INFLUENCE OF NANOFILLERS ON THE PROPERTIES OF UREA FORMALDEHYDE RESIN AND MEDIUM DENSITY FIBERBOARD

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ABSTRACT

Wood based panel is typically a panel manufactured with wood in the form of fibers combined with a thermoset resin, and bonded at an elevated temperature and pressure in a hot press. The density of boards lie in the range of 600-800 kg/m^3 are known as Medium Density Fiberboard (MDF). The required pressing time depends on the curing time of thermoset resin (UF resin). The thermal conductivity of wood fibers is low due to which long duration for the complete curing is required. Several methods and heat transfer models were tested to increase the heat transfer for attaining proper cure of the fiber matrix with steam injection, electromagnetic heating, longer pressing time, etc. Further, emission of formaldehyde with the use of resin is observed. To overcome the problem, wood based composite industries have initiated with reduced formaldehyde content in the resin and included formaldehyde scavengers in the manufacture of MDF. These measures decrease the formaldehyde emissions to a certain extent, but adversely affect the mechanical properties of the boards.

In the present work three different types of nanofillers such as multiwalled carbon nanotubes (CNTs), aluminum oxide nanoparticles and nanosize activated charcoal were mixed with UF resin and used in the preparation of MDF. The process has improved heat transfer during hot pressing and achieved proper curing due to enhanced thermo physical properties of wood fibers. The influence of the nanofillers on the curing behaviour, cross-link density of UF resin and visco-elasticity properties were investigated using differential scanning calorimetry (DSC) and dynamical mechanical analysis (DMA). To improve the dispersion of nanofillers into UF matrix, high speed mechanical stirring and ultrasonic treatments were used. The CNTs were oxidized with nitric acid and the functional groups formed on its surface improved the dispersion and interaction with UF matrix. The dispersion of nanofillers in UF resin matrix was confirmed with XRD, FESEM, and DMA tests undertaken. The mixing of CNTs and Aluminum oxide with UF resin have reduced the curing time due to enhanced thermal conductivity of MDF matrix. The heat transfer during hot pressing of MDF improved significantly with the addition of CNTs and Al_2O_3 nanoparticle and activated charcoal did not have effect on heat transfer. The curing rate of UF resin improved with all the three nanofillers, as the activation energy of UF curing decreased by the DSC results. The physical and mechanical properties of MDF have improved significantly with CNTs and Al_2O_3 nanoparticle. The activated charcoal has significantly decreased the formaldehyde emission of MDF.

The RSM models were developed to optimize the use of CNTs in the production of MDF because CNTs has gave the best results in three nanofillers. The regression models were developed with three independent variables (Pressing time; CNTs% and UF %) for two responses IB and MOR. The optimum values for each variable are 238 s pressing time, 3.5% CNTs and 8.18% UF resin with the predicated values for IB 0.71 MPa and 48.78 MPa for MOR.

ABSTRAK

Panel berasaskan kayu merupakan panel yang diperbuat dengan menggunakan kayu berbentuk gentian yang digabungkan dengan resin termoset, dan diikat pada suhu dan tekanan tinggi dengan menggunakan penekan panas. Ketumpatan panel tersebut yang terletak dalam lingkungan 600-800 kg/m^3 dikenali sebagai Papan Serat Ketumpatan Sederhana (MDF). Tempoh masa kenaan tekanan bergantung kepada masa pengawetan resin termoset (resin UF). Kekonduksian haba gentian kayu adalah rendah yang mana tempoh yang panjang diperlukan untuk proses pengawetan lengkap berlaku. Terdapat beberapa kaedah dan model pemindahan haba telah diuji untuk meningkatkan pemindahan haba dalam mencapai pengawetan yang sesuai bagi matrik berserat termasuk kaedah suntikan wap, pemanasan elektromagnetik, tempoh kenaan tekanan yang lebih lama, dan lain-lain lagi. Tambahan pula, pelepasan formaldehid dengan penggunaan resin juga diperhatikan. Untuk mengatasi masalah ini, industri komposit berasaskan kayu telah mengambil langkah dengan mengurangkan kandungan formaldehid dalam resin dan memasukkan pemungut formaldehid dalam pembuatan MDF. Langkah-langkah ini didapati dapat mengurangkan pelepasan formaldehid sehingga ke tahap tertentu, namun sebaliknya menjejaskan sifat-sifat mekanikal papan.

Dalam kajian ini, tiga jenis partikel nano telah digunakan iaitu *Multiwalled Nanotube Carbon* (CNTs), partikel nano aluminium oksida dan arang bersaiz nano yang diaktifkan telah dicampur dengan resin UF dan digunakan dalam penyediaan MDF. Proses ini telah meningkatkan pemindahan haba semasa proses penekanan dan mencapai proses pengawetan lengkap yang disebabkan oleh peningkatan ciri-ciri termo-fizikal. Kesan partikel nano terhadap sifat-sifat tingkah-laku pengawetan, ketumpatan sambung silang resin UF dan juga visco-elastik diuji dengan menggunakan kalorimeter pengimbasan pembezaan (DSC) dan analisis mekanikal dinamik (DMA). Untuk meningkatkan penyebaran partikel nano dalam UF matriks, pengadun mekanikal berkelajuan tinggi dan rawatan ultrasonik telah digunakan. Partikel nano CNTs telah dioksidakan dengan menggunakan asid nitrik di mana kumpulan berfungsi yang terbentuk di permukaan partikel telah meningkatkan penyebaran dan interaksi dengan UF matriks. Penyebaran partikel nano dalam UF resin matriks telah disahkan melalui analisis XRD, FESEM, dan ujian DMA yang telah dijalankan. Pencampuran antara CNTs dan aluminium oksida dengan resin UF telah mengurangkan masa pengawetan yang mana ia disebabkan oleh peningkatan kekonduksian haba MDF matriks. Pemindahan haba semasa penekanan panas MDF meningkat dengan ketara dengan penambahan partikel nano CNTs dan Al_2O_3, manakala panambahan arang yang telah diaktifkan pula tidak memberi kesan ke atas pemindahan haba. Kadar pengawetan resin UF telah meningkat bagi ketiga-tiga partikel nano di mana tenaga pengaktifan untuk pengawetan UF menurun berdasarkan keputusan DSC. Ciri-ciri fizikal dan mekanikal MDF juga telah meningkat dengan ketara dengan kandungan CNTs dan Al_2O_3 partikel nano. Arang yang diaktifkan juga telah mengurangkan pelepasan formaldehid dengan ketara dalam MDF.

Model RSM telah dibangunkan untuk menoptimumkan penggunaan CNTs dalam pengeluaran MDF kerana CNTs didapati dapat memberikan hasil yang baik di antara tiga jenis pengisi nano. Model regresi telah dibangunkan dengan menggunakan tiga pembolehubah bebas (tempoh penekanan; CNT % dan UF %) untuk dua keadaan iaitu IB dan MOR. Nilai optimum untuk setiap pembolehubah adalah 238 s untuk tempoh penekanan, 3.5 % CNT dan 8.18 % resin UF dengan nilai jangkaan untuk IB 0.71 MPa dan MOR 48.78 MPa.

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NOMENCLATURES

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Symbol	Meaning
A	Frequency factor
a	Thickness of sample (m)
b	Width of sample (m)
d	spacing between atomic planes or lattice spacing (A^o)
E'	Storage modulus resins(MPa)
E''	Loss modulus of resins (MPa)
E^*	Complex modulus
Ea	Activation Energy (kJ/mol)
k	Rate constant
L	Length of span (m)
l	Length of specimen (m)
P	Peak load (N)
R^2	Coefficient of determination
t	Thickness of specimen (m)
$\tan \delta$	Loss factor or loss tangent
T_f	Final thickness of sample (mm)
T_i	Initial thickness of sample (mm)
T_P	Peak curing temperature (^{o}C)
w	Width of specimen (m)
w_f	Final weight of sample (g)
w_i	Initial weight of sample (g)
w_p	Weight of nanofillers (g)
w_R	Weight of resins (g)
$\Delta E'$	Rigidity of resins (%)

Greek Symbols

Symbol	Meaning
α	Extent of the curing reaction in Kissinger's equation

β	Heating rate of sample in DSC (^{o}C/min)
λ	X-ray wavelength
ϖ	diffraction angle (degree)
φ	Volume concentration of nanofillers (%)
σ_A	Sinusoidal stress
ε_A	Sinusoidal strain
ρ	Density of MDF sample (Kg/m^3)
ρ_p	Density of nanofillers (Kg/m^3)
ρ_R	Density of UF resin (Kg/m^3)
ΔH	Cure enthalpy (J/g) of UF curing reaction
ΔH_t	Cure enthalpy at time t (J/g)
ΔH_{Total}	Cure enthalpy at the end of curing process of UF resin in DSC

LIST OF ABBREVIATIONS

AC	Activated charcoal
AC0	Sample having 0.0 wt% loading of activated charcoal in UF resin
AC1	Sample having 1.0 wt% loading of activated charcoal in UF resin
AC2	Sample having 2.5 wt% loading of activated charcoal in UF resin
AC3	Sample having 5.0 wt% loading of activated charcoal in UF resin
AL0	Sample having 0.0 wt% loading of Al_2O_3 nanoparticles in UF resin
AL1	Sample having 1.0 wt% loading of Al_2O_3 nanoparticles in UF resin
AL2	Sample having 2.5 wt% loading of Al_2O_3 nanoparticles in UF resin
Al_2O_3	Aluminum oxide nanoparticles
AL3	Sample having 5.0 wt% loading of Al_2O_3 nanoparticles in UF resin
ANOVA	Analysis of Variance
BET	Brunauer, Emmett and Teller
BET	Surface area
CARB	California Air Resources Board
CNT1	Sample having 1 wt% loading of CNTs in UF resin
CNT2	Sample having 2.5 wt% loading of CNTs in UF resin
CNTs	Multiwalled carbon nanotubes
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
DTG	Derivative thermogarvimetry
EM	Electro-magnetic
F/U	Formaldehyde/urea molar ratio
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectoscopy
IB	Internal bonding (MPa)
LCL	Lower control limit in Tukey's test
MC	Moisture content (%)
MDF	Medium density fiberboard
MOE	Modulus of elasticity
MOR	Modulus of rupture (MPa)

MUF	Melamine urea formaldehyde resin
OSB	Oriented strand board
PF	Phenol formaldehyde resin
pMDI	Polymeric 4, 4 –diphenylmethane diisocyanate
R_{IB}	Regression model equation of RSM model for IB
R_{MOR}	Regression model equation of RSM model for MOR
RSM	Response surface methodology
SWCNTs	Single walled carbon nanotubes
TGA	Thermogravimetry
TMP	Thero-mechanical pulping
TS	24 hrs Thickness swelling (%)
UCL	Upper control limit in Tukey's test
UF	Urea-formaldehyde resin
UTM	Universial Testing Machine
VDP	Vertical density profile
WA	24 hrs Water absorption (%)
WBC	Wood based composites
XRD	X-ray diffraction

CHAPTER- 1

INTRODUCTION

1.1. BACKGROUND

Over the last decades, there is a growing interest in the development of wood based panels (WBP). These industries are continuously seeking ways for increased productivity; cost effectiveness, higher quality of the boards and at the same time safeguard the environment.

The WBP industry currently has 15 plants with a total annual installed capacity of 2.9 million m^3 in Malaysia (MIDA, 2012). In 2011, exports of MDF from Malaysia amounted to RM1.1 billion**.** Currently, Malaysia is the world's third largest exporter of MDF, after Germany and France (MIDA, 2012). The global wood-based composites market is valued over US$ 80 billion in 2011 (New markets research report, 2012). Since the eighties large scale production of WBCs began in North America and Europe and over time MDF has become a general name for processed fiberboard panels.

The bonding of wood materials (fibers, flakes, particles, chips, wood powder) together with the help of adhesives is termed as wood based composites (WBC). The WBCs have been classified based on the type of wood materials used ranging from fiberboards to laminated beams used for structural, non-structural purposes, exterior and interior grade panels. The WBP have certain advantages over natural wood. The properties of wood being highly variable between species to trees of same species and even pieces of the same tree. The natural wood defects such as growth stress and knots affect the end uses. The WBP can also be recycled and manufactured by using wood wastes from various industries, small diameter wood, forest residues, and barks.

Maloney (1989) classified WBPs according to the type of raw materials and process of manufacturing namely dry and wet processing methods. Further he proposed the division of panels according to their density and specific gravity. However, he also classified the WBC according to composites types such as veneers, particleboards and plywood, all of which may be fashioned into different shapes and sizes required for a variety of industrial and domestic purposes.

Medium-density fiberboard (MDF) is an engineered wood breakdown product from hard and soft wood residuals combined with wax and resin binders to form panels by application of high temperatures and pressures. Fiberboards are wood based composite products specially engineered from fibers of wood. MDF is called an engineered wood product primarily because it is composed of fine wood fibers unlike plywood, combined with a synthetic resin, and subjected to heat and pressure to form boards (Irle and Barbu 2010). Heavily used in furniture, fiberboards are classified based on their density into low density particle boards, medium density fiberboards (MDF) and high density hard boards. Plywood, commonly confused as fiberboard, is actually made up of layers of thin sheets of wood and is not made of wood fibers. Economical, easily produced and easy to fabricate, MDF and rarely hardboards are used in the manufacture of expensive furniture. The MDF board can be easily moulded into many shapes and sizes as per requirements. Apart from extensive use in the packaging and insulation industry, home interiors and exteriors from floors to doors and roofs to cabinets are fashioned with different kinds of fiberboards. Thus, in MDF manufacturing, the boards with controlled density, desired thickness, and dimension can be prepared, but in case of natural wood these properties cannot be maintained.

Many types of organic (urea formaldehyde UF, phenol formaldehyde) and natural adhesives (lignin, tannin, soya adhesives) are extensively used by the WBP industries. The MDF and particle board manufacturing units consume 68% of UF resins produced in the world while 23% of it is used in plywood manufacturing (SRI, 2009). Although minimally used, other types of adhesives used in the manufacturing of wood