A STUDY OF THE MICROSCOPIC CHARACTERISTICS OF FRACTURE SURFACE OF MDI-BONDED WOOD FIBER/RECYCLED TIRE RUBBER COMPOSITES USING SCANNING ELECTRON MICROSCOPY

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ABSTRACT

Scanning electron microscopy (SEM) was utilized to observe the microstructure and fracture surfaces of tensile, bending, and internal bonding specimens of diphenylmethane diisocyanate (MDI) bonded wood fiber/recycled tire rubber composites. Microscopic characteristics of the composites, such as interface bonding between fibers and between fiber and rubber, geometry changes of wood fibers and rubber crumbs, and density profile along the thickness direction of composites, were examined. Four fracture types were classified by the observation of micrographs of various samples: fiber pull-out, fiber breakage, fiber partial pull-out and then breakage, and fiber split. The effects of two important factors, fiber to rubber ratio and MDI level, on bonding quality and fracture type were studied. The results illustrated that excellent bonding was formed between fibers, and good bonding was also observed between fiber and rubber in the micrographs. The degree of wood fiber densification varies along the thickness direction of the composites, forming a density profile. Fiber-slippage and density profile formed during the hot-press process give the composite a layerlike structure. Fiber breakage often occurs in high-densified layers or the layers with high resin content. Fiber pull-out often occurs in low-densified layers or the layers with low resin content.

Keywords: Microstructure, fracture surfaces, wood fiber, tire rubber, MDI, composites, SEM.

INTRODUCTION

In recent years, there has been widespread interest in the manufacture of products from recycled materials. Advantages of doing this are that material recycling makes the technology more economically and environmentally attractive. A new technology that combines wood fibers and recycled tire rubber crumbs to produce wood fiber/tire rubber composites has been successfully developed (Song 1995). Major mechanical properties of the composites are presented in Table 1. In order to study the effects of microstructure of the composites on macro-properties, scanning electron microscopy (SEM) was applied to observe fracture surfaces of tensile, bending, and internal bonding specimens of the composites. As soon as the relationships between macro-properties and microstructure and between microstructure and main process parameters are clearly understood, an analytical model can be established and used to simulate the composite properties and to control the manufacturing process.

Wood fiber/tire rubber composites are composed of wood fibers, recycled tire rubber crumbs, and diphenylmethane diisocyanate (MDI) resin. In the hot-press process of manufacturing the composites, both physical and chemical changes occur in the components

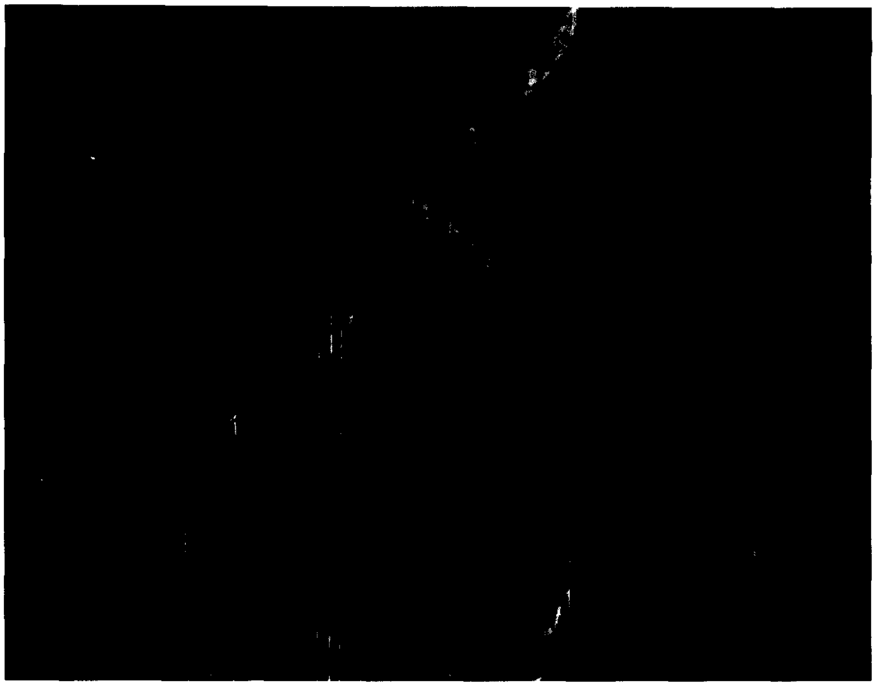

FIG. 2. A fracture surface of an internal bonding test specimen. The wood fiber to tire rubber ratio in the composite is 50:50 based on a total oven-dry weight, and MDI level is 10% based on the total oven-dry weight of wood fibers and rubber crumbs. The smooth bonding surface is shown in the figure by (1).

scope was used at 15 kV to observe microstructure and fracture types. The secondary-electron micrographs were recorded at magnifications of 300× to 3500× on polaroid-type film.

RESULTS AND DISCUSSION

Interface bonding between components generated by MDI resin

In short-fiber composites, the load is transferred from the matrix to the fiber via shear stress at the interface, so that interface bonding between fibers, and between fiber and rubber crumb greatly affects the strength of the composites. Table 1 shows tensile, bending, and internal bonding strengths of the composites with varied fiber to rubber ratio and MDI level. From Table 1, most mechanical properties of the composites were improved by increasing either fiber to rubber ratio or MDI level. The SEM micrograph in Fig. 1 shows that strong interface bonding was developed between fibers. The MDI resin surrounded wood fibers and formed a smooth interface between the fibers; no cracks were observed from the interface zone. In this case, the load was sufficiently transferred from the interface to fibers, and finally resulted in fiber breakage. The smooth bonding surfaces were also formed between wood fibers and rubber crumbs (Fig. 2).

Considering each component in the composites, the wood fibers play a critical role in determining mechanical properties of the composites due to their greater strength (Jayne 1959). The rubber crumbs are filled between wood fibers and make only a little contribution to the strength of the composites because of their low strength and large deformation. From the morphology point of view, the wood fibers are lightweight material with long and thin figures; whereas rubber crumbs are round particles and their aspect ratios are near one. Compared to rubber crumbs, light and slender wood fibers have quite a larger volume of

FIG. 1. A fracture surface of a tensile test specimen. The composite is composed of wood fibers and 15% MDI resin based on the total oven-dry weight of wood fibers. The figure shows smooth bonding surface formed by MDI resin (1) and fiber breakage (2).

- Fracture types and characteristics.

MATERIALS AND METHODS

Commercially produced thermomechanical pulp (TMP) fibers, consisting of 72% aspen (*Populus* spp.), 17% maple (*Acer* spp.), 10% oak (*Quercus* spp.), and 1% ash (*Fraxinus* spp.), were used in this study. All fibers were air-dried to a moisture content (MC) of 6 to 9% prior to further processing. Rubber crumbs of waste tires from Whirl Air Rubber in Minnesota, with sizes passing 30-mesh, were used and air-dried to an MC between 2 to 3% prior to processing. Liquid MDI resin of 100% solids content, manufactured for the wood composite industry, was used to bond wood fibers and rubber crumbs.

The manufacturing process of wood fiber/recycled tire rubber composites follows: 1) Wood fibers and rubber crumbs were uniformly mixed in a rotating drum blender. 2) After blending, MDI resin was sprayed over the surface of the mixture. 3) A semiautomatic mat former was employed to form a loose mat. 4) The mat was then prepressed at 0.843 MPa for 30 s at room temperature. 5) The prepressed mat was consolidated in a hot-press for 360 s, with 30 s of decompression time at 150°C, and 30 s press closing time. The maximum pressure used in the hot-press was 13.1 MPa. 6) All the composite panels were conditioned in a 20 ± 3°C and 50 ± 2% RH environment to equilibrium moisture contents before testing.

The composite samples for tensile, bending, and internal bonding strengths were prepared and tested following the ASTM-D 1037 (1989) standard methods. After mechanical testing, the samples were cut into 12-× 12-× 6-mm small specimens along the fracture surfaces and stored in sealed plastic bags. A sputter coater was used to precoat conductive gold onto the fracture surface of the nonconductive composite specimens before observing their microstructure. A JSM-820 scanning micro-

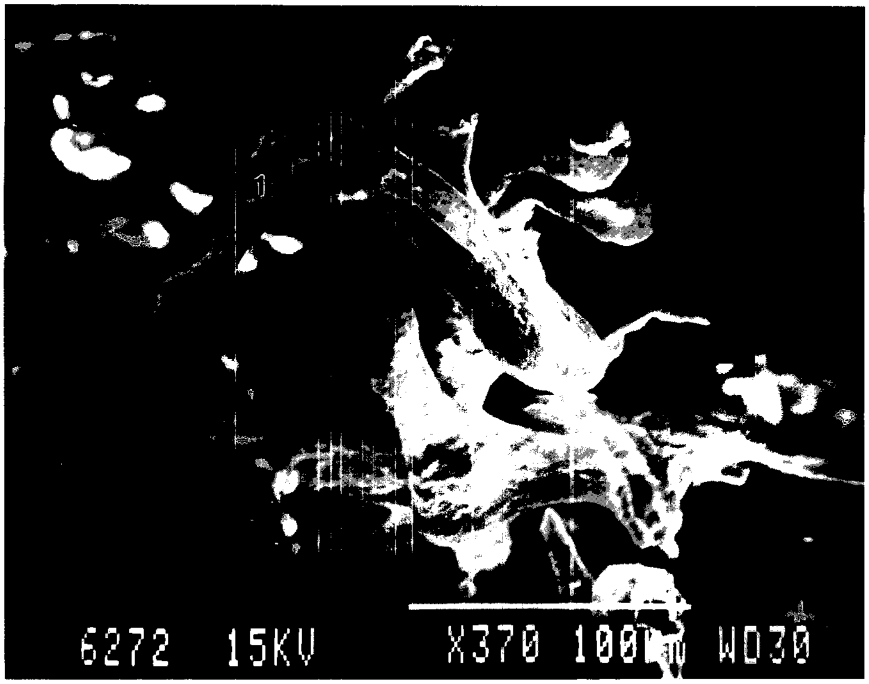

FIG. 5. A fracture surface of a tensile test specimen. The composite is composed of wood fibers and 5% MDI, based on the total oven-dry weight of wood fibers. Fiber pull-out occurs in the layers with lower density or layers with lower resin volume level (1).

fraction and specific surface areas, which greatly contribute to the mechanical properties of the composites. Therefore, increasing fiber to rubber ratio improves the mechanical properties of the composites.

From observation of the fracture surfaces of wood fibers, no MDI droplets were found in cell lumina (Figs. 3 and 4). When MDI is applied at a low level, the surfaces of fibers and rubber crumbs can not be sufficiently covered by the resin, so that the composite has low strength (Fig. 5). By increasing MDI to a high level as much as 20%, the surfaces of fibers and rubber crumbs are well covered, and even some voids in the composite can be partially filled by surplus resin to form a smooth surface which reduces stress concentrations formed by voids (Fig. 6).

Deformation and densification of wood fiber and rubber crumb

Both wood fibers and rubber crumbs deform during the hot-press process. Figure 1 shows that the cross sections of fibers varied from round to ellipse, and some cell lumina were almost closed. Compared to single fibers, fiber bundles show higher resistance to compressive deformation (Fig. 4). Because of the porous structure of wood cells, deformation of fibers results in their densification, which reduces sizes of cell lumina and increases the bulk density of the fibers (Figs. 1 and 3).

In the mat-forming process of wood fiber/tire rubber composites, fibers are randomly oriented parallel to the mat surface. Many voids exist between fibers and between fibers and rubber crumbs in the mat. During the hot-press process, the voids are first diminished and the fibers brought closer together; then the fibers are compacted and deformed to further reduce free voids in the mat; finally, the fibers are densified as cell lumina are compressed even more or even vanish. Fiber-slippage, which enlarges contacts between fibers, takes place in the initial stage of fiber deformation and assists in the formation of a layerlike

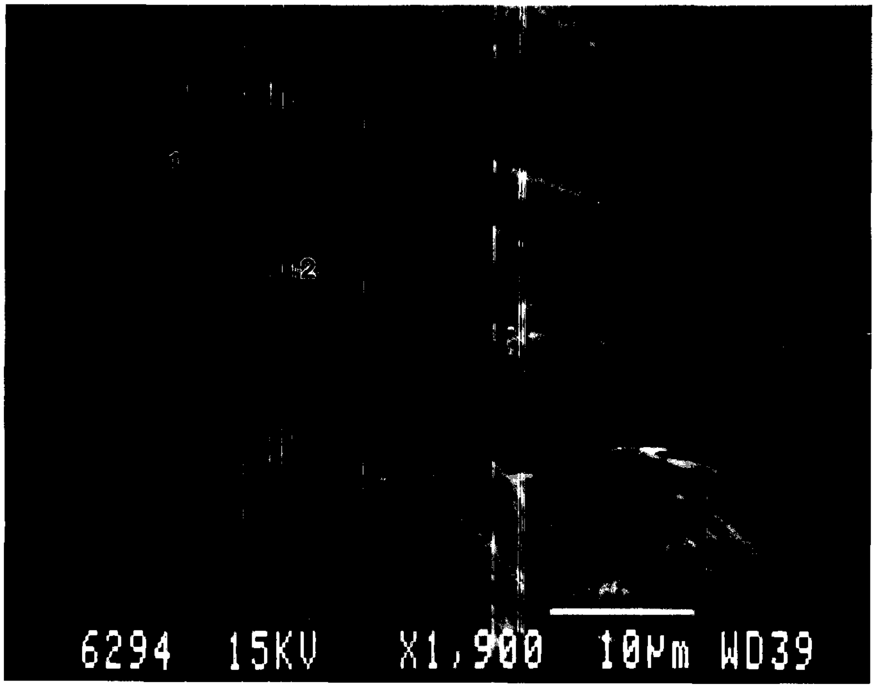

FIG. 3. A fracture surface of a tensile test specimen. The composite is composed of wood fibers and 15% MDI based on the total oven-dry weight of wood fibers. The figure shows the change of fiber cross section (1) and fiber breakage (2)

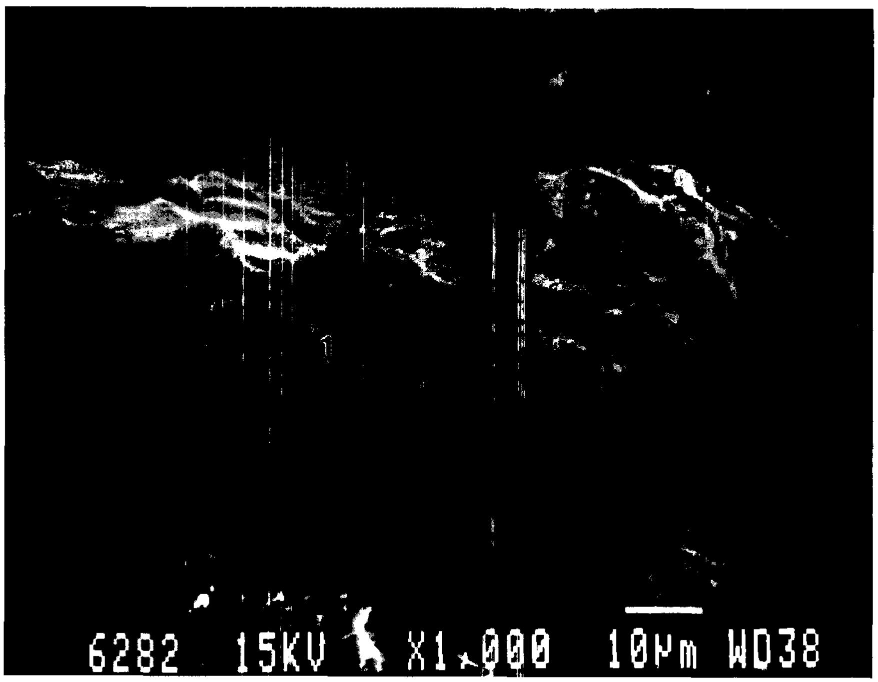

FIG. 4. A fracture surface of a tensile test specimen. The composite is composed of wood fibers and 15% MDI, based on the total oven-dry weight of wood fibers. The fiber bundle exhibits high resistance of compressive deformation (1).

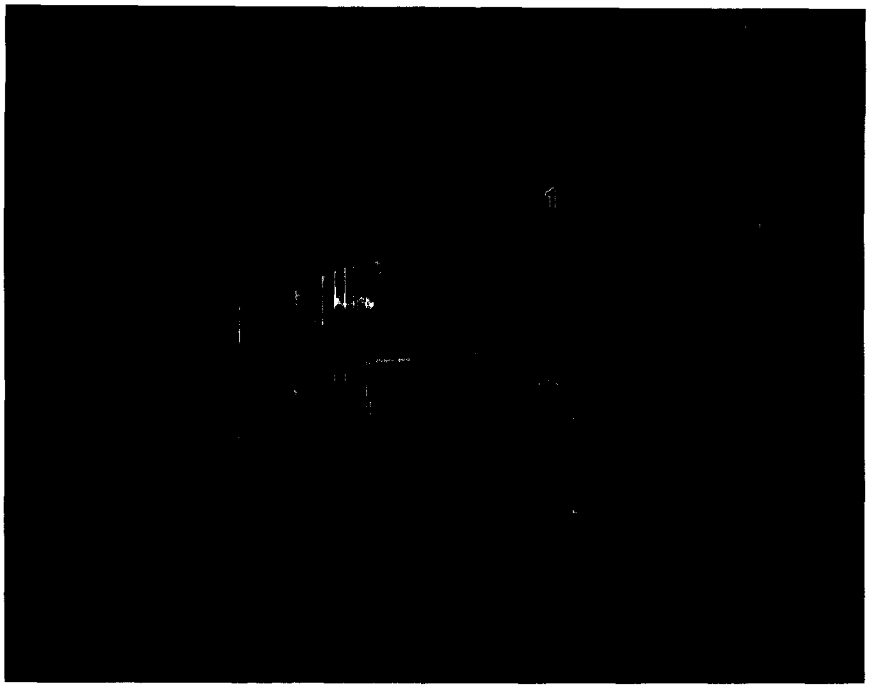

FIG. 7. A fracture surface of an internal bonding test specimen. The wood fiber to tire rubber ratio in the composite is 50:50 based on a total oven-dry weight, and MDI level is 5% based on the total oven-dry weight of wood fibers and rubber crumbs. The rubber crumb is compressed from round to thin, flat particles (1). There is no sufficient resin distributed at interface between fibers or between fiber and rubber crumb due to low resin level.

the cross section of a panel due to the variation of strain during the hot-press process. Overall, the highly densified fibers form the layers with fewer voids, and less compressed fibers form the layers with more voids.

The density profile formed in the composites also results in MDI redistribution. The highly densified layers in composites have a relatively high volume proportion of MDI resin in comparison to the low densified layers, because densification reduces fiber volume, which relatively increases the resin volume ratio.

Figure 7 shows the deformation of rubber crumbs. During the consolidating process, the rubber crumbs were compressed from round to thin, flat particles. From the observation of the rubber surface, no cracks or other damage generated by the hot-press process were found. Also, no densification occurred on the rubber crumbs because of their impressible property (Poisson ratio is near 0.5). The changes in rubber geometry increase the contact area between rubber and wood fibers, which assists in forming the bonds between them.

Fracture types and characteristics

Four types of fractures were observed from the fracture surfaces of tensile, bending, and internal bonding specimens. They are wood fiber pull-out, wood fiber breakage, wood fiber partial pull-out and breakage, and wood fiber split. The fractures of rubber crumbs are also observed, but not shown in this paper because of their negligible effect on the strength of the composites. The fracture types of the composites are strongly affected by composite density profile, MDI level, as well as test methods, i.e. bending, tensile, and internal bonding tests.

Figure 5 is a micrograph showing fiber pull-out from the matrix. The fracture only occurred on the interface bonding surface between wood fibers or between fiber and

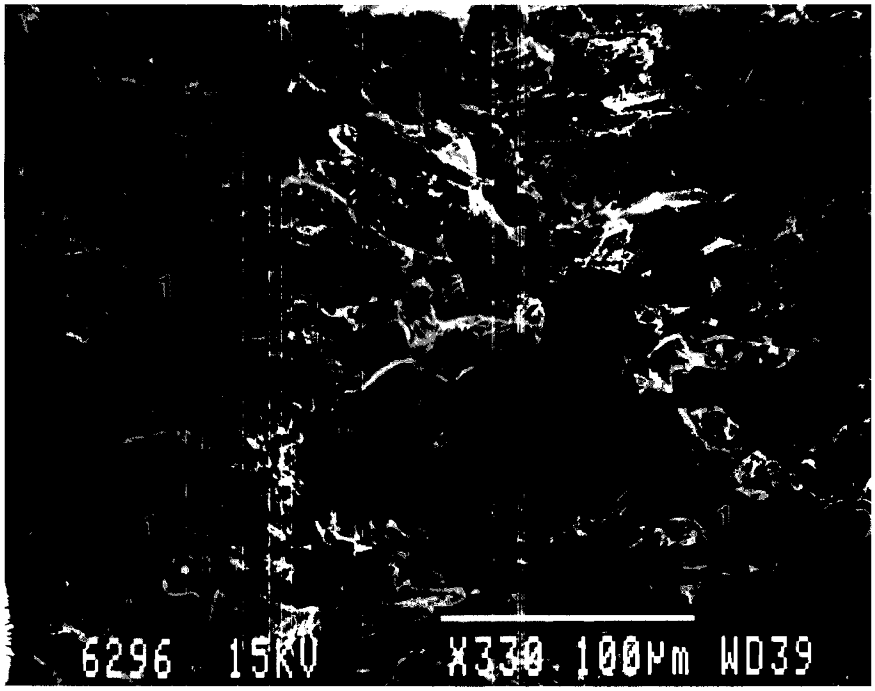

FIG. 6. A fracture surface of a tensile test specimen. The wood fiber to tire rubber ratio in the composite is 75:25 based on a total oven-dry weight, and MDI level is 20% based on the total oven-dry weight of wood fibers and rubber crumbs. The figure shows that free voids in the panel can partially be filled by surplus resin to form a smooth surface (1).

structure. The degree of fiber densification varies through the cross section of the composites and forms a graduated density profile. The density profile in the thickness direction also helps to form the layerlike structure of the composites; fibers with the same degree of densification can be assumed to form a layer perpendicular to the thickness direction of the composites. From the above assumption, the composite is composed of numerous layers and each layer has the same degree of densification. Because of the variation of densification and resin redistribution through the thickness of the composites, each layer has its unique mechanical properties. This unique layerlike structure results in composites with various fracture types in the same fracture surface (detail in following paragraphs). However, bundles of TMP fibers and inconsistent mat-forming may interrupt the layerlike structure (Fig. 4).

The density profile is formed by the temperature gradients, moisture gradients, resin curing rates, and press closing time, which cause wood fibers to have varied stress and strain behavior along the thickness direction of the mat. The temperature and the moisture gradients formed through the thickness of the mat during the hot-press result in a gradient of fiber compliance through the thickness of the mat. Although stress in the mat varies with time before the press is closed, the stress at any given moment can be assumed constant in any spot of the cross section of the mat. The empirical equation describing the relation between stress and strain follows:

$$\epsilon = J\,\sigma^{\eta}$$

where: ϵ = strain, unitless, σ = stress, Pa, η = coefficient, and J = compliance, Pa^{-1}.

From the equation, strain is related to the compliance only if the coefficient (η), which is related to raw material property, is known. Therefore, a density profile is formed along

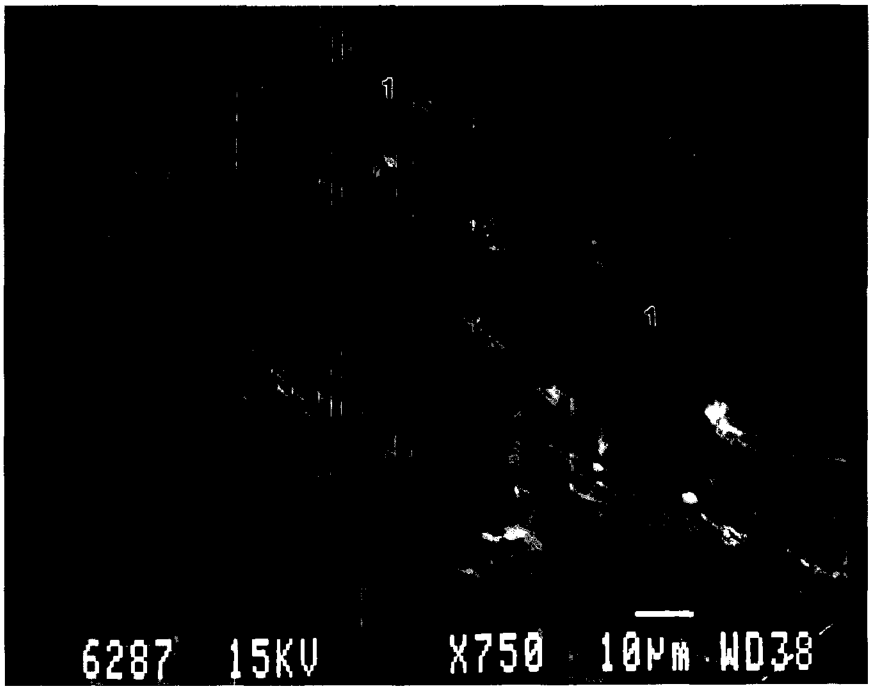

FIG. 8. A fracture surface of a tensile test specimen. The composite is composed of wood fibers and 10% MDI based on the total oven-dry weight of wood fibers. The fibers are partially pulled out and broken (1).

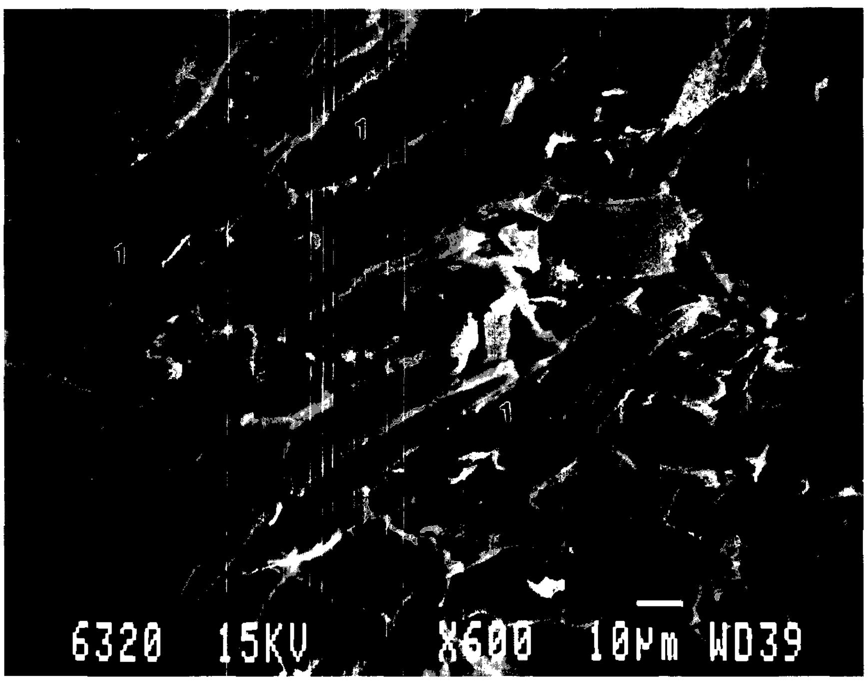

FIG. 9. A fracture surface of an internal bonding test specimen. The composite is composed of wood fibers and 5% MDI based on the total oven-dry weight of wood fibers. Fiber split occurs in the fracture surface (1).

rubber, and the fibers were not broken. In this case, the fibers did not have a reinforcing function, and the fracture stress in the interface zone was quite low. Fiber pull-out often occurs in the low density layers or in the layers with lower resin volume ratio in the composites. The low density layers result in poor bonding quality and bonding efficiency because the fibers can not closely contact each other and the voids existing between fibers are partially filled by resin. The lower resin volume ratio also results in lower bonding strength because the amount of the resin is not adequate to cover the fiber surface and form strong interface bonding. If the resin is not uniformly sprayed on the fiber surface, some fiber surfaces may not have resin or do not have enough resin. In those cases, the load can not be completely transferred to the fibers.

Figures 3 and 4 show single fiber and fiber bundle breakage, respectively. The fracture surfaces of fibers were perpendicular to the fiber lumina. The interface bonding between fibers was very strong so that the load was entirely transferred through the interface to fibers, and finally resulted in fiber breakage. Fiber breakage often occurs in high density layers or layers with higher resin volume ratio in the composites. The higher density layer can result in high-bonding efficiency and good bonding quality because of fewer voids and closer contact between fibers. The higher resin volume ratio also results in good bonding strength because the amount of resin on the surface of fibers is sufficient to form a strong bonding in the interface. The load is wholly transferred to the fibers and finally results in fiber breakage.

Figure 8 is an example showing fiber partial pull-out and breakage. In this case, the load was transferred through the interface to the fibers and ultimately resulted in fiber breakage. However, interface bonding between fibers was not very strong so that fibers were partially pulled out before fiber breakage occurred. In fact, this type of fracture is the most common in wood particulate composites. Traditionally, the wood composite industry has mainly produced price-driven products. Due to the high cost of resin, only limited resin level is used in these products. The low resin level only acts as point welding and can not cover the total surface of wood material.

Figure 9 shows fiber split parallel to fiber length direction. This type of fracture usually takes place when the load is parallel to the fiber length direction. Because of the effect of microfibril angle in the wood cell wall, the strength of fiber split is lower than fiber breakage. The macro-strengths in Table 1 show that internal bonding strengths of the composites are much lower than tensile and bending strengths.

CONCLUSIONS

From the observations of fracture surfaces of tensile, bending, and internal bonding specimens, several conclusions follow:

1. Excellent interface bonding was formed between fibers, and good bonding was also observed between wood fiber and rubber crumbs.
2. During the hot-press process, the cross sections of the fibers varied from round to ellipse, and cell lumina were decreased or even closed. The rubber crumbs were compressed from round to thin, flat particles. The fiber bundles in TMP fibers showed higher resistance to compressive deformation than single fibers. The deformation of the fibers resulted in their densification, which reduces the fiber lumina and increases their bulk density. The degree of fiber densification varies along the cross section of the composites and causes the density profile formed in the composites.
3. Four types of fractures were observed on the fracture surfaces of tensile, bending, and internal bonding specimens: wood fiber pull-out, wood fiber breakage, wood fiber partial pull-out and breakage, and wood fiber split.
4. The types of fracture were strongly affected by the panel density profile, MDI level, and test method. In general, fiber breakage of-

ten occurs in highly densified layers or layers with high resin content. Fiber pull-out often occurs in low-densified layers or layers with low resin content. Fiber split often occurs in internal bonding specimens.

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