/18OH at different ratio.

4.5 The Effect of Grafting Procedure

Since there are two approaches, studied the effect of order of adding chemicals on the grafting reaction was studied; details are shown in Chapter III. The grafting efficiency and grafting yield are shown in Table 4.8. CMF-g-TDI/18OH refers to the TDI coupling with 18OH first then grafted onto the CMF surface, meanwhile 18OH-g-TDI/CMF means the reaction of TDI coupling agent and CMF then grafted with 18OH.

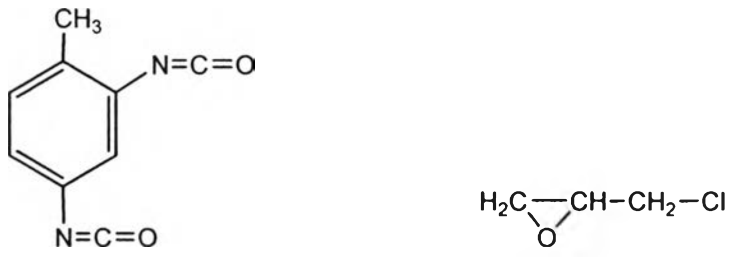
Table 4.8 The grafting efficiency and grafting yield of CMF-g-TDI/18OH and 18OH-g-TDI/CMF approach

Approach	Grafting Efficiency (%)	Grafting Yield (%)
CMF-g-TDI/18OH	23.93	5.98
18OH-g-TDI/CMF	14.60	3.65

The results show that CMF-g-TDI/18OH performed a better grafting efficiency and grafting yield, two times higher, than 18OH-g-TDI/CMF. Since the isocyanate group is very reactive with the hydroxyl group, both 18OH and CMF also contained hydroxyl groups in their molecule. Due to a linear chain structure of 18OH, so the hydroxyl groups on its surface can be led to react with isocyanate group of TDI easier than CMF which has a complex structure.

4.6 The Effect of Coupling Agents

Two different types of coupling agent were also studied. The structure of those two coupling agents is shown in Figure 4.12.



Tolylene 2,4–diisocyanate (TDI) Epichlorohydrin (EP)

Figure 4.12 Tolylene 2,4–diisocyanate (TDI) and Epichlorohydrin (EP) structure.

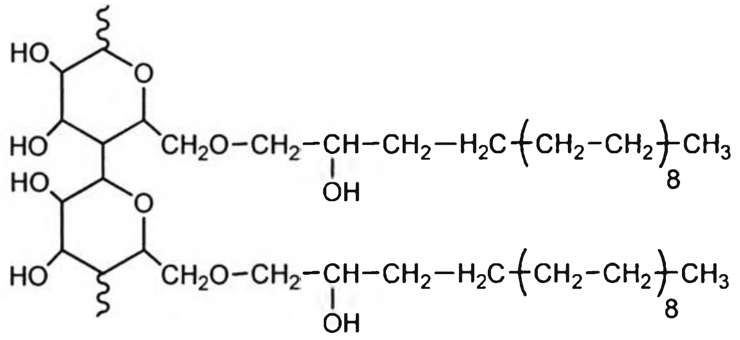
Each of the isocyanate functional groups in TDI can react with a hydroxyl group to form a urethane linkage; therefore isocyanates are chemically linked to the cellulose fiber matrix. The 2,4–TDI is an asymmetrical molecule and thus has two isocyanate groups of different reactivity. The 4–position is approximately four times more reactive than the 2–position. However, since both isocyanate groups are attached to the same aromatic ring, reaction of one isocyanate group will cause a change in the reactivity of the second isocyanate group (Randall, D. *et al.* 2002). Epichlorohydrin is an organochlorine compound, an organic compound containing at least one covalently bonded chlorine atom, and an epoxide, a cyclic ether with three ring atoms. It is a water insoluble chemical but miscible in most polar organic solvents. However, epichlorohydrin is also a highly reactive compound that is used in plastic processing.

Table 4.9 The grafting efficiency and grafting yield of TDI and EP coupling agents in the grafting reaction of CMF and 18OH

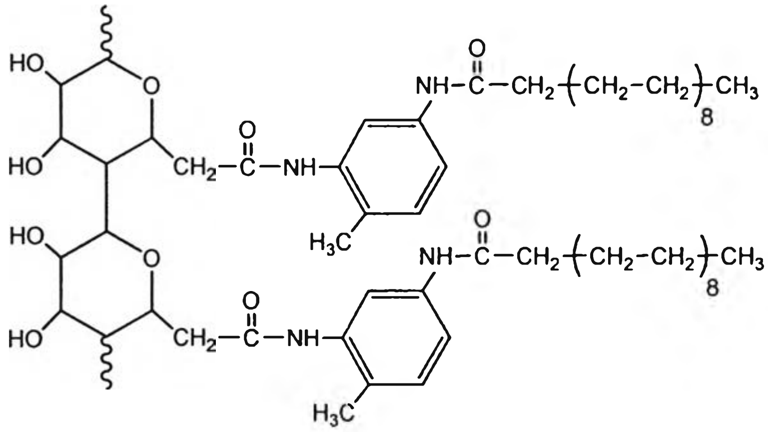
Coupling Agent	Grafting Efficiency (%)	Grafting Yield (%)
CMF-g-TDI/18OH	23.93	5.98
CMF-g-EP/18OH	8.49	16.98

The grafting efficiency and grafting yield of these two coupling agents are shown in Table 4.9.

The results show that the TDI coupling agent gave a better grafting efficiency, 23.93%, than EP due to the strongly reactive of isocyanate groups. On the other hand, EP shows a greater grafting yield than TDI due to the less used in the grafting reaction. The final products of each coupling agent are shown in Figure 4.13.



CMF-g-EP/18OH



CMF-g-TDI/18OH

Figure 4.13 The final structure of CMF-g-EP/18OH and CMF-g-TDI/18OH.

4.7 The Effect of Cellulose Fiber Characteristics

Two difference characteristics of cellulose fibers were investigated in order to compare the grafting efficiency and grafting yield. The morphology of these two fibers is characterized by SEM, shown in Figure 4.14. Cellulose microfibrils (CMF) size is around 3–5 μm diameter, whereas cellulose fibers (CF) is around 29 μm diameter which appear as long fibers. The chemical compositions of CMF and CF contain mainly carbon, hydrogen and oxygen atoms at the same ratio as shown in Table 4.10.

Table 4.10 The grafting efficiency and grafting yield of CMF-g-TDI/18OH and CF-g-TDI/18OH

Sample	Grafting Efficiency (%)	Grafting Yield (%)
CF-g-TDI/18OH	5.84	4.38
CMF-g-TDI/18OH	7.73	5.79

The results show a better performance of CMF, around 30% grafting efficiency and a grafting yield of CMF-g-TDI/18OH greater than CF-g-TDI/18OH. In order to graft with TDI/18OH, because the smaller size of CMF, it made the grafting reaction easier to perform.

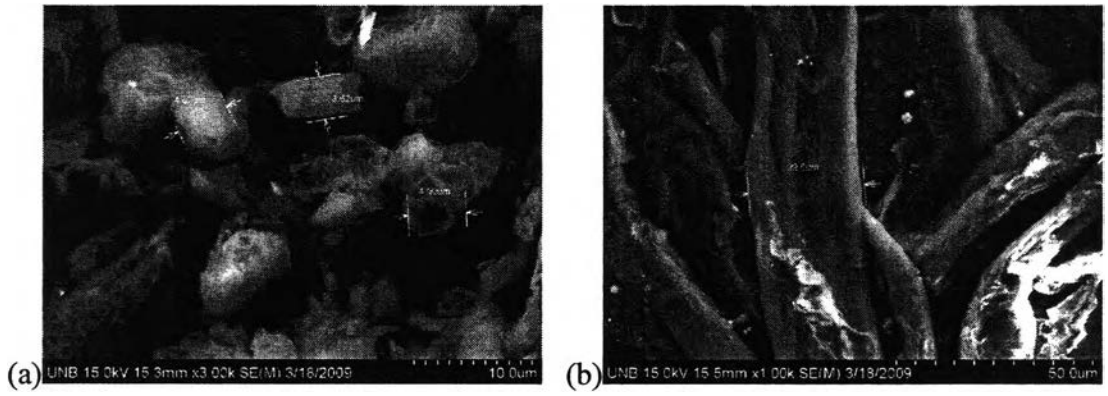


Figure 4.14 The morphology of CF and CMF.