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Location and characterization of flame retardant in medium density fiberboard

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Introduction

Medium density fibreboard (MDF) is a widely used wood composite in furniture manufacture and building construction. In such application resistance to flame spread and fire is an advantage. The properties of MDF can be improved with the use of flame retardant chemicals and several studies have investigated the fire retardant treatment of wood based composites (Hashim et al. 2002; Grexa, et al. 2003; Kozlowski et al. 1999). There are three main groups of flame retardant chemicals; a) inorganic eg. metal hydroxides, antimony compounds, boron compounds and phosphorus compounds; b) halogenated products based primarily on chlorine and bromine; c; organophosphorus products which primarily rely upon phosphate esters (Anon., 1997). For wood and wood products, the most commonly used fire retardant chemicals include borax-boric acid, zinc borates, chromated zinc chloride, ammonium sulphate, and nitrogen-phosphate mixtures (Holmes, 1977; Myers and Holmes, 1975; Winandy et al. 1988; White and Sweet, 1992; Sain, et al., 2004). The main ways of application of flame retardant to wood and wood products are by impregnation of wood with flame retardant materials, incorporation of the flame retardant into the glue system or surface treatment of the products. There are many

Sweet, 1992, Le Van and Winandy, 1989; Le Van et al., 1996) but very little has been reported on the distribution and characterization of the flame retardant materials in MDF (Grexa and Lubke , 2001).

The present work investigates the characterization and distribution of flame retardant materials in MDF. The materials used were zinc borate and sodium aluminate. The location and distribution of chemicals were determined by scanning electron microscope (SEM) coupled with energy dispersive X-ray analysis (EDAX). This technique has been found useful in furnishing the information for the preservative distribution as being done by Helsen and Bulck (1998) and in detecting UF resin penetration in particleboard (Bolton, et al. 1988). Fourier transform infrared spectroscopy (FTIR) correlates with functional groups. It has been used by several researchers in examining lignocellulosic materials (Smith, 1996). Zhang and Kamden (1999) used DRIFT-IR to characterize interaction between copper ethanolamine and wood. Michelle (1993) used FTIR to study the reaction of wood and lignin model compounds with inorganic chromium trioxide and concluded that the main reaction was with wood via aromatic ring of lignin. Liu, et al. (2002) used FTIR to investigate thermal properties of boron containing phenol formaldehyde. In this study FTIR is used to characterise and monitor the alteration in wood components in MDF treated with these flame retardant materials. Absorption sites such as phenolic hydroxyl, carboxylic, and ester groups in wood components were examined.

Experimental

Board types

Experimental MDF of dimension 21.2 x 21.2 x 0.5 cm and target density of 0.7 gm/cm^3 were made using a small scale laboratory press. The boards were made from

thermomechanically processed either rubberwood fibres (*Hevea brasiliensis*) or oil palm empty fruit bunches fibres (*Elaeis guineensis*).

Two types of adhesives were used that is urea formaldehyde and phenol formaldehyde adhesives at 15 % resin level based on oven dry weight of the boards. Fire retardant chemicals used are zinc borate and sodium aluminate incorporated in the resin mix during fibre blending.

SEM - EDAX

The location and distribution of the fire retardant chemicals were viewed with SEM. Presence of chemicals were confirmed using EDAX.

FTIR

FTIR analysis was performed on a Nicolet 510P spectrometer equipped with Spectra-Tech diffuse reflectance accessory (DRIFT). Potassium bromide (KBr) was used to collect the background. The samples were obtained by scraping with a fresh razor blade throughout the cross section. The air dried samples were mixed with KBr before spectrum collection. The spectra was collected using diffuse reflectance FTIR (DRIFT). Spectra were acquired for a total of 64 scans between a 400 to 4000 cm^{-1} wave number range with a resolution of 4 cm^{-1}. The intensity of the selected bands was determined. It was obtained by measuring the peak height, from the absorbance after auto base line correction using OMNIC E.S.P. 5.2a.

Results and discussion

SEM - EDAX

The presence of flame retardant chemicals was detected across the samples at random locations. Figure 1, 2 and 3 show representative SEM photomicrographs from the samples viewed. At low magnification (160x), it was seen that zinc borate was distributed evenly on the fibres as small particles. Zinc borate particles were also seen in the lumen and also in between fibres. (See Figure 1c). No such particles was seen in the control samples (Figure 1a). Examination using EDAX of the MDF control samples made from rubberwood using urea formaldehyde show that the major elements present are C, O, and apart of Au from the coating media as shown in Figure 1b. No peak of zinc was detected from this sample. Zinc element peak however is seen present in the flame retardant treated MDF as shown in Figure 1d with the board treated with zinc borate made using PF resin.

Figure 2 shows the SEM photomicrographs of MDF made from zinc borate at maginification x 2500. At higher maginification, zinc borate was seen encrusted at the cell wall for both rubberwood and oil palm fibers. Zinc borate particles were present on the fibres in the treated MDF either sitting on the cell walls, or on the pits. It seems that there is not much different in the distribution with the types of resin used.

Figure 3a shows the SEM photomicrographs of MDF made from EFB using PF resin (control) and Figure 3b shows SEM photomicrographs of the flame retardant treated MDF with sodium aluminate. It can be seen that presence of sodium aluminate as small particles and also as small crystals like substance on the cell wall of the MDF made from EFB. A clear encrustment was seen on the cell wall forming a crystal on the surface of the cell wall of EFB. Present of this crystal like substances probably reduce the flame spread. The EDX spectrum of the treated board confirms presence of aluminum and sodium which can be seen in Figure 2C.

Two types of distribution were observed from the micrographs (Figure 1-3). One is in the form of particles. Second in the form of crystal on the wall surface. This distribution of the flame retardant chemicals provide better flame retardant properties.

FTIR

The FTIR spectra of MDF obtained from the study are shown in Figure 4 to 7. The absorption bands put forward for examinations were assigned based from various literatures is tabulated in Table 1.

Figure 4 and 5 shows the FTIR spectra of flame retardant MDF made from either rubberwood or oil palm empty fruit bunch treated with zinc borate together with the MDF control using either PF or UF resin along with pure zinc borate with KBr. Analysis of the FTIR spectrum of Figure 4 shows that a sharp peak was seen at 1251 cm^{-1} for the pure zinc borate spectra and become gradually wide for other MDF spectra. According to Liang et al. (1960) peak around 1263 cm^{-1} is the C-O stretching vibration in lignin and hemicellulose. A sharp peak is seen at 805 cm^{-1} of the pure zinc borate and it becomes wider for MDF treated with zinc borate using PF resin and also wider peak at this point for MDF treated with zinc borate using UF resin. The peak becomes much wider for the MDF control using PF resin and UF resin. According to Michelle (1989) peak at 809 cm^{-1} is due to vibration of O mannan in hemicellulose. At peak 756 cm^{-1} a sharp peak is seen for the pure zinc borate and gradually becomes less in other MDF spectra. According to Liu, et al. (2002) and Gao, et al. (1999), a peak at 750 cm^{-1} maybe attributed to the presence of benzene ring. The same trend is seen in Figure 2 for MDF made from similar specification but made from oil palm empty fruit bunches.

Figure 6 and 7 show the FTIR spectra of flame retardant MDF made from either rubberwood or oil palm empty fruit bunch treated with sodium aluminate together with the MDF control using either PF or UF resin along with pure sodium aluminate with KBr. The results show that at 903 cm^{-1} there is a transition in peak for pure sodium aluminate and a wide peak is seen here for all other spectra of MDF. The peak at 895 cm^{-1} may accounts for the presence of C1 group frequency in cellulose and hemicellulose (Michell, 1989; Michell et al. 1965; Bolker and Somerville, 1963). The same trend is seen in Figure 7 for spectra of MDF made from oil palm empty fruit bunches.

Conclusions

The flame retardant chemicals were present as small particles distributed in between the fibres .

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Table 1 Assignments of infrared absorption bands

Position in cm^{-1}	Band assignments	Reference
1739	Carboxyl stretching vibration in carboxylic acid	Tolvaj and Faix,(1995); Michelle et al. (1965)
1730	C=O stretching in xylan	Michell et al. 1965; Bolker and Somerville, 1963
1710	1-ethoxy-1guaiacyl-2-propanone	Hergert, (1971)
1709	B-hydroxylconiferyl alcohol	Hergert, (1971)
1700-1715	Ketones in lignin stretching	Hergert, (1971)
1700-1600	H-O-H bending band	Johnston et al. 2002.
1705	Guaiacyl acetone	Hergert, (1971)
1660	Keto-carbonyl conjugated with benzene ring	Harrington et al. 1964
1650	Carbonyl group	Liu, et al., (2002) ; Gao, et al. 1999
1643	H-O-H deformation in absorbed water in carbohydrate	Michell, 1989
1640	H-O-H bending mode for sorbed water only	Johnston et al. 2002.
1600	Benzene ring stretching in lignin	Harrington et al. 1964; Michell, 1989; Michell et al. 1965; Bolker and Somerville, 1963
1600	Benzene ring	Liu, et al., (2002); Gao, et al. 1999
1511	Lignin	Silva, et al. 1999
1505	Benzene ring stretching in lignin	Harrington et al. 1964; Michell, 1989; Michell et al. 1965; Bolker and Somerville, 1963
1460	CH_3 deformation in lignin and CH_2 in xylan	Michell, 1989; Michell et al. 1965; Bolker and Somerville, 1963
1453	Benzene ring stretching in lignin and CH_2 vibration in cellulose	Michell, 1989
1450	$-CH_2-$ group	Liu, et al., (2002); Gao, et al. 1999
1425	CH_2 scissor vibration in cellulose /C=C stretch in aromatic ring lignin	Michell, 1989; Michell et al. 1965; Bolker ; Somerville, 1963 and Liang, et al. 1960
1400	-CH bond	Trepper, 2001
1370	CH_2 bending in cellulose and hemicellulose	Michell, 1989; Michell et al. 1965; Bolker and Somerville, 1963
1370,1221	Phenolic O-H deformation	Hergert, (1971); Sarkanen et al.1967
1350	Phenol-borate B-O	Liu, et al., (2002); Gao, et al. 1999
1330	OH in plane deformation in vibration in cellulose and hemicellulose	Michell, 1989
1325	CH_2 wagging vibration in cellulose	Michell et al. 1965; Bolker and Somerville, 1963
1315	CH_2 wagging vibration in cellulose	Michell, 1989
1275	Guaiacyl nuclei in lignin	Sarkanen et al. 1967
1263	C-O stretch vibration in lignin and hemicellulose	Liang, et al. 1960
1230	Phenol hydroxyl group	Liu, et al., (2002) ; Gao, et al. 1999
1230	Syringyl nuclei in lignin and C=O in xylan	Michell et al. 1965 ; Sarkanen et al.1967

1160	C-O-C asymmetric bond in cellulose and hemicellulose	Michell, 1989; Michell et al. 1965
1110	O-H association bond in cellulose and hemicellulose	Michell, 1989; Michell et al. 1965
1050	Ether linkage C-O	Liu, et al., (2002) ; Gao, et al. 1999
1050	C-O strectching in cellulose and hemicellulose	Michell, 1989; Michell et al. 1965; Bolker and Somerville, 1963
1020	Benzene hydroxyl group	Liu, et al., (2002); Gao, et al. 1999
Below 1000	oxides	Tepper, 1999
895	C1 group frequency in cellulose and hemicellulose	Michell, 1989; Michell et al. 1965; Bolker and Somerville, 1963
870	1,3,4 substituted benzene ring in softwood lignin (out of plane bending)	Michell, 1989
810	1,3,4 substituted benzene ring in softwood lignin (out of plane bending)	Michell, 1989
809	Vibration of O mannan in hemicellulose	Michell, 1989
775	Vibration of galactan in hemicellulose	Liang et al. 1960
750	Benzene ring	Liu, et al., (2002); Gao, et al. 1999
680	COH out of plane bending in cellulose	Bolker & Somerville, 1963

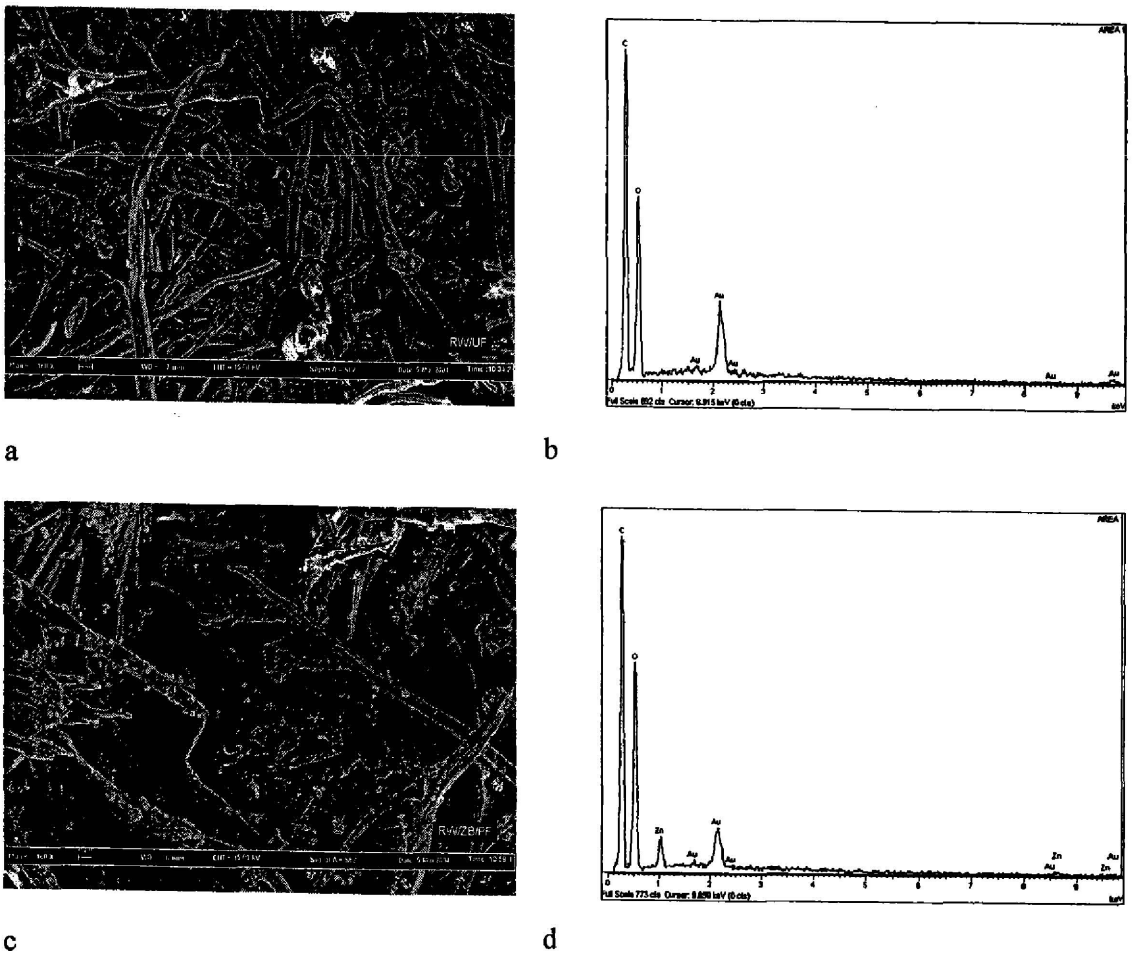
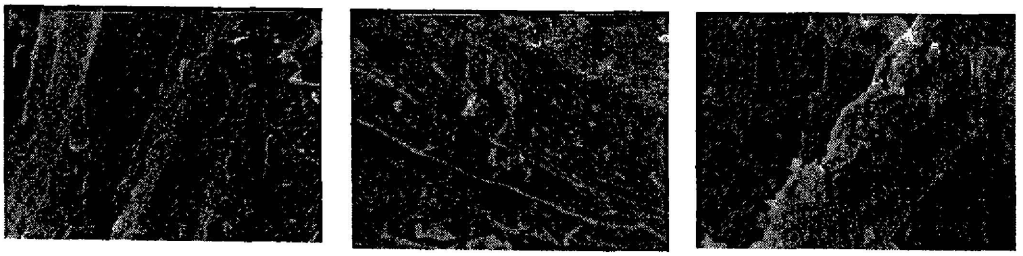
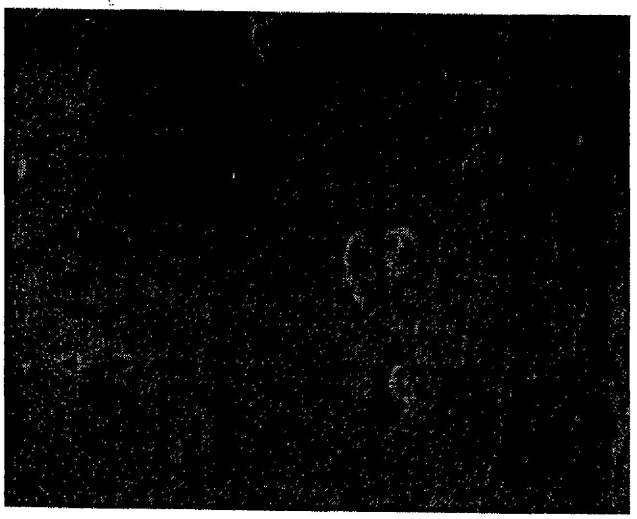


Figure 1: SEM photomicrographs and EDAX spectrum of MDF a) made from rubberwood (control) using UF resin and b) made from rubberwood treated with zinc borate using PF resin

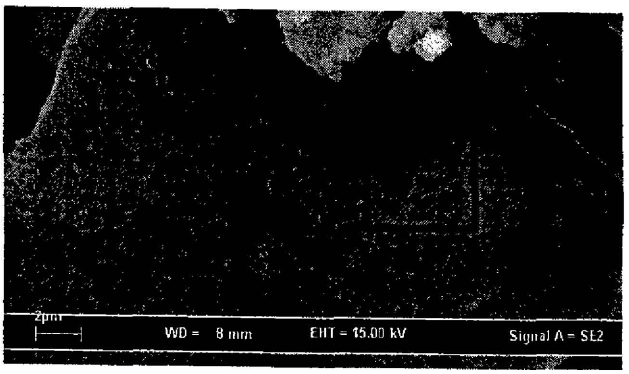


a) b) c)

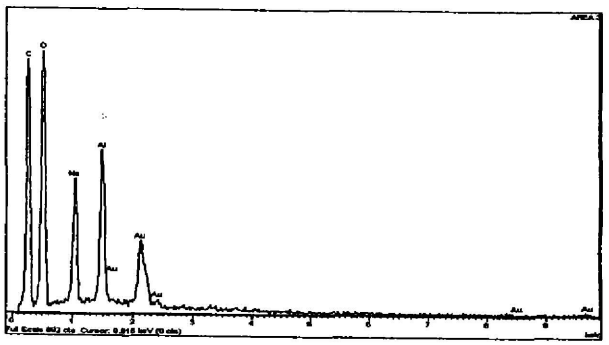
Figure 2: SEM photomicrographs of MDF a) made from rubberwood using UF resin as a control x 2500, b)made from rubberwood treated with zinc borate using UF resin x 2500 and, c) made from oil palm empty fruit bunches treated with zinc borate using PF resin x 2500



a



b



c

Figure 3: SEM phtomicrographs of MDF made from EFB (control) using PF resin x 2500 (a), MDF made from EFB treated with sodium aluminate (b) and the EDAX spectrum from b (c)

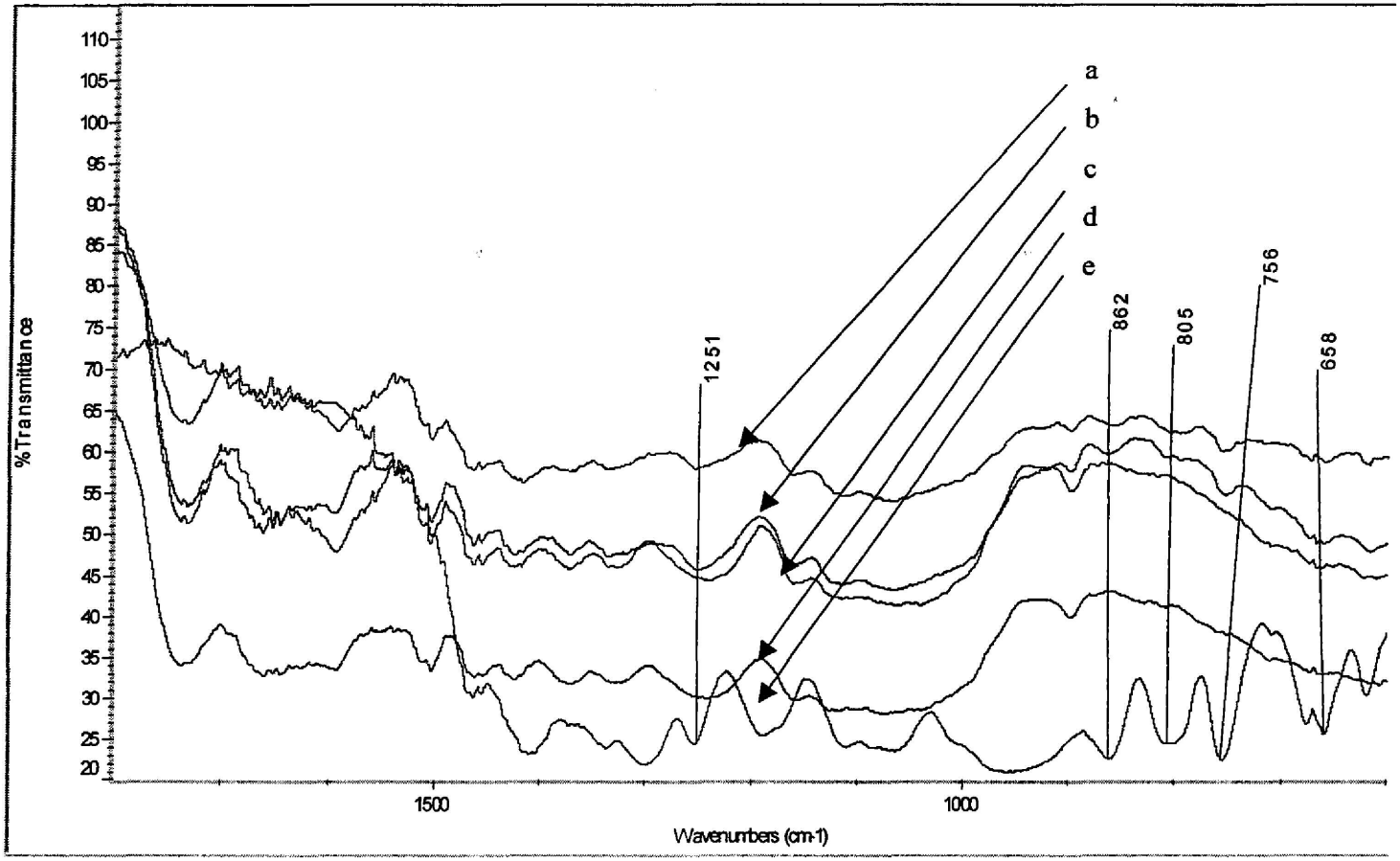


Figure 4: FTIR spectra of MDF made from rubberwood

a= MDF treated with zinc borate using PF resin
b= MDF treated with zinc borate using UF resin
c= MDF control using PF resin
d= MDF control using UF resin
e=pure zinc borate

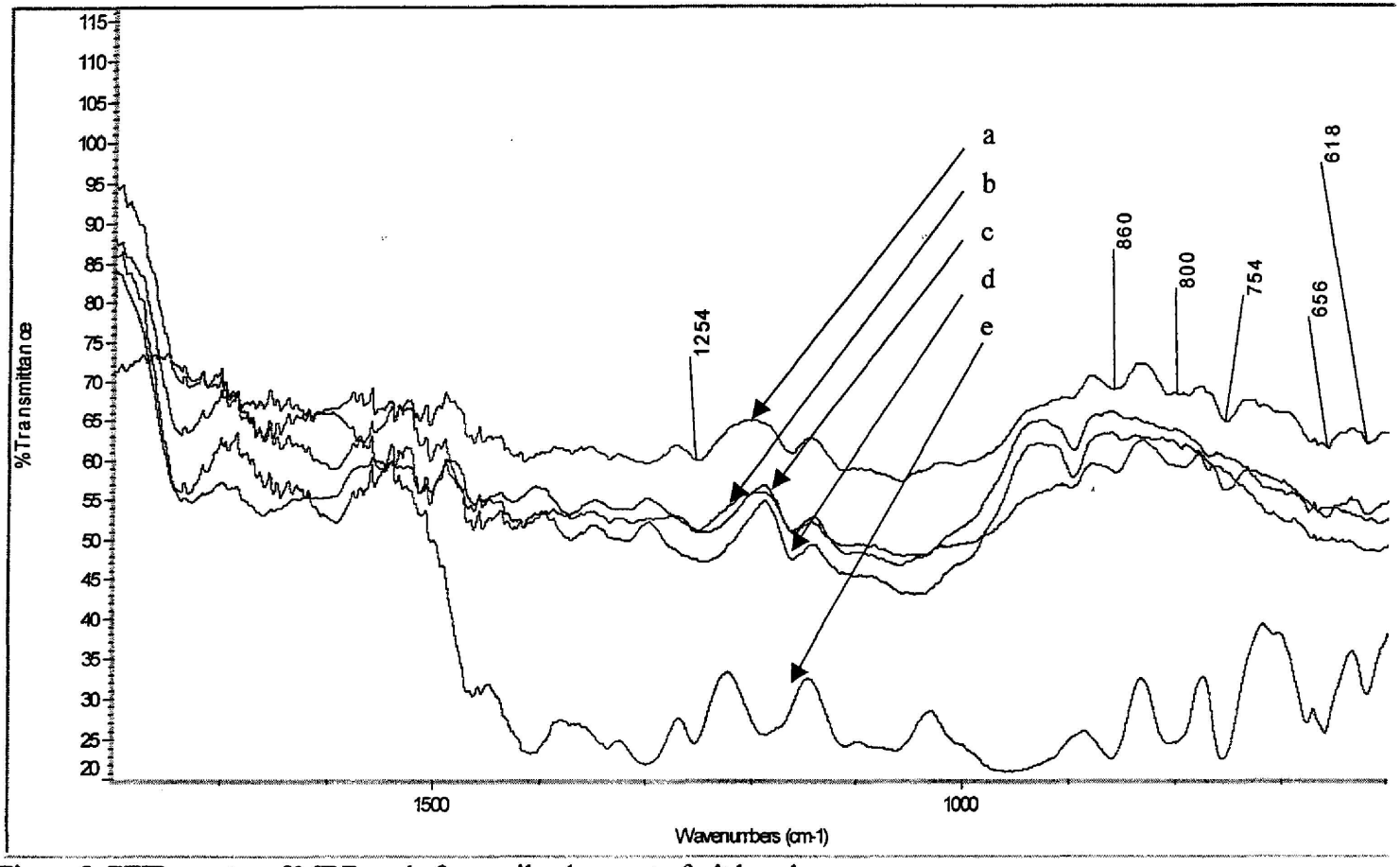


Figure 5: FTIR spectra of MDF made from oil palm empty fruit bunches

a= MDF treated with zinc borate using UF resin
b= MDF treated with zinc borate using PF resin
c= MDF control using UF resin
d= MDF control using PF resin
e=pure zinc borate

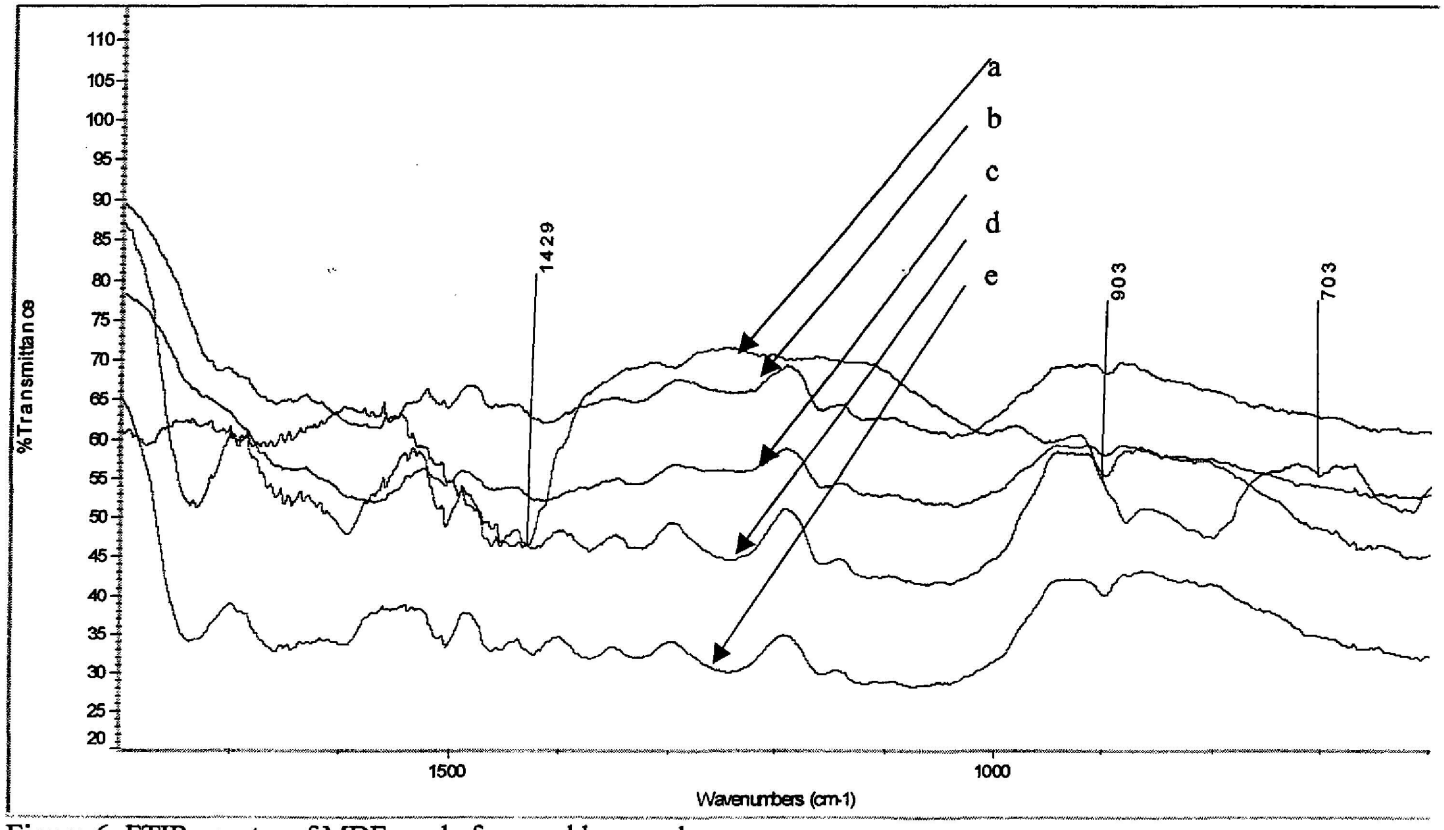


Figure 6: FTIR spectra of MDF made from rubberwood

a= pure sodium aluminate
b= MDF treated with sodium aluminate using UF resin
c= MDF treated with sodium aluminate using PF resin
d= MDF control using PF resin
e= MDF control using UF resin

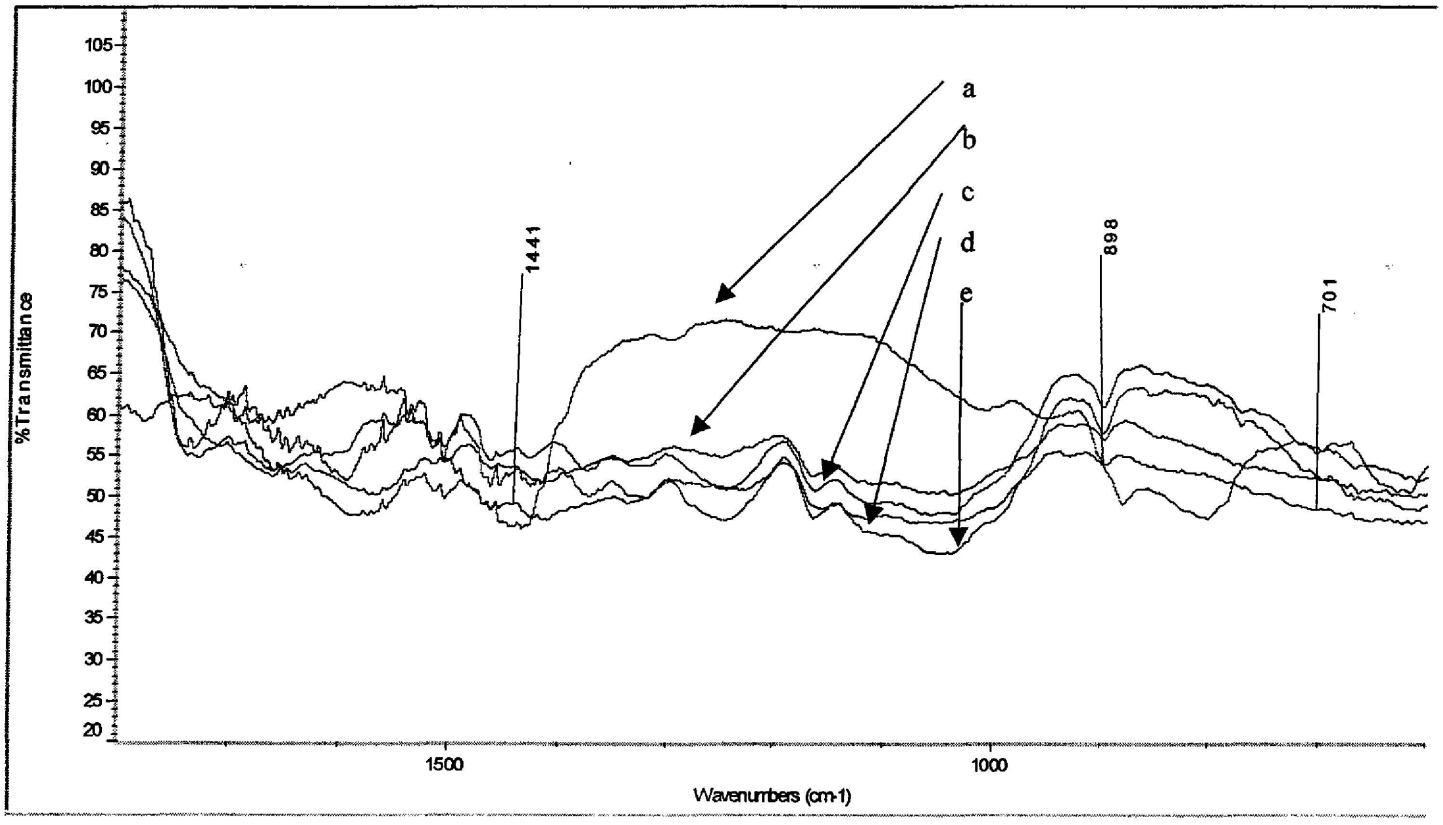


Figure 7: FTIR spectra of MDF made from oil palm empty fruit bunches

a= pure sodium aluminate
b= MDF treated with sodium aluminate using UF resin
c= MDF control using UF resin
d= MDF treated with sodium aluminate using PF resin
e= MDF control using PF resin