Table Captions

Table 1. Types of particles or fibres of composite wood products.

Table 2. The results of weight percent gained after modification.

Table 3. Peak assignments for several major absorption bands typical for agricultural fibres.

Figure Captions

Figure 1. Chemical reaction of acetic anhydride modification of MDF fibres.

Figure 2. Chemical reaction of propionic anhydride modification of MDF fibres.

Figure 3. FT-IR spectra of unextracted, extracted, acetylated and propionylated MDF fibres.

Figure 4. Effect of fibre modification on tensile strength of agro-composites.

Figure 5. Effect of fibre modification on tensile modulus of agro-composites.

Figure 6. Effect of fibre modification on elongation at break of agro-composites.

Figure 7. Effect of fibre modification on flexural strength of agro-composites..

Figure 8. Effect of fibre modification on flexural modulus of agro-composites.

Figure 9. Effect of fibre modification on impact strength of agro-composites.

Figure 10. Effect of fibre modification on internal bond strength of agro-composites.

Figure 11 (a-d). SEM micrographs of internal bond fractures (see circle), of (a) non-extracted, (b) extracted, (c) propionic anhydride (extract) and d) acetylated anhydride (extract) fibre modification (2cm length on photos represents 50μm), at 500 magnification.

Figure 12. Effect of fibre modification on water absorption of agro-composites.

Figure 13. Effect of fibre modification on thickness swelling of agro-composites.

HIGH-PERFORMANCE AGRO-COMPOSITES FROM NON-TOXIC CHEMICALLY MODIFIED MDF FIBRES.

-Flexural properties

-Impact properties

-Internal bond strength

Physical Properties

CONCLUSION

ACKNOWLEDGEMENT

REFFERENCES

TABLE 1

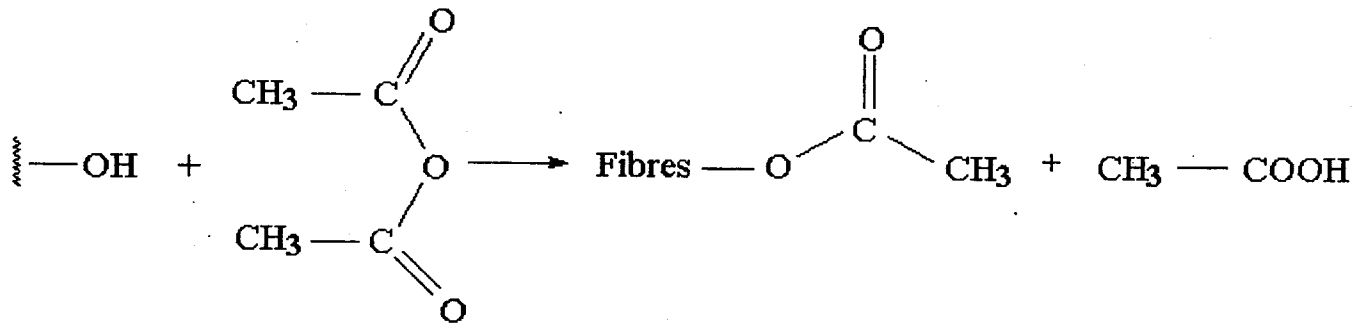
Composite wood product	Types of particles or fibres
Medium Density Fibreboard	Constructed from thermo-mechanical pulp fibres
Particleboard	Constructed from wood or non-wood flakes, shavings or splinters
Chipboard	Constructed from wood or non-wood flakes, shavings, splinters or paper
Plywood	Constructed from one or more wood or non-wood veneers

TABLE 2

Fibres modification	Weight percent gain (%)
Unextracted	Not applicable
Extracted	Not applicable
Acetylated (with extracted fibres)	5.4%
Propionylated (with extracted fibres)	6.7%

TABLE 3

Frequency (cm^{-1})	Assignments
3500 – 3100	OH stretching
3090 – 2600	CH stretching of CH_2 and CH_3
1750 – 1700	C = O stretching
1600 – 1400	Aromatic ring stretching in lignin
1400 – 1300	CH deformation of CH_2 and CH_3
1300 – 1000	C – O stretching
1280 – 1070	C – O – C stretching
1300 - 1030	OH deformation



Agro-fibres Acetic anhydride Modified agro-fibres Acetic acid

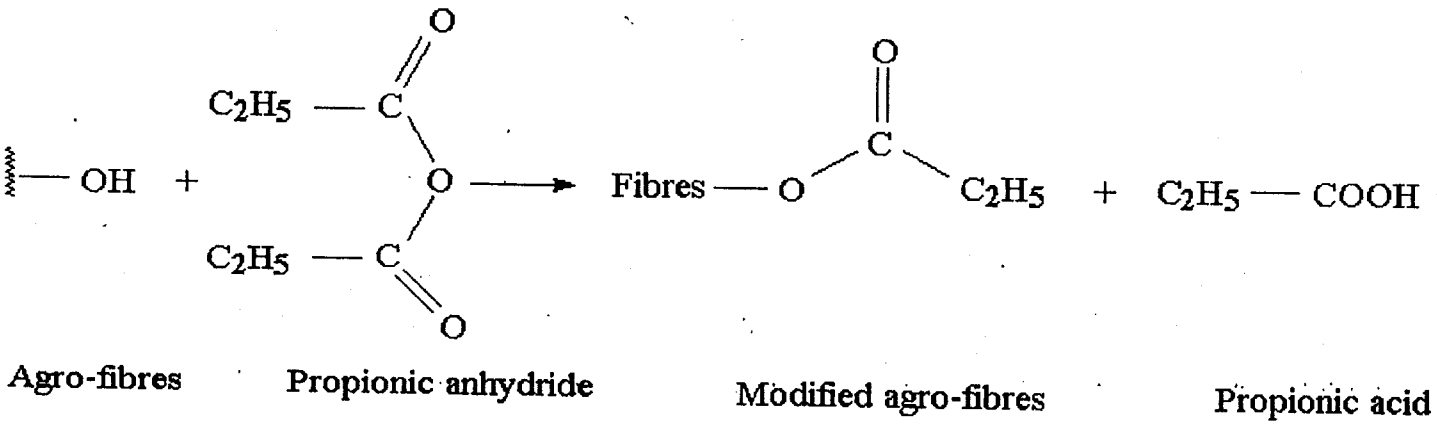
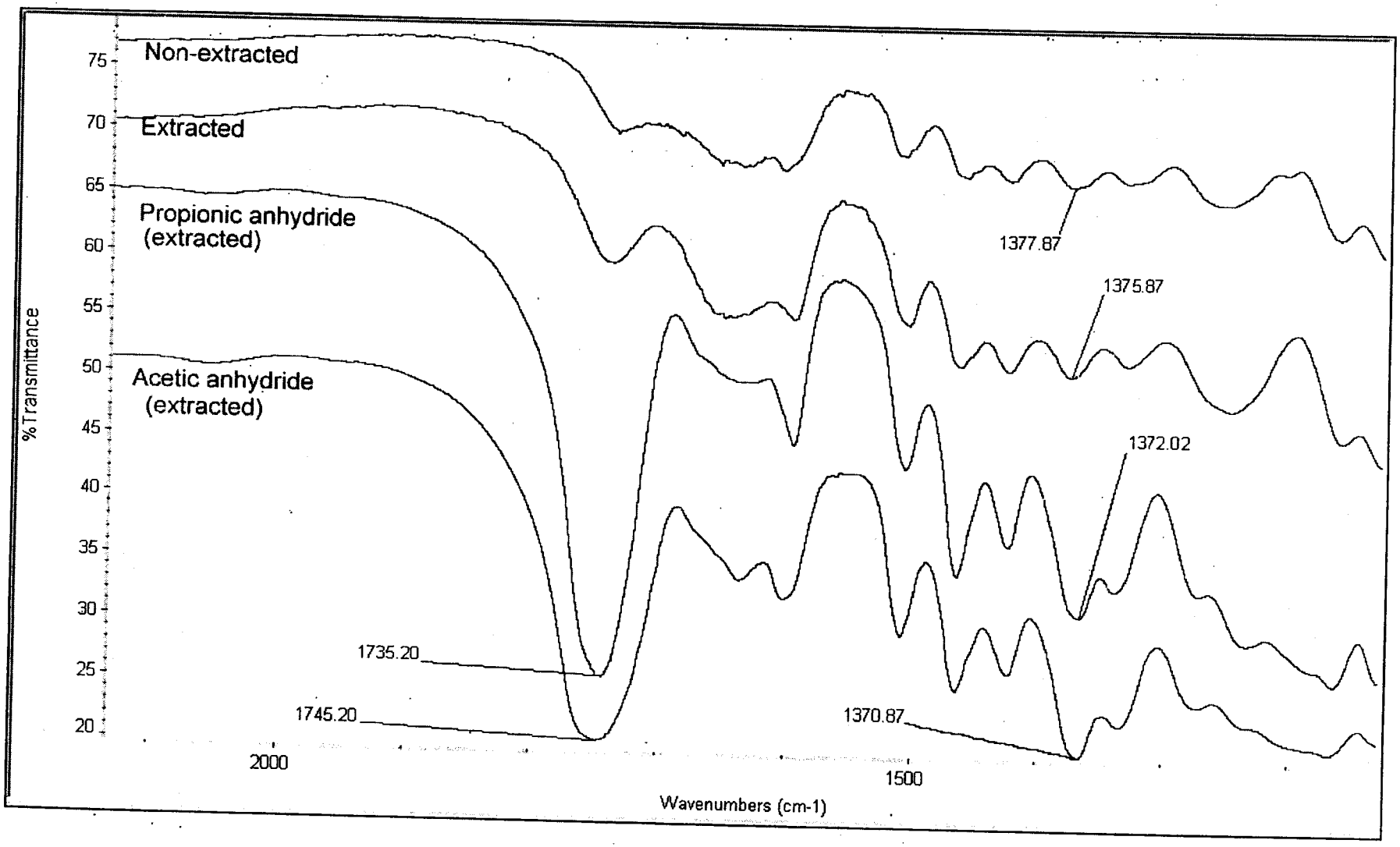
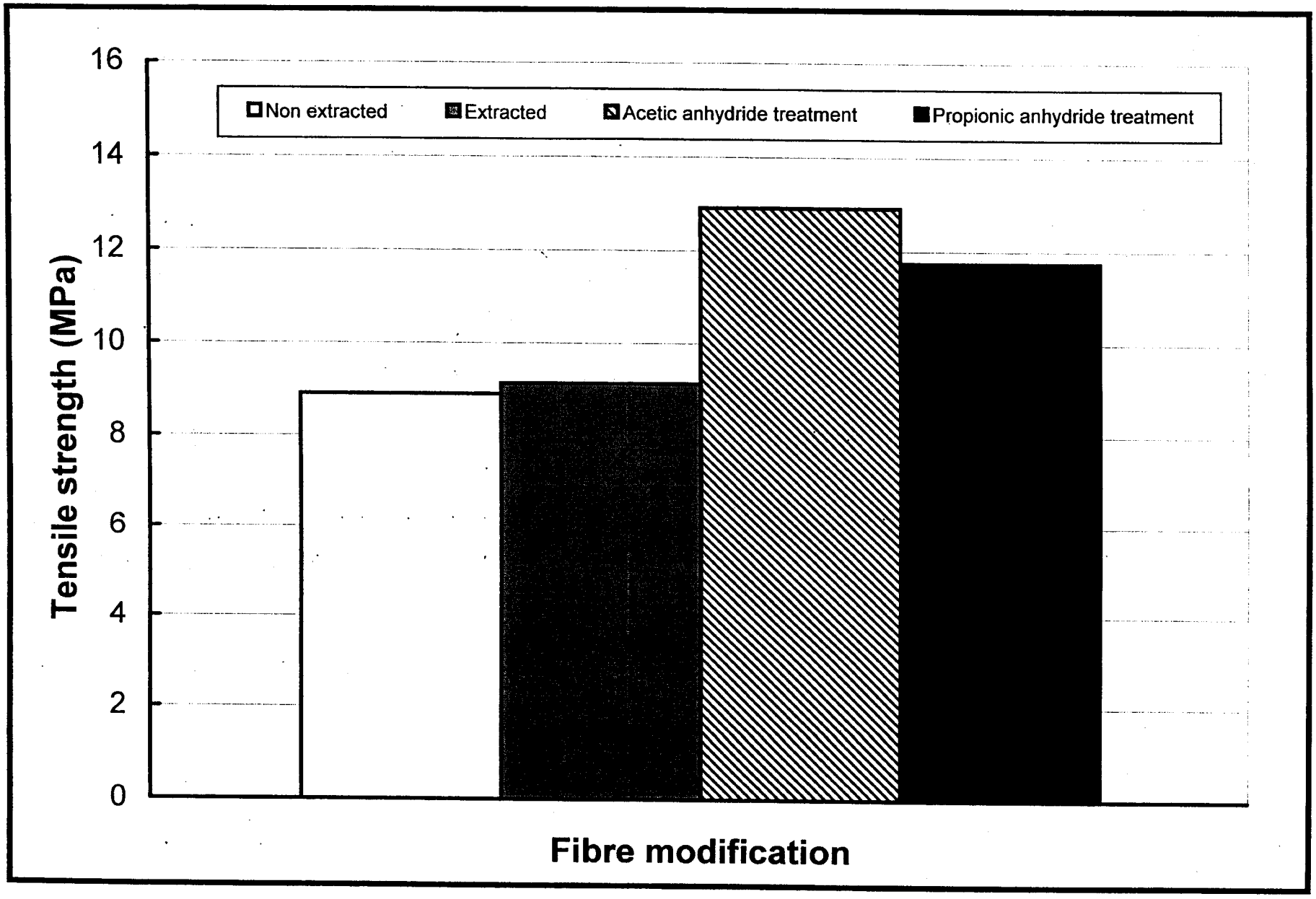
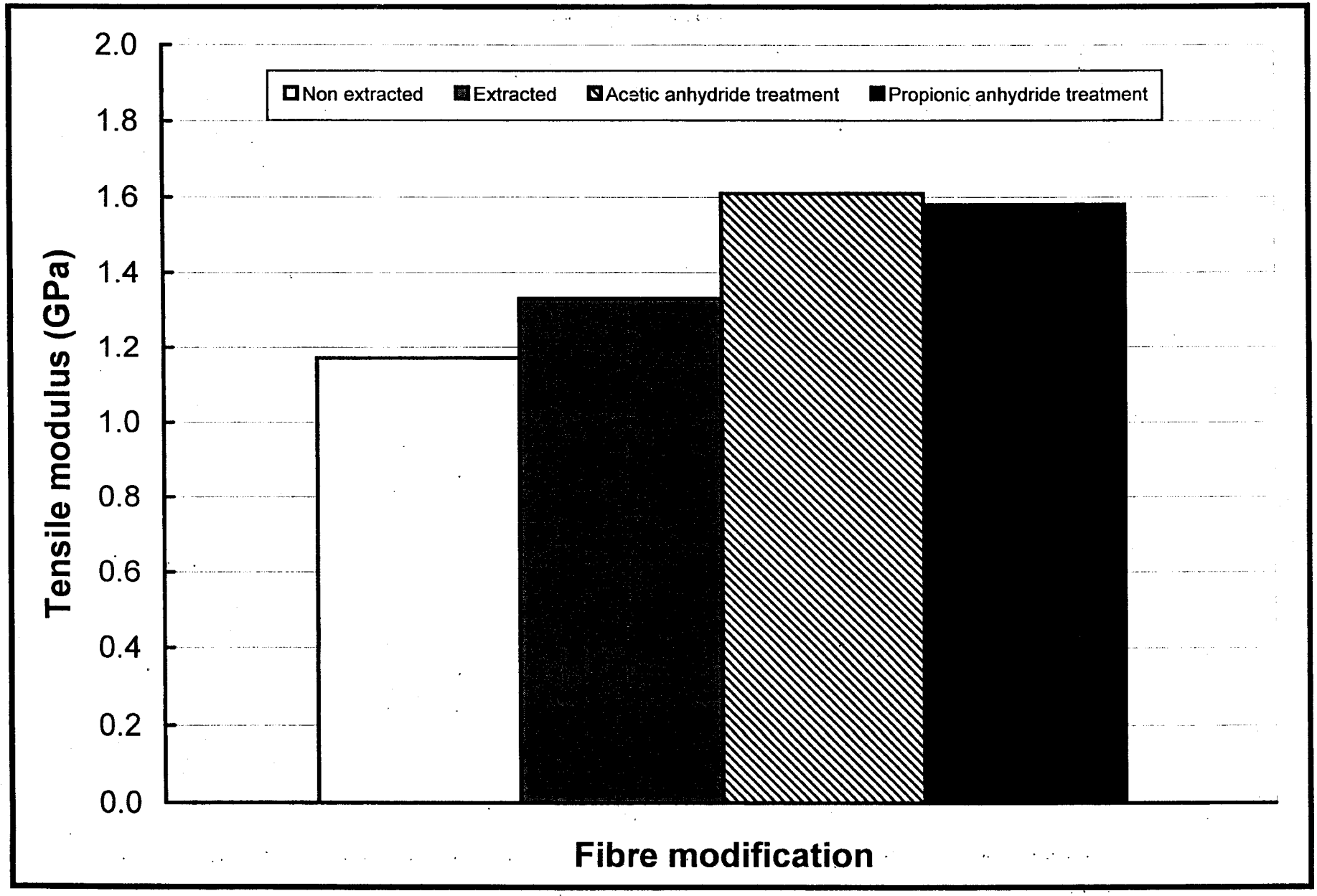
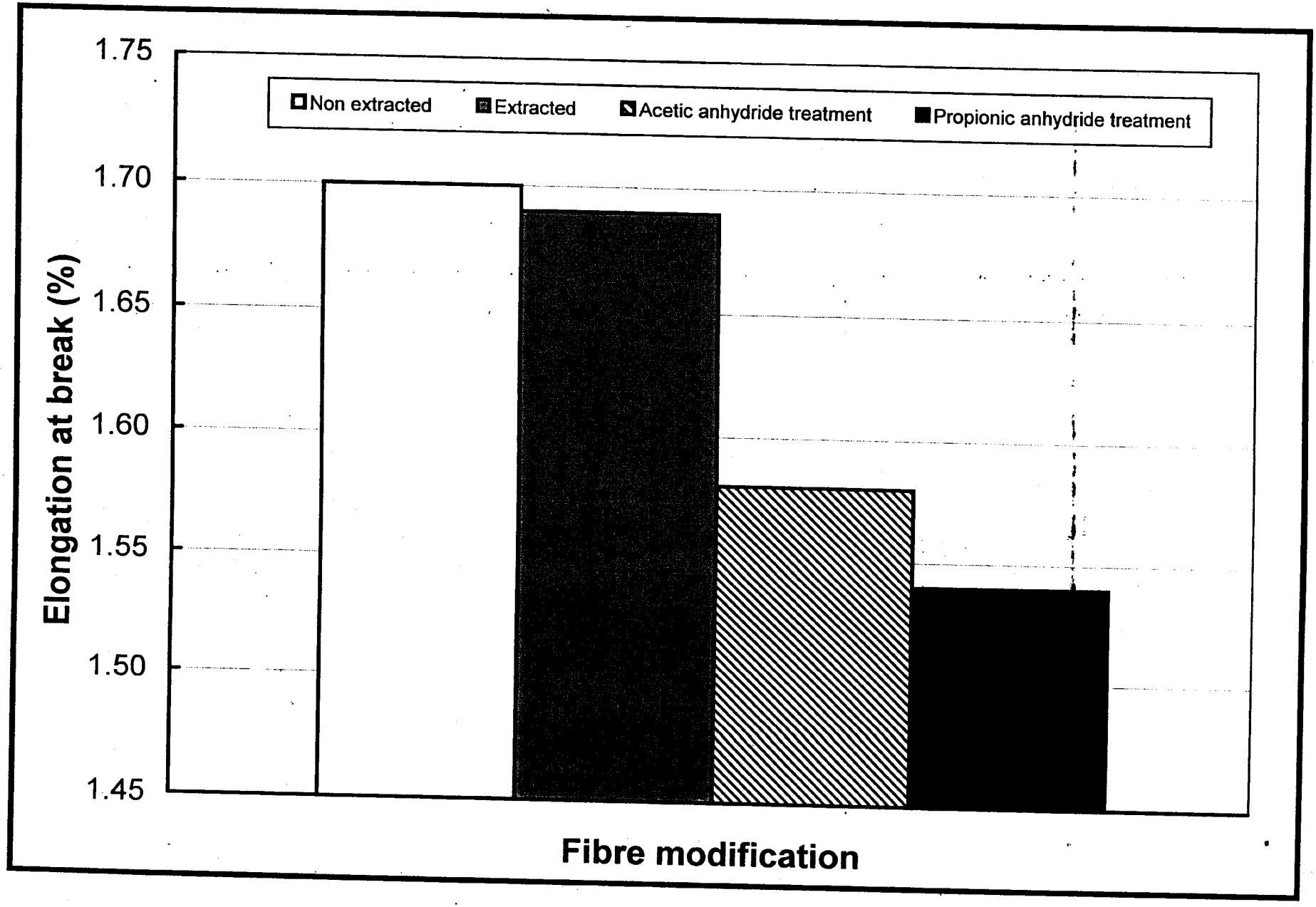

OH
+
C2H5 — C
O
C2H5 — C
O
O
Fibres — O
C
O
C2H5
+
C2H5 — COOH
Agro-fibres
Propionic anhydride
Modified agro-fibres
Propionic acid

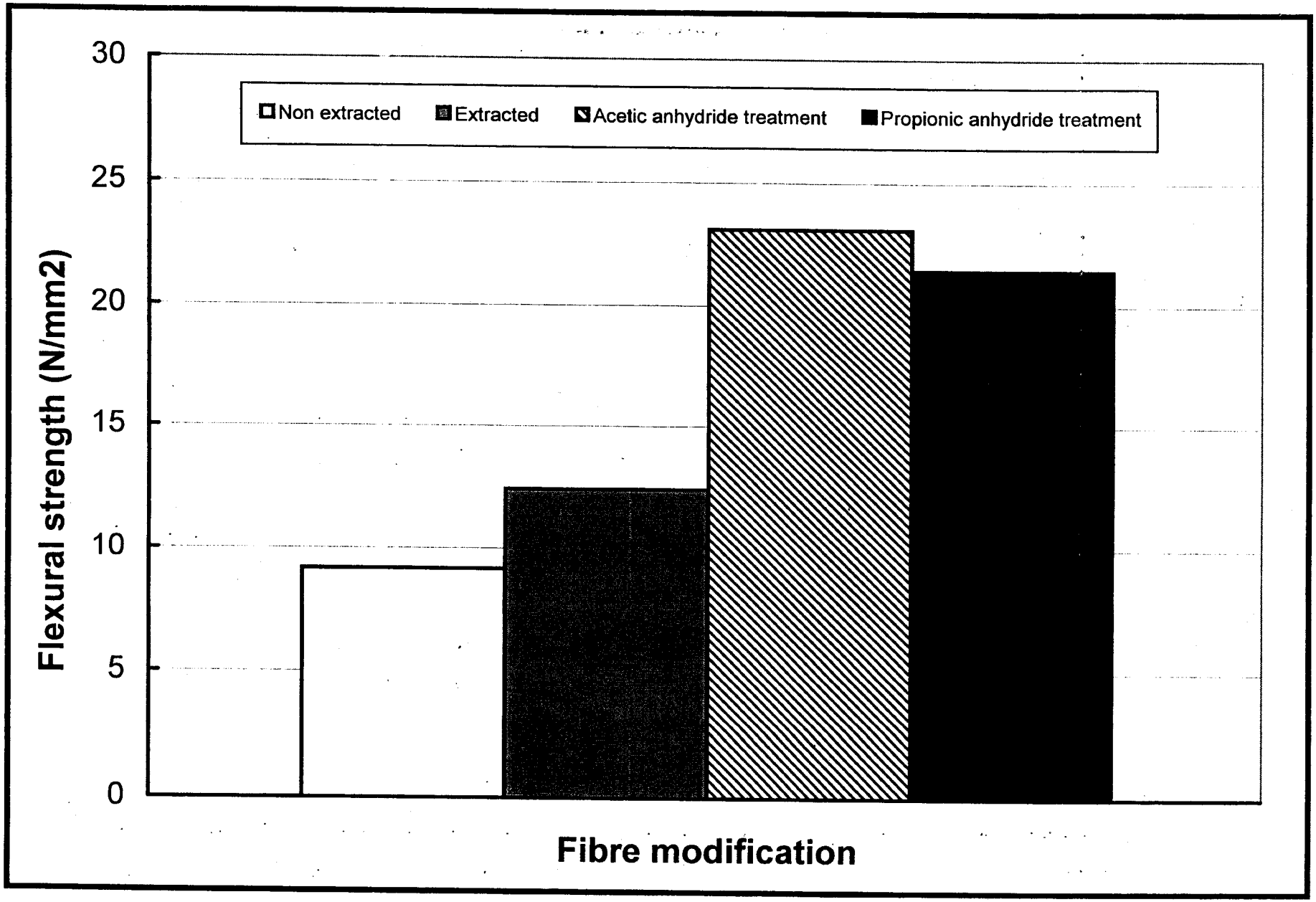
FIGURE 3

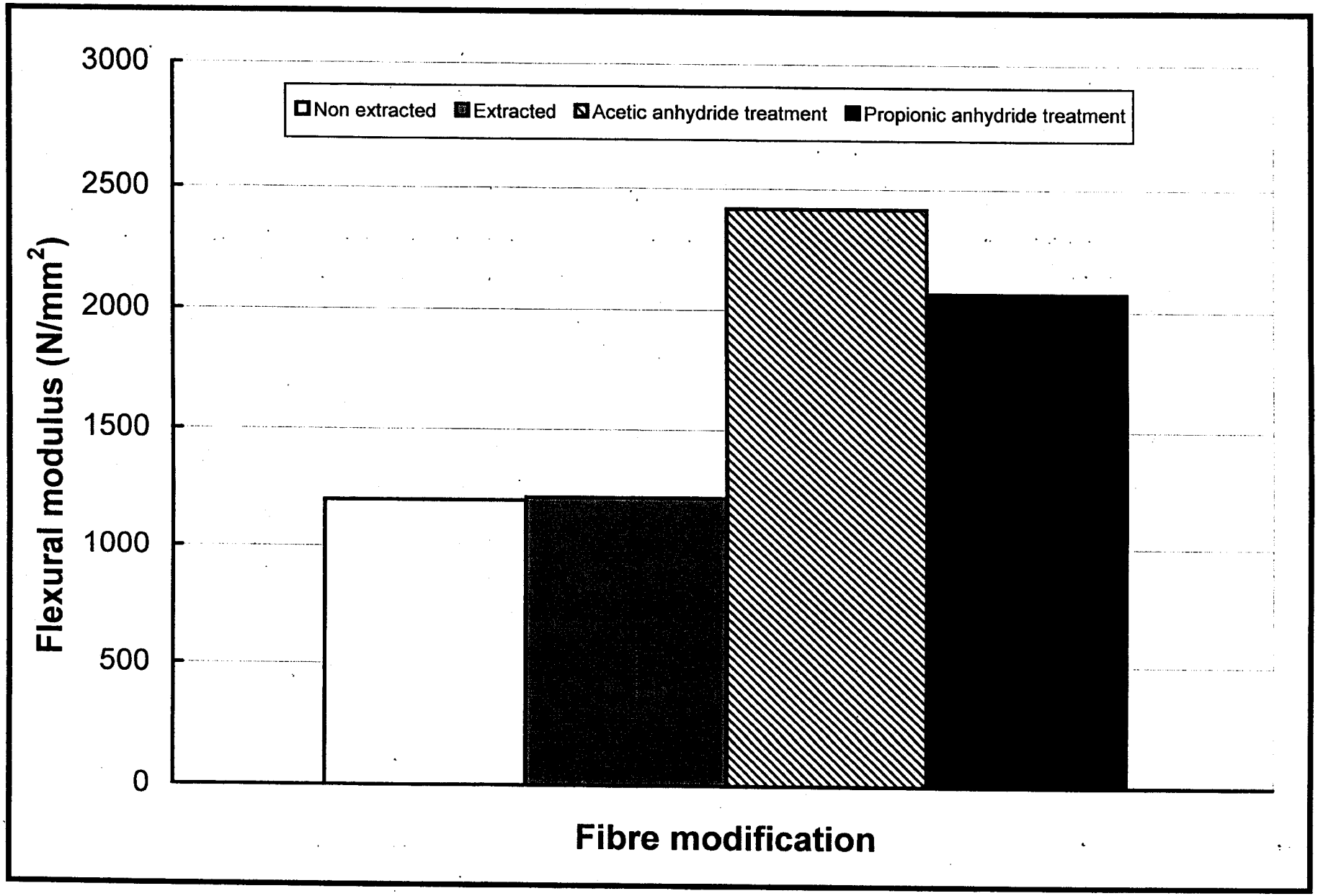

Non-extracted
Extracted
Propionic anhydride
(extracted)
Acetic anhydride
(extracted)
% Transmittance
75
70
65
60
55
50
45
40
35
30
25
20
1377.87
1375.87
1372.02
1735.20
1745.20
1370.87
2000
1500
Wavenumbers (cm-1)

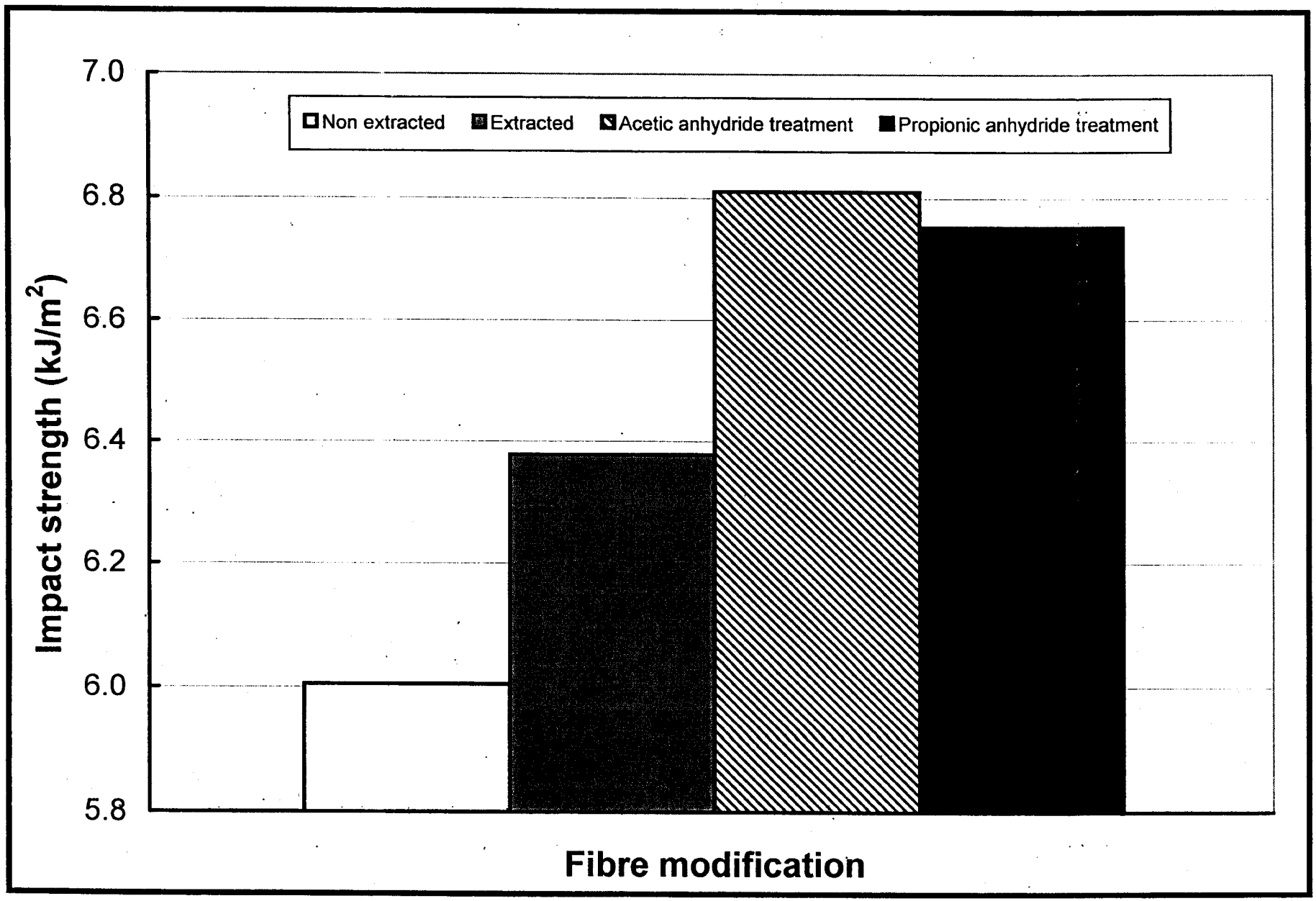

16
14
12
10
8
6
4
2
0
Tensile strength (MPa)
Non extracted
Extracted
Acetic anhydride treatment
Propionic anhydride treatment
Fibre modification

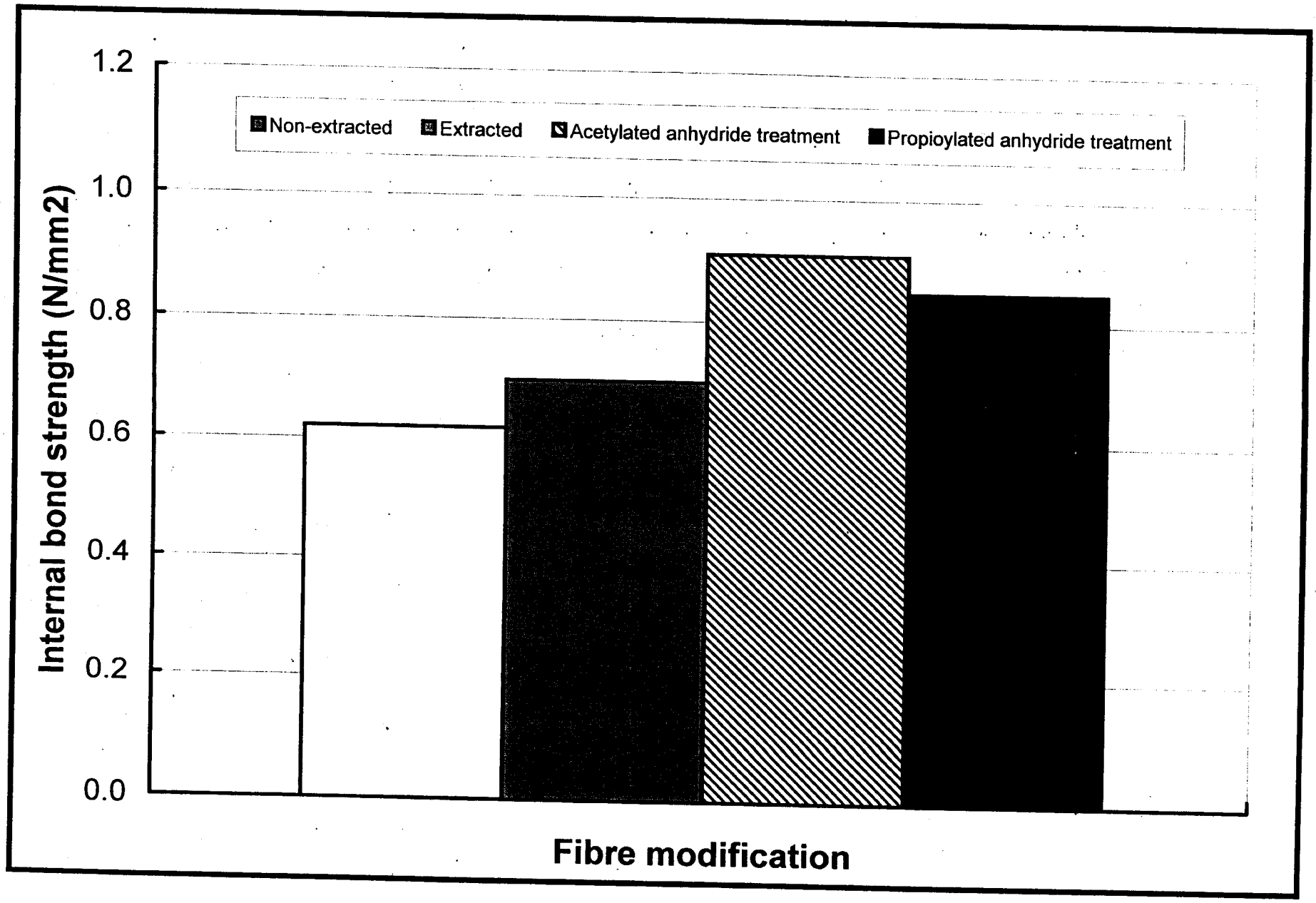

Non extracted
Extracted
Acetic anhydride treatment
Propionic anhydride treatment
Tensile modulus (GPa)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Fibre modification

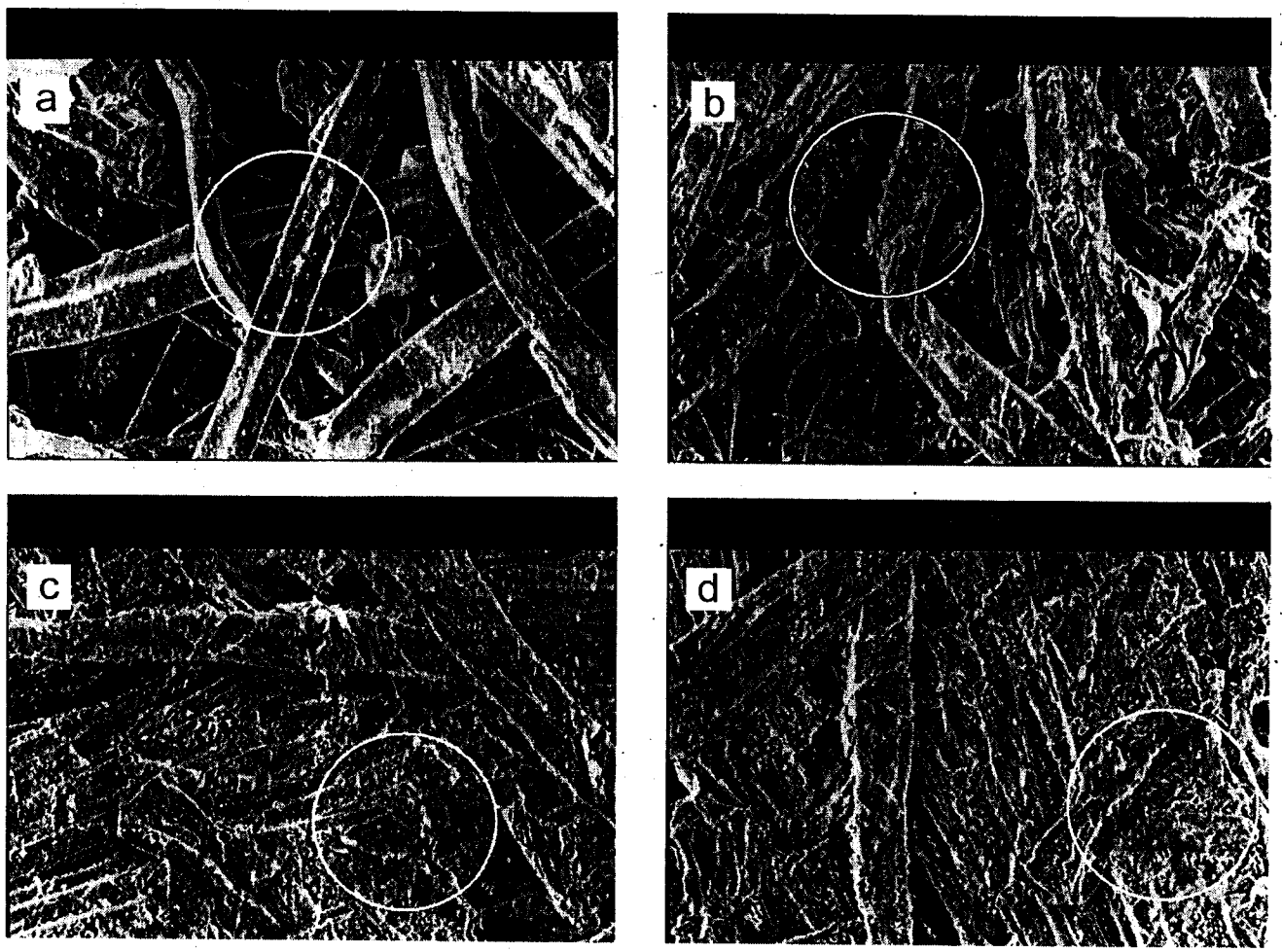

1.75
1.70
1.65
1.60
1.55
1.50
1.45
Elongation at break (%)
Non extracted
Extracted
Acetic anhydride treatment
Propionic anhydride treatment
Fibre modification

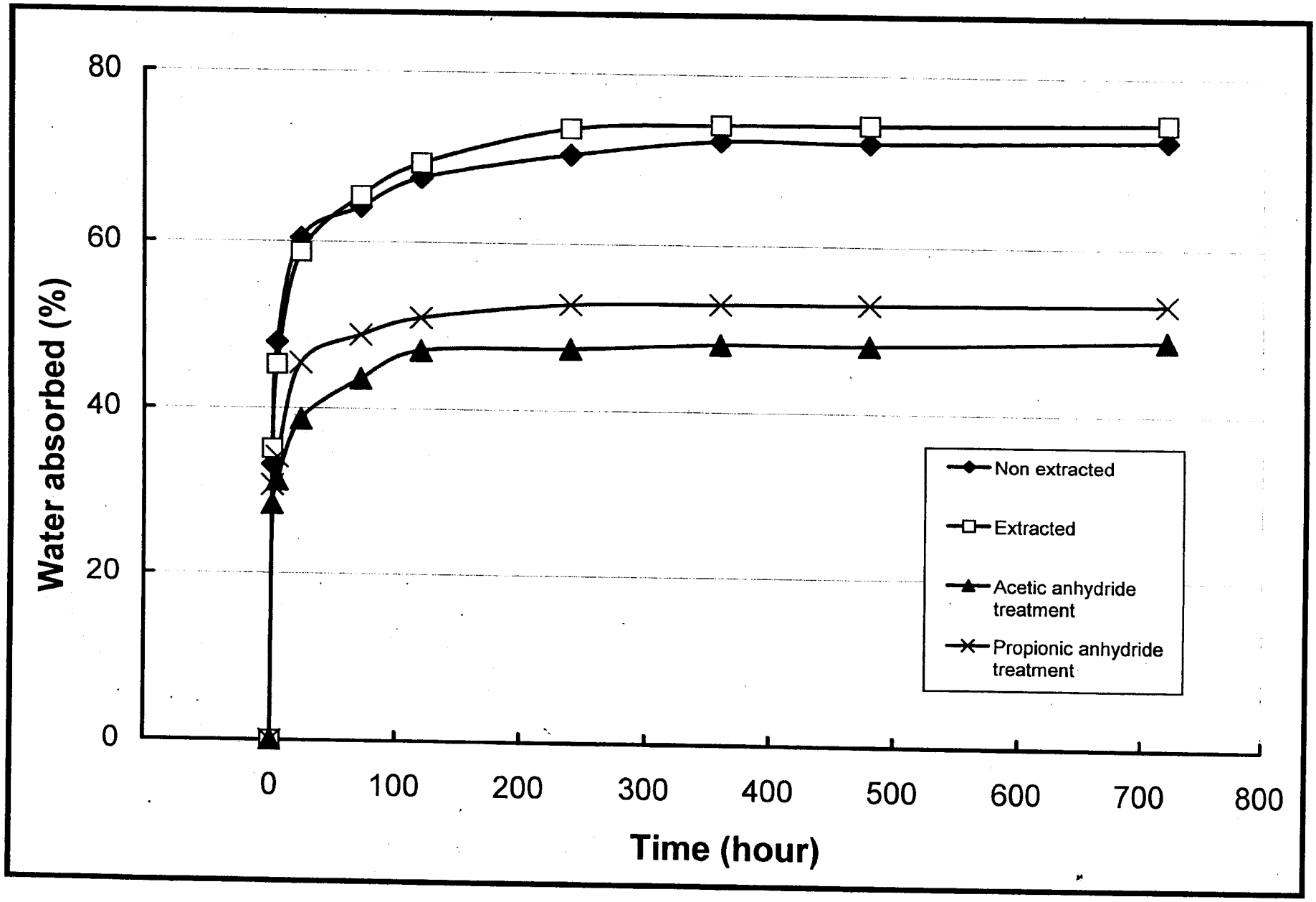

30
25
20
15
10
5
0
Flexural strength (N/mm2)
Non extracted
Extracted
Acetic anhydride treatment
Propionic anhydride treatment
Fibre modification

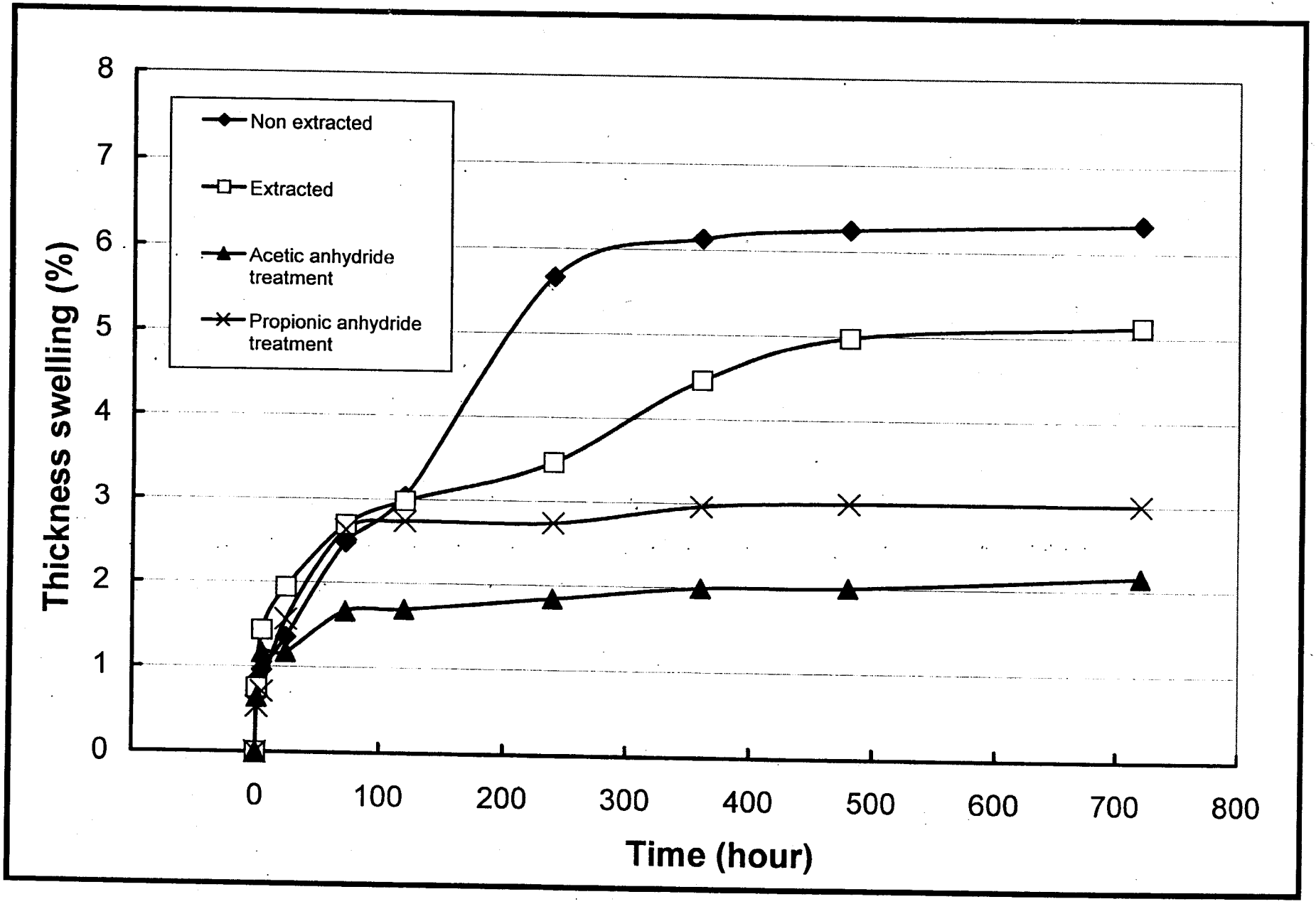

3000
2500
2000
1500
1000
500
0
Flexural modulus (N/mm2)
Non extracted
Extracted
Acetic anhydride treatment
Propionic anhydride treatment
Fibre modification


7.0
6.8
6.6
6.4
6.2
6.0
5.8
Impact strength (kJ/m2)
Non extracted
Extracted
Acetic anhydride treatment
Propionic anhydride treatment
Fibre modification


1.2
1.0
0.8
0.6
0.4
0.2
0.0
Internal bond strength (N/mm2)
Non-extracted
Extracted
Acetylated anhydride treatment
Propioylated anhydride treatment
Fibre modification


a
b
c
d


80
60
40
20
0
Water absorbed (%)
0
100
200
300
400
500
600
700
800
Time (hour)
Non extracted
Extracted
Acetic anhydride treatment
Propionic anhydride treatment


Thickness swelling (%)
0
1
2
3
4
5
6
7
8
0
100
200
300
400
500
600
700
800
Time (hour)
Non extracted
Extracted
Acetic anhydride treatment
Propionic anhydride treatment

HIGH-PERFORMANCE AGRO-COMPOSITES FROM NON-TOXIC CHEMICALLY MODIFIED FIBRES.

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ABSTRACT

The effects of chemical modification on high-performance agro-composites from non-toxic chemically modified fibres by using oil palm empty fruit bunches MDF fibres and phenol formaldehyde as matrix were investigated. Four types of composite boards were produced (extracted; non-extracted; acetylated; and propionylated) and each mechanicals and physical properties were compared accordingly. Proof of modification was indicated by increased of weight and was confirmed by Fourier-Transform Infrared Analysis (FT-IR). The modification enhanced the composites properties, while unmodified MDF fibres composite showed lower mechanical properties and higher water absorption. The changes in mechanical properties followed the order: acetylated (highest) > propionylated > extracted > non-extracted (lowest). However, water absorption showed different

phenomena, the changes followed in the order: extracted (highest) > non-extracted >propionylated > acetylated (lowest).

Keywords: Agro-composites; MDF fibres; Non-toxic-chemical; Phenol formaldehyde; Acetylation; Propionylation.

INTRODUCTION

Agricultural fibres wastes (oil palm fibres, pineapple fibres, banana stem fibres, etc.) are produced in vast quantities all over the world. In the industry, there are many types of agricultural based composites product such as particle board, medium density fibre board (MDF), conventional plywood, laminated veneer lumber (LVL), strand-, wafer-, chip-, particle-, and fibreboard. In global perspectives, fibreboard, with a current market shares of approximately 15 % and expected to increase its market share the most (1). Below are some examples of major composite agricultural products and type of material available in the markets (2).

Agricultural fibres such as oil palm fibres and pineapple leaf fibres are produced in quantities of the order of over 50 million of tones per annum. The use of such materials have been so attractive as they offer a number of advantages, such as low production costs, easy processing (3,4), light weight (4), very high strength–to-weight ratio (5,6), low density, derived from a renewable resources and they can be burned at the end of their product life cycle (7). Agricultural fibres are known today as alternatives to replace man-made fibres (3-8). However, the main disadvantage of agricultural fibres is the hydrophilic properties of the cell wall polymers, due to the associated abundant hydroxyl functionality. This leads to undesirable changes in mechanical and dimensional properties such as function of relative humidity and degradation by decay organisms.

Chemical modifications have been made to improve the decay and moisture resistance of agricultures fibres, by modifying the properties so that they become hydrophobic (7). Agricultural fibres, hydrophobic in nature because of an abundance of hydroxyl groups are not compatible with hydrophobic matrices such as polyester, formaldehyde etc. This incompatible leads to low fibre-matrix interfacial bond strength, poor wetting of the fibres by the matrix resin, and a reduction of its mechanical performance when exposed to moisture (8,9). The ability of chemical modification to increase the resistance of agricultural fibres to moisture has been widely studied (5,10,11), but very few of them have studied anhydride modification of fibre-matrix bonding, which might lead to the improvement of the composites of using phenol formaldehyde as binder properties (7).

A number of reviews have showed various improvements on composites features through chemical modifications (using acetic anhydride, phthalic anhydride, propionic anhydride, succinic anhydride etc). However, acetylation was the most studied because it is known to significantly develop the properties of the composites (12). The purpose of the study reported here was to determine the effect of various anhydride modifications of agricultural fibres to any improvement in the mechanical properties, physical properties and water absorption of composites so formed. Moreover, the overall aim was to produce high performance conventional composites from EFB MDF fibres and evaluate their properties in comparison with those achieved with present technology using non-modified fibres.

EXPERIMENTAL

Materials and Methods

The medium density fibreboard (MDF) oil palm empty fruit bunches (EFB) fibres was supplied by Malaysia Palm Oil Board (formerly known as Palm Oil Research Institute Malaysia). Prior to modification, the MDF fibres was extracted in Soxhlet apparatus using a mixture solvent of toluene, methanol and acetone (4:1:1 by volume) for 5 hours at 70^{O}C. The extracted fibres was dried overnight in oven at 105^{O}C and allowed to cool in desiccators before preparing the composite.

Anhydride modifications

For the modifications, a quantity of extracted oven-dried fibres was put in 3-litre reaction flask and the weight of the dry contents determined on a four-figure balance. The flask was then placed in an oil bath set at 100^{O}C for 1 hour. Reaction with acetic or propionic anhydride was performed as the flask was filled and a reflux condenser fitted. After refluxing process completed, the flask was removed from the oil bath the hot reagent decanted off. The fibres was then washed by refluxing in acetone for 3 hour to remove unreacted anhydride and acetic acid by-product, then the solvent decanted off. The flask containing the modified fibres was oven-dried overnight before transferred to cool in to ambient temperature in the dessicator. The fibres then were weighted to determine the weight percent gain of the fibres due to the modification.

Composite preparation

Weighted amount of fibres and 7 % phenol formaldehyde resin of the fibres weight were mixed by spread the pulp on a mat and sprayed the resin with a sprayer. The mixer was hand-formed in a deckle box with internal dimensions of 200 x 200 mm. It was pre-pressed for 5 minutes. Then the pre-pressed mixer was hot-pressed (platen temperature, 150 °C) to 5 mm thick with targeted density of 0.7 g/cm^3 for 10 minutes. After that, it was cold-pressed for overnight. The boards were cut into specimens for evaluating their properties.

TESTING AND ANALYSIS

Fourier-Transform Infra-Red Analysis (FT-IR)

This procedure was employed to characterize the product of the reaction. The analysis was carried out on a Perkin Elmer System 2000 FT-IR spectrometer using a potassium bromide disc method.

Mechanical Testing

Tensile test

Tensile tests were carried out on an Instron model 4301 according to Japanese Industrial Standard for Fibreboards (JIS A5905). Each batch, 10 specimens were cut from a

composites board using a Beaver NC5 router connected to a CRUSADER II-computer controlled system. Tests were performed using a cross head speed of 2 mm/min, gauge length of 50 mm using a load cell of 500 N.

Flexural test

Flexural tests were performed according to JIS A5905. Approximately, samples of 95 mm x 15 mm x 5 mm (length x width x thickness) were used for the bending test. Tests were conducted on an Instron model 1195, with strain rate of 2 mm/min.

Impact test

Impact tests were conducted based on JIS A5905. Test was carried out using Impact Pendulum Tester (Zwick Model 5101). Ten specimens were prepared from rectangular bars of dimensions 65 x 15 mm, chopped off in a Charpy pendulum device and the absorp energy was measured as the reduction in pendulum energy. The Charpy impact strength on unnotched specimens in kilojoules per square meter was calculated.

Internal bond strength test

Internal bond strength determined the tensile strength perpendicular to the board plane. Test was performed accordance with JIS A5908-1994, using Instron model 1195

machine. Ten samples with density of 750 kg/m^3 were glued to metal holder with epoxy resin

Water Absorption And Thickness Swelling Test

Samples with approximate dimensions of 20 x 15 x 5 mm were used for the measurements of water absorption and thickness swelling according to JIS A5908-1994. The composite samples were vacuum-dried at 70°C to a constant weight, and then immersed in distilled water at 30 °C and 55 humidity for 100 days. The samples were periodically taken out of the water, surface dried with absorbent paper, and reweighed and remeasured the thickness, and immediately put back into the water. The water absorption was determined by weighing the samples at regular intervals. A Mettler balance type AJ150 was used, with a precision of 1 mg. water absorption and thickness swelling were calculated according to the following formula.

$$\text{Water absorption, WA(\%)} = \frac{M_2 - M_1}{M_1} \times 100 \qquad (1)$$

Where M_2 is the mass of samples after immersion (g) and M_1 is the mass of the samples before immersion (g).

The thickness swelling was determined by measured the dimensions of the samples at regular intervals. The calculation for the measurement shown below.

$$\text{Thickness swelling (\%)} = \frac{t_w - t_0}{t_0} \times 100 \qquad (2)$$

Where t_0 is the initial thickness of the samples and t_0 is the thickness of wetted samples.

Scanning Electron Microscope Analysis

The fracture surface of the composite were mounted onto holders electrically conducting carbon adhesive tab. Specimens were coated with Polaron Equipment Lt model E500 coater at a voltage of 1.2kV (10mA) in a vacuum at 25Pa for 5 minutes. After that, the samples were observed in Leica Cambridge S-360 S scanning electron microscope to study the fibre-matrix bonding.

RESULTS AND DISCUSSION

Reaction and Fourier-Transform Infra-Red Analysis (FT-IR)

The weight of fibres increased after modification with acetic anhydride or propionic anhydride. Table 2 below showed the results of weight percent gained for each samples tested. The calculation according to equation 3 below:

$$\text{WPG (\%)} = [\text{ (weight gain/original weight) }] \times 100 \quad (3)$$

Figures 1 and 2 below displayed the reaction schemes for acetic and propionic anhydride modifications, respectively. Propionylation have showed the higher weight percent gain (WPG) as compared with acetylation. This was due to adduction of 3-carbon hydrophobic group to the propionilated fibres, whereas acetic modification adducted 2-carbon hydroxyl group during modification.

Figure 3 showed the evidence of the anhydride modification (acetylation and propionylation) by comparing the FT-IR spectra of the product (non-extracted, extracted, acetylated and propionilated). Upon modification of MDF fibre with anhydrides, a new peak appeared in the range 1734-1745 cm^{-1} due to carbonyl group (13), and an increased in the carbon-hydrogen (C – H) region (1370-1378 cm^{-1}). Table 3 below was referred for the typical guidance for several major absorption bands for agricultural fibres from the previous study (14). With all anhydride modifications, an increased of the hydrophobicity of the fibres occurred and thus the degree of moisture absorption was reduced accordingly.

Mechanical Properties

Tensile properties

The effect of fibres acetylation and propionic modification, extracted and non-extracted was compared. Properties of fibreboards were strongly dependent on the interfacial interactions between the fibres and the resins. Dispersability of the fibre in the resin also depends to a large extent on the wettability of the fibre surface by the resin. There was a relationship between tensile strength (TS), modulus (TM) and elongation at break (EOB). The effect of anhydride modifications as compared to non-extracted and extracted on TS and TM of MDF fibreboards were illustrated in Figure 4 and 5 respectively. The changes in TS and TM followed the order: acetylated (highest) > propionylated > extracted > non-extracted (lowest). This was probably due to the modified fibre were rendered more hydrophobic and thus enhanced compatibility between fibre and matrix resin

consequently. The improvement of fibre-matrix bonding would lift the strength, stiffness and interfacial bond of the composites. Whereas, from Figure 6, with all modified fibres (acetyl, propionyl and extracted), the result was decreased in elongation compared with unmodified fibres (non-extracted). This was due to the improved fibre-matrix adhesion (to give more stiffness to the composites) and because modified fibre were prone to split and fall apart, so that, fibre was more brittle after modification. Consequently, we can conclude that in this case improved wetting of the treated fibres by the matrix was responsible.

Flexural properties

Figure 7 and 8 showed the effect of fibre treatment on the flexural strength and modulus, respectively, of the fibreboards. The poor flexural properties showed by the composites were attributed to the weak fibre/matrix bonding. In production of fibreboards, poor wetting was expected due to deficient compatibility between polar nature of MDF fibres and non-polar PF resin that lead to the weak interfacial regions. These weak interfacial regions would reduce the efficiency of stress transferred between resin and fibre, thus poor strength properties can be anticipated. The quality of interfacial bonding was determined by several factors, such as, the nature of the fibre and binder as well as their compositions, the fibre aspect ratio, the types of mixing procedures, processing conditions employed and on the treatment of the polymer or fibre with various chemicals, coupling agents, compatibilizers, etc. Modification was made to chemically modified the fibres surface with acetic and propionic anhydride.

The results showed that composites with acetylated and propionylated fibres showed higher flexural strength than those without such modifications (Figure 7). The anhydride was able to chemically attach to fibres. This was possible through the reaction of fibres hydroxyl groups with the carboxyl groups of the anhydride. This indicated that the modification might improve the hydrophobicity of the pulp surface, which consequently results in the improved compatibility with the PF resin.

Figure 8 illustrated the results of the modulus of the fibreboards increased as the modifications were done to the MDF fibres. The effect on flexural modulus was more significant than on flexural strength because the incorporation of modified fibre was still able to instill stiffness into the composites. The acetylated and propionylated fibre displayed higher stiffness as compared to those with unmodified fibre. This might contributed to the increased compatibility between the resin and the fibre. The increased compatibility results in the formation of a continuous interfacial region, which permitted a better and efficient stress transferred in the samples.

Impact properties

The toughness of a composite was substantially influenced by the strength of the fibre-adhesive bond. The effect of the modifications (extracted, acetylated and propionylated) on the impact properties (Charpy) of the MDF fibreboards was presented in Figure 9. The impact properties of fibreboards in the following order: non-extracted (lowest) <

extracted < propionyl < acetyl (highest). The results clearly indicated poor energy-absorbing capabilities of the unmodified fibres. There were two mechanisms by which fibres can reduced the impact strength of the composite (15): Fibres tend to inhibit deformation and ductile mobility of polymer molecules, which lowered the ability of the composite to absorb energy during crack propagation; and fibre also created high stress concentration regions that required less energy to initiate a crack. Such regions might occur at fibre ends, areas of poor interfacial adhesion and regions where fibres contact each other. Therefore, it suggested that modification improved fibre wettability so that the produced composites had less void spaces, which provided sites for crack initiation. Less void spaces will then mean that there are fewer flaws in the composites. This lead to a further increase in impact strength of the composite.

Internal Bond Strength

Figure 10 was the plot of the internal bond strength of non-extracted, extracted, acetylated and propionylated MDF fibres. Modification of the fibre with acetic anhydride and propionic anhydride improved the internal bond strength of the composite system. The phenomena were caused by better compatibility between fibre and matrix resin surface. Previous study (16) also stated that the internal bond strength depended on the duration of the modification and the size of the fibre used. When it comes to internal bonding, slightly finer fibres were more favorable. The changes of the internal bond strength were as followed: acetylated (highest) > propionylated > extracted > non-

extracted. Modification improved the internal bond due to the increasing of the hydrophobic properties of the fibre surface.

The internal bond fractures of non-extracted, extracted, propionic (extract) and acetic (extract) composites were showed in Figure 11 (a-d), respectively. The non-extracted fibres composites showed poor fibre-matrix bonding. The same phenomenon exhibited for extracted fibres with modification. Figure 11 (c and d) showed good bonding between the modified fibre (hydrophobic) and phenol formaldehyde matrix. These properties behavior influenced the mechanical and physical properties of composites.

Physical properties

Agricultural fibres are hydrophilic and readily absorb water, which leads to swelling of the fibres. This effected dimensional stability of composites when continuously exposed to high humidity environments. Thus, composites suffered loss of mechanical properties due to deficient wet fibre properties and degradation of fibre/matrix resin interaction. The increased hydrophobicity by the acetyl groups produced an obvious effect on the water absorption (Figure 12) and thickness swelling (Figure 13) behaviours of the fibreboards. The rate of water uptake decreased in the order: extracted (highest) > non-extracted > propionylated > acetylated (lowest). The water absorption behaviour of the fibreboards depends on the ability of the fibre to absorb water due to the presence of hydroxyl groups. The hydroxyl groups absorbed moisture or water through the formation of hydrogen bonding. Treatment of the fibre was carried out by reacting the hydrophilic

hydroxyl groups with acetic anhydride or propionic anhydride. Acetic and propionic anhydride modifications reduced the number of hydrophobic groups in the fibres when it reacted with the fibres. The blocking of hydroxyls groups also changes the hydrophilic nature of the fibre, which leads to exclusion of water from the substrate. The acetyl groups would be replacing hydroxyl groups on the fibre surface (7). Thus, this would produce more hydrophobic surface as compared to the unmodified fibre. Acetylation, which resulted the best-lowered thickness swelling properties, imparted a permanent swelling because the ester-bonded acetyl group was larger than the hydrogen of the hydroxyl group it was substituting. Since the maximum swelling of the fibre wall at equilibrium with water is only slightly higher than the permanent swelling caused by the acetylation treatment, while actual swelling of an acetylated fibre in contact with water was very small (17). The treated fibreboards showed lower absorption and thickness swelling than the unmodified.

CONCLUSIONS

The studies have looked at the use of chemically modified fibre from MDF pulp in phenol formaldehyde fibreboards. It can be concluded that acetic and propionic anhydrides have been found to react with the MDF pulp. Modification resulted in hydrophobic fibres and improved fibre-matrix bonding. From the modified fibres investigated, acetylated fibres showed the highest tensile, flexural, impact and internal bonding properties, followed by propionylated and then extracted, due to improving the

compatibility between fibre and resin. The changes of moisture absorption and thickness swelling were also dependent upon fibre modification. These properties followed the order unmodified (highest) > extracted > propionylated > acetylated (lowest).

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