DEVELOPMENT OF NEW GENERATION COUPLING AGENTS FOR WOOD-PLASTIC COMPOSITES

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DEVELOPMENT OF NEW GENERATION COUPLING AGENTS FOR WOOD-PLASTIC COMPOSITES

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ABSTRACT

Advanced high performance coupling agents were developed for wood-plastic composite (WPC) applications. These new products utilize a proprietary composition and grafting process that provides superior performance compared to typical maleic anhydride grafted coupling agents.

In this paper a series of polyethylene based coupling agents were tested for performance in WPC. First, the effect of coupling agents on enhancing the mechanical properties and in reducing water sorption of WPC was investigated in injection molding as well as profile extrusion processes. Second, the mechanism of coupling and the relationship to enhancement in performance was studied using several analytical techniques: small strain oscillatory rheology; dynamic mechanical analysis (DMA); scanning electron microscopy (SEM); Fourier Transform Infrared Spectroscopy (FTIR); and thermo gravimetric analysis (TGA).

The effect of lubricants on WPC performance was thoroughly evaluated. It was determined through molecular investigations that certain lubricants can have a detrimental effect on the performance of coupling agents. Recommendations on how to optimize WPC performance through the selection of proper formulation components are presented.

INTRODUCTION

Wood-polymer composites (WPC) have gained a lot of interest in the last decade. Most recently, the WPC market has taken off due to the optimization and development of machinery, material, and processing conditions. Applications for these composites include a variety of building products, consumer, industrial and automotive. Polymer composites made with wood and natural fibers such as rice hulls, flax, hemp, jute, or kenaf are environmentally sound due to their biodegradability. They are less abrasive on processing equipment and are lower in density compared to mineral filled composites. Most importantly, WPC do not have the typical problems that treated wood has in outdoor applications such as wrapping, twisting, cupping, and splitting. The wood-polymer composites are promoted as low maintenance products for outdoor applications.

In 2002 these products continued their excellent growth with combined North American and Western Europe demand reaching 1.5 billion lb., according to a study recently published by Principia Partners[1]. The North American market is by far the biggest and accounts for about 1.3 billion lbs. in 2002 [1]. Building products is the largest application and accounts for about 80% of consumption of WPC products as decking and railing systems, window and door profiles, and shingles [1].

In this paper, the effect of the Integrate™ coupling agents on the overall performance of WPC was thoroughly investigated. Integrate products are maleic anhydride grafted polyolefin. Polyethylene based products are studied in this report. The uniqueness of these new products comes from the high efficiency of grafted functionality.

In general, maleated products such as maleated polyethylene and polypropylene are typically added in small percentages to the WPC to reduce the interfacial tension between the non-polar polyolefin matrix and wood filler and thereby enhance the mechanical properties of the polymer composites. In addition to the coupling effect, these additives enhance composites morphology by evenly dispersing the discontinuous filler into the dominant polymer matrix. The combined effect of coupling agents and lubricants on the final performance of the wood composites was also investigated.

EXPERIMENTAL

Materials/Processing

PE-Based Integrate Coupling Agents:

Product Name	Base Polymer	MI	Density	Maleic Anhydride Level
NE 556-004	HDPE	3.8	0.956	High
NE 558-004	HDPE	3.9	0.958	Very High
NE 433-003	LLDPE	2.7	0.933	High
NE 534-003	LLDPE	2.6	0.934	Very High

HDPE:

Equistar Alathon® M 5040: MI = 3.8 g/10 min. and density = 0.950 g/cc
Equistar Petrothene® LB 0100-00: MI = 0.3 g/10 min. and density = 0.950 g/cc

PROCESSES

A- Injection Molding

Composite Structure / Components:

0-2% Integrate NE 556-004 (HDPE-based, MI = 3.8 g/10min.)
40% HDPE Equistar M 5040 (MI = 4 g/10 min.)
60% Pine Flour (60 mesh and 0.5 wt. % moisture)

Compounding:

Twin Screw Extruder
Production Rate = 1160 Lbs./hr.
Pellets dried to < 0.5 wt. % moisture
Injection Molded into Test Specimens

B- Profile Extrusion

Raw Materials:

Coupling Agents:
HDPE Based: NE 556-004 and NE 558-004
LLDPE Based: NE 443-003 and NE 534-003
HDPE: LB 0100-00 (MI = 0.3 g/10 min., Density = 0.952 g/cc)
Lubricants: EBS/ZS and Non-metal Stearate Lubricant
Wood Flour: 40 mesh pine wood

Basic Formula:

40% HDPE
56 - 60% wood flour
0, 2% coupling agent
0 or 2% lubricant

Raw materials were first dry blended for 5 minutes and then fed into a 55 mm Cincinnati-Milacron® twin-screw extruder. The barrel, screw and die temperatures were held constant between 300-325°F, while the screw speed ranged between 5-10 rpm's. The extruded 0.5 x 6.0" cross-section was then cooled via a water spray chiller at the outfeed of the extruder die.

EXPERIMENTAL TECHNIQUES

Fourier Transform Infrared Spectroscopy (FTIR):

FTIR Nicolet 760 Magna-IR spectrometer purged with nitrogen was used to record the IR spectra. Sixty four scans of both the sample and the reference were collected at a resolution of 2 cm^{-1} with double precision throughout the range 4000 – 400 cm^{-1}.

Scattering Electron Microscopy (SEM):

Wood filled polymer samples were fractured and then mounted on aluminum stub using carbon tape and then gold coated. SEM was carried out on a Philips SEM at 30kV voltage and 85mA current. Images were taken at 100 and 200 times magnification.

Dynamic Rheology:

A TA Instruments (formerly Rheometrics) ARES Melt rheometer was used in dynamic mode with a Nitrogen blanket. All measurements were performed with 25mm parallel plates. The samples were found not to have a linear viscoelastic regime in the measurement range of this rheometer, so maximum strain amplitude of 1% was chosen in order to be consistent within the sample set. The samples were measured in frequency-sweep mode from 0.025 rad/sec to 400 rad/sec, at 150° Celsius and 1% strain. The stability tests were carried out with an unstabilized compression molded plaque at 5 rad/sec, 1% strain and 150°C.

TGA:

A TA Instruments 2910 Series TGA was used. The measurements were done with a Nitrogen environment. The sample was then brought to equilibrium at 30°C for 15 minutes. The sample was then subjected to a temperature ramp of 10°C / minute up to 800°C. The weight loss as a function of time and temperature was recorded.

DMA:

A TA Instruments DMA Q800 was used in a temperature ramp mode. The sample was loaded and brought to thermal equilibrium at –150°C. The sample was then ramped at 3°C / minute to 100°C. The sample was measured at a frequency of 1Hz.

RESULTS AND DISCUSSION

The effect of coupling agents on enhancing the mechanical properties of wood-plastic composites (WPC) has been the subject of many publications [2-9]. Several functional groups as well as base resins were used in developing coupling agents. Results generated so far indicate that maleic grafted polyolefin gives the best performance in WPC. Enhancement of performance is related to the concentration of the coupling agent and the efficiency of the product. Typically 1 – 3 % by weight is used with an average of about 2% of the total weight. Also, it was found that the higher the molecular weight of the coupling agent the better the performance. By reviewing the results of existing coupling agents, it was concluded that a new technology is needed to impart high performance in WPC. Integrate coupling agents were developed using a unique grafting technique that makes them highly efficient in WPC compatibilization. Two product lines were developed: polyethylene and polypropylene based grafted with maliec anhydride. The uniqueness of these products is attributed to the high grafting efficiency and low residual maleic.

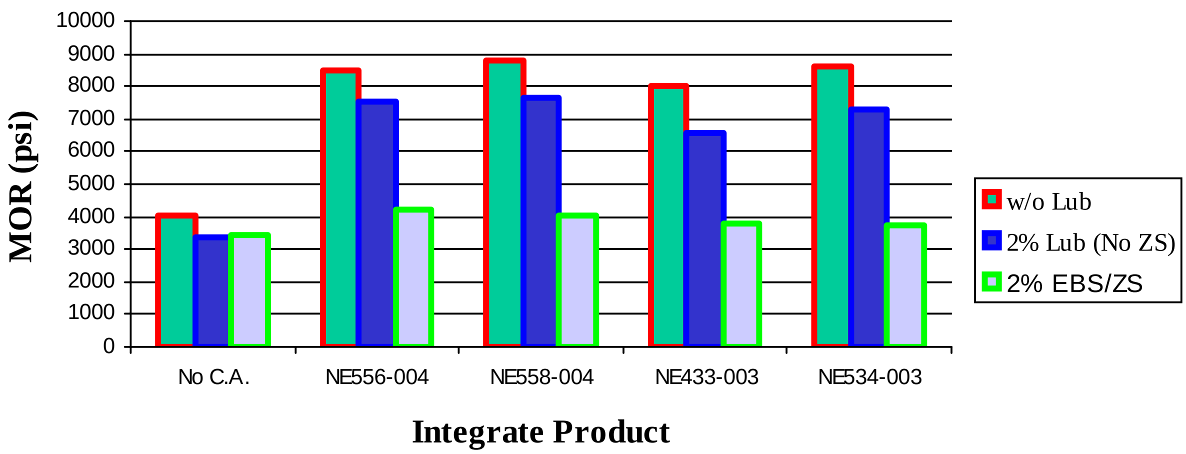
In this study, only PE-based Integrate coupling agents were studied. Injection molding as, well as profile extrusion processes, were utilized. Table (1) below summarizes the results generated for the injection molding experiment. The ratio of HDPE to wood flour was 40:60 by weight. Results indicate that significant enhancement in tensile strength as well as Izod impact with the addition of 2 wt. % coupling agent to the WPC formulation.

Table (1): Effect of Coupling Agent on Performance Enhancement of WPC

Sample	Coupling Agent (Wt. %)	Tensile Strength (PSI)	Elongation @ Break (%)	Izod Impact (ft-lbs./inch)
WPC Control	None	3,200	0.98	0.32
WPC Coupled	2% NE556-004	5,200	1.80	0.70

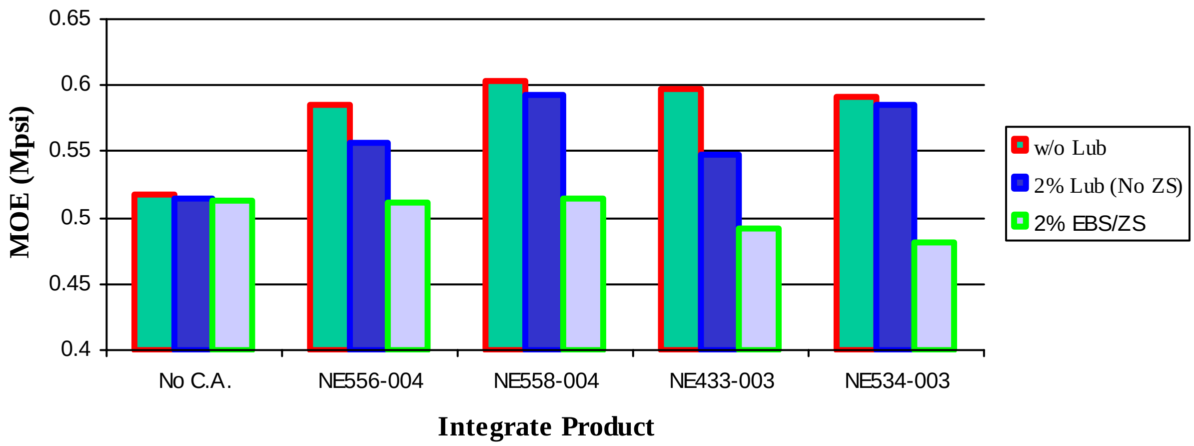
In the profile extrusion experiments, the percentage of HDPE was held constant at 40% throughout all of the trial runs, while pine wood flour was varied from 54-60% depending on the additive loading. Figure (1) indicates that over 100% improvement in modulus of rupture (MOR) (ASTM D 790) was observed when Integrate was added at 2 wt.% to the WPC formulation. In this Figure, four Integrate coupling agents were used. NE 556-004 and NE558-004 are HDPE-based and NE433-003 and NE534-003 are LLDPE-based. All coupling agents were equally high in performance when used in HDPE-based WPC formulation. Over 100% improvement in strength was observed in all coupled formulations. Figure (1) also shows the effect of lubricant on the performance of coupling agent. Two lubrication systems were utilized throughout the extrusion runs, 1.33% EBS wax mixed with 0.67% zinc stearate (ZS) and a 2% non-metal stearate lubricant. It was found that zinc stearate has an antagonistic effect on the performance of coupling agents. On the other hand, the performance was maintained when a non-metal stearate lubricant was used.

Figure (1): Effect of Coupling Agents and Lubricants on MOR Performance of WPC Formulations



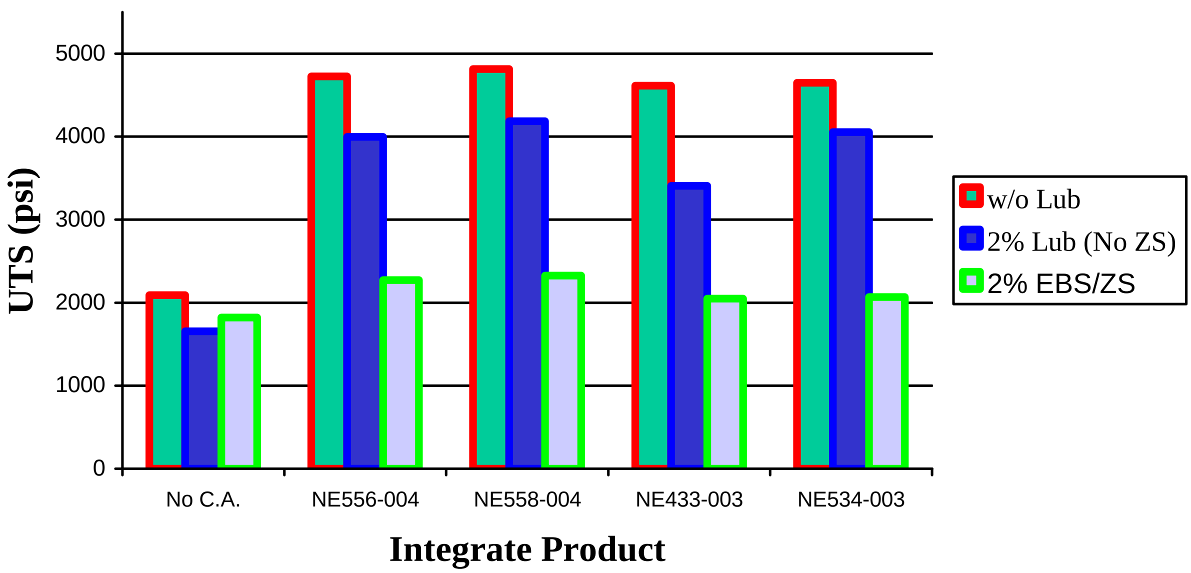
In addition to strength improvement evident from the increase of MOR when coupling agents were used, stiffness enhancement was also detected as measured by the modulus of elasticity (MOE) (ASTM D 790). Figure (2) indicates similar trends observed in Figure (1).

Figure (2): Combined Effect of Coupling Agents and Lubricants on MOE Performance of WPC Formulations



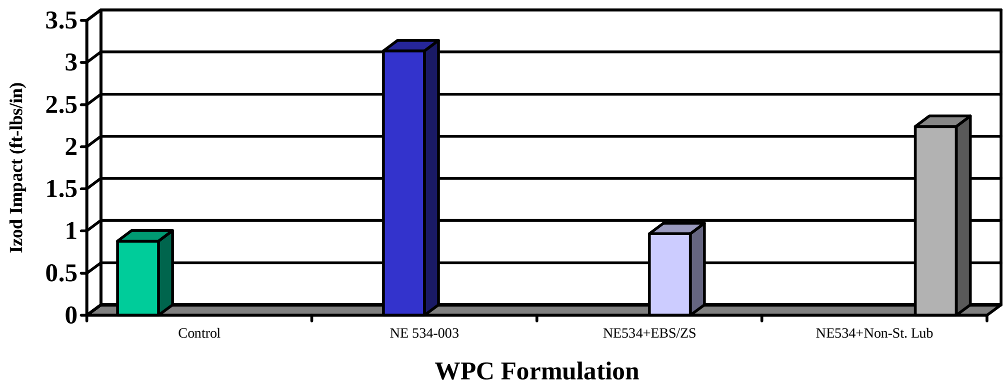
Moreover, tensile measurements were conducted on the four WPC formulations with and without lubricant and coupling agent according to ASTM D 638-96. Figure (3) illustrates that ultimate tensile strength was more than doubled when 2% coupling agent was used. The effect of lubricant followed the same trend observed in previous Figures.

Figure (3): Combined Effect of Coupling Agents and Lubricants on Ultimate Tensile Strength of WPC Formulations



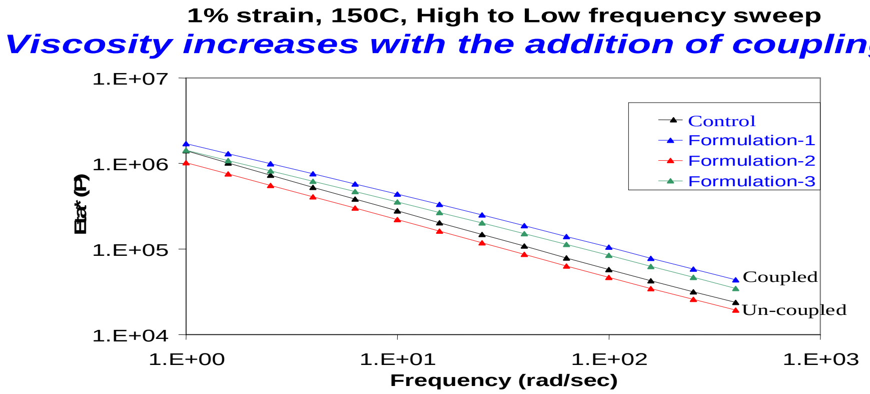
Integrate coupling agents were also tested for impact performance, Figure (4). It was found that over 300% increase in Izod impact strength was detected in coupled WPC formulations compared to the un-coupled control sample. Balance of performance enhancement between strength and stiffness to impact is a unique characteristic of the new technology. The substantial boost in mechanical properties of the extruded composites when coupling agents were added to the formulations is much higher than what is found when traditional coupling agents are used. The high performance is attributed to the high concentration of effective maleic functionality present at the wood/polyolefin interface. Maleic anhydride reacts with the hydroxyl polar groups in wood and forms strong covalent ester bonds [10-14]. It was also proven[10], that H-bonding, dipole-dipole, as well as Van der Waals forces take place between the anhydride functionality and the hydroxyl groups. The high molecular weight backbone of the coupling agent co-crystallizes with the non-polar polyethylene matrix to form an inseparable bond. Lower molecular weight coupling agents tend to form weak boundary layers and phase separate from the polyolefin matrix.

Figure (4): Combined Effect of Coupling Agents and Lubricants on Izod Impact Strength of WPC Formulations



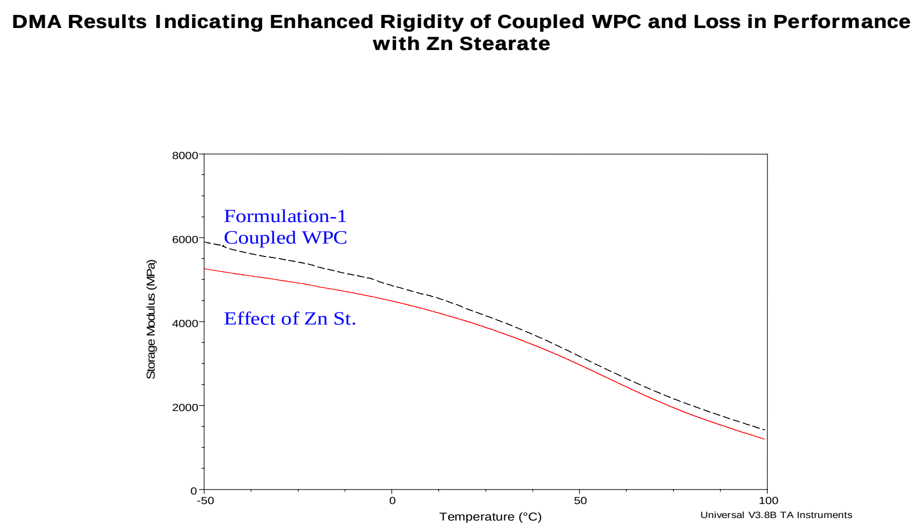
To further understand the effect of coupling agents and lubricants on WPC performance, several analytical techniques were employed including small strain oscillatory rheology, TGA, DMA, FTIR and SEM. Storage modulus G' was measured at 5 rad/s, 1% strain and 150 °C versus time to determine the optimum processing and testing conditions. No significant change in G' was detected versus time indicating composite stability at the chosen experimental conditions. The same rheological setup was then used to measure the complex viscosity (Eta*) versus frequency for the coupled and uncoupled formulations, Figure (5). Results indicate that the coupled formulations have higher viscosity compared to the un-coupled. This result indicates efficient coupling of the polar wood flour to the non-polar HDPE matrix. Figure (5) also explains the loss in performance for the formulation containing zinc stearate lubricant as having the lowest viscosity of all measured formulations. On the other hand, the formulation containing the non-metal stearate exhibited high viscosity compared to the control.

Figure (5): Dynamic Rheology - Measurement of Complex Viscosity versus Frequency



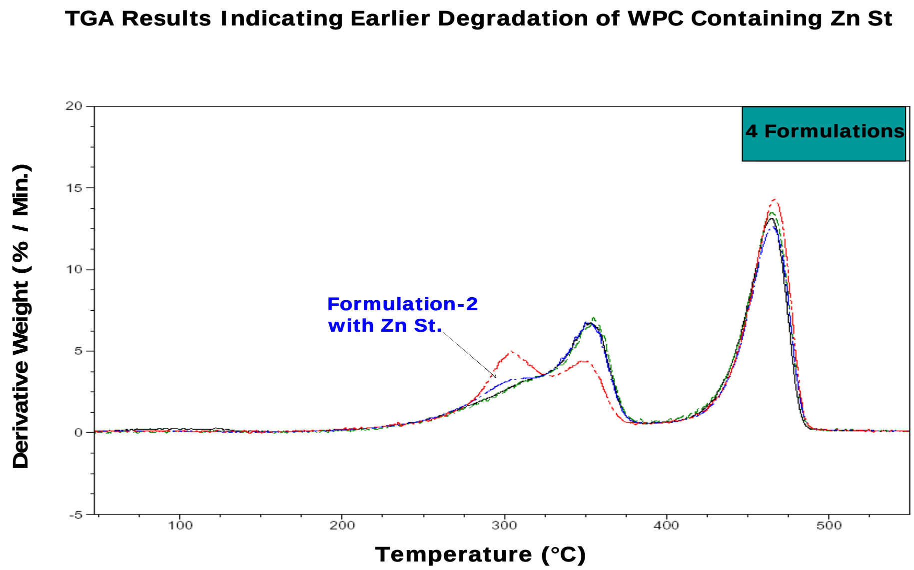
The antagonistic effect of zinc stearate on the maleated polyolefins in WPC compositions was further proven using the DMA technique. The storage modulus of the coupled WPC and of the coupled with zinc stearate formulations were measured in the temperature range -50 °C – 100 °C. The graph undoubtedly shows that this category of lubricant negatively affects the performance of the coupled WPC structures.

Figure (6): DMA Storage Modulus versus Temperature for Coupled WPC with and without Zinc Stearate



TGA results given in Figure (7), shows that the formulation containing zinc stearate starts to decompose at lower temperature compared to all other formulations indicating the likelihood of formation of new chemical species. This result suggests that a chemical reaction is taking place between the lubricant and the coupling agent.

Figure (7): TGA Results for the Four WPC Formulations



Other researchers have observed the negative effect of the stearate on the maleic anhydride coupling agents [15], but the main reason was still not clearly identified. To determine the root cause for the loss in performance, the following experiment was conducted using FTIR spectroscopy. A mixture of maleic anhydride and zinc stearate was heated in presence of water and the IR spectra were recorded. Figure (8) shows a good spectral match with zinc ionomer. This result indicates that maleic anhydride, in presence of moisture from wood, converts to maleic acid which is then reacted with zinc stearate to form zinc ionomer. Another potential side reaction, but to a lesser extent, is the formation of stearic acid. This FTIR experiment clearly explains the root cause for performance loss when metal stearates are used with maleic anhydride coupling agents.

Figure (8): FTIR Spectra Indicating Reaction between Maleic Acid and Zinc Stearate

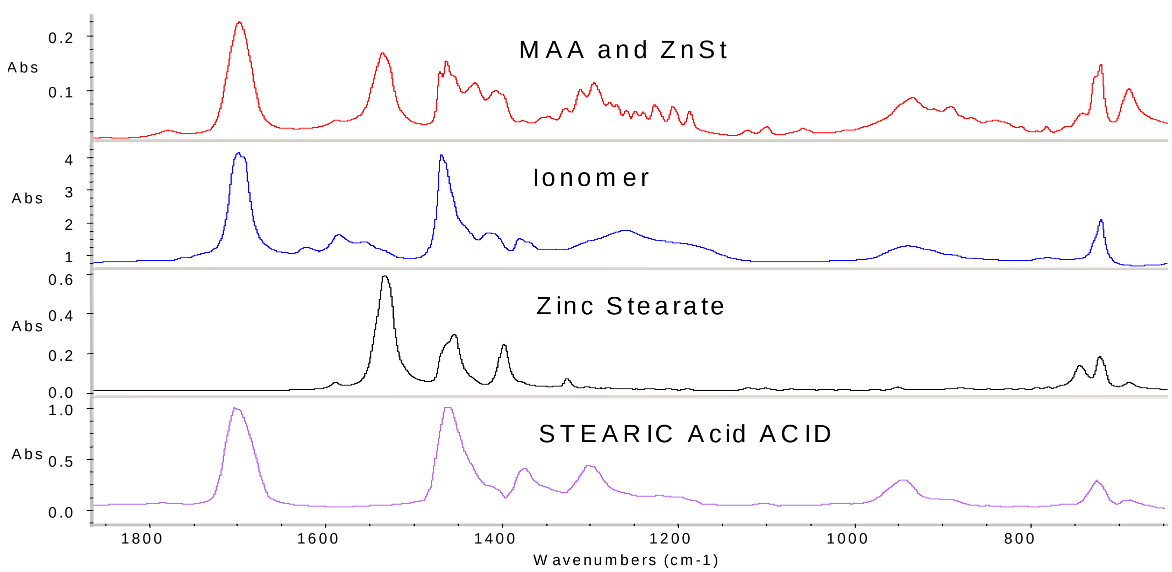


Figure (9): SEM Micrograph of Un-Coupled WPC

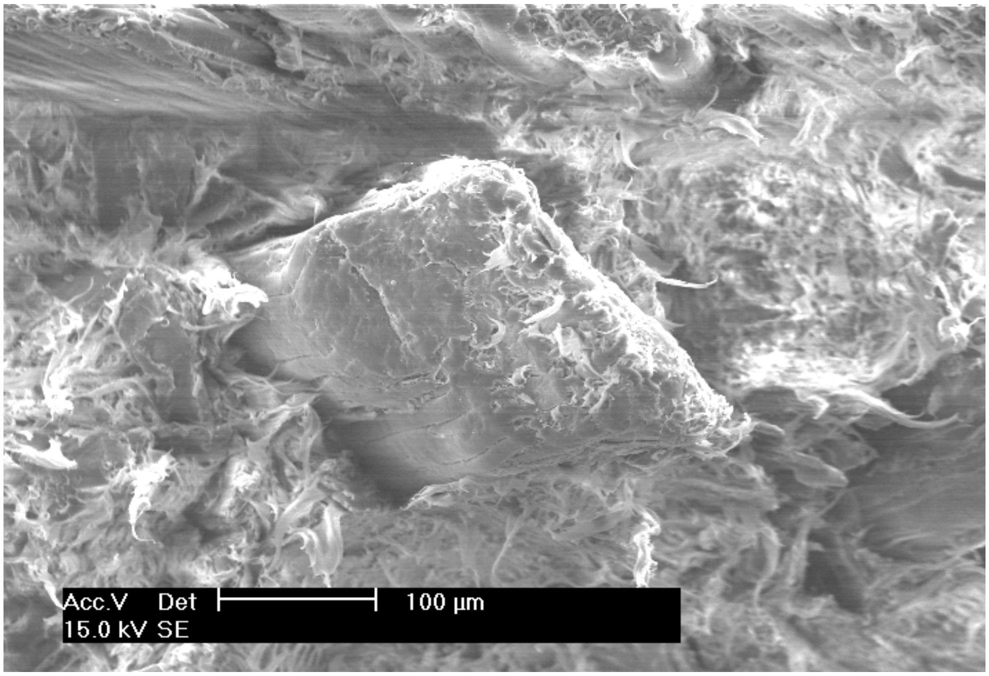


Figure (10): SEM Micrograph of WPC Containing 2% Integrate

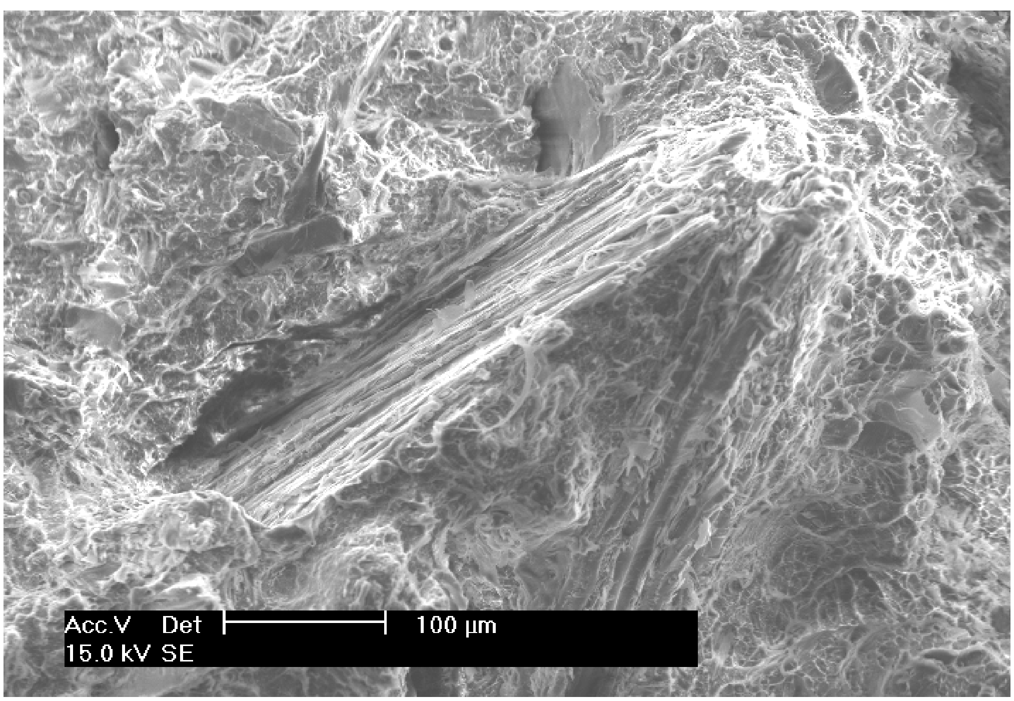
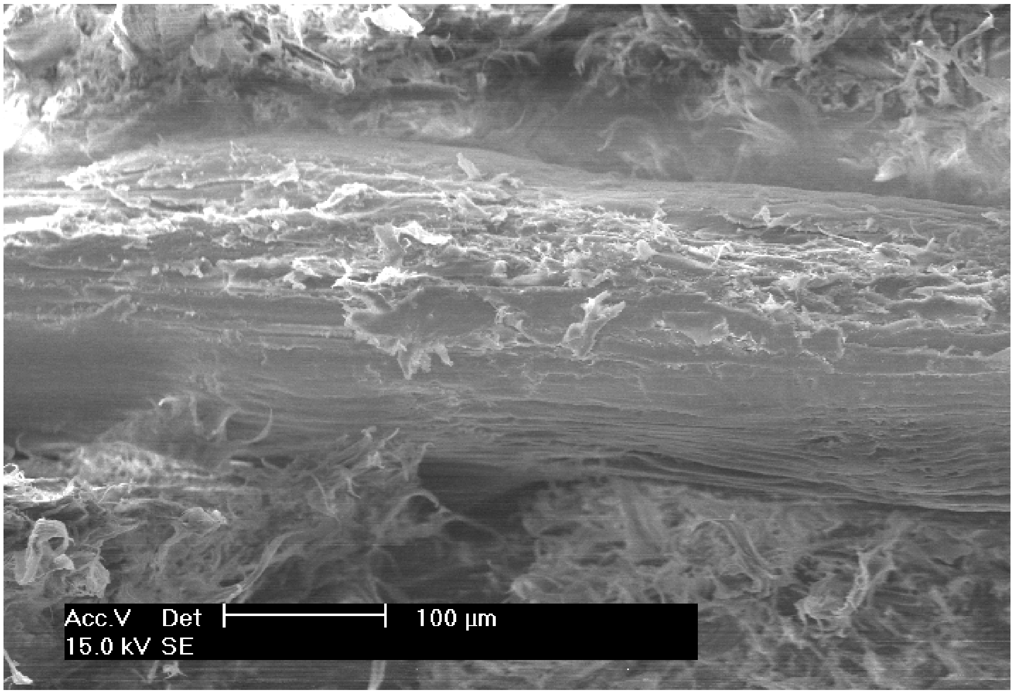


Figure (11): SEM Micrograph of WPC Containing 2% Integrate and 2% EBS/Zinc Stearate Lubricant



SEM micrographs Figures (9 – 11) visually describe the above findings. The wood particles were found un-bound in Figure (9) when no coupling agent was used. Figure (10) shows the strong bonding between the polar wood and the non-polar HDPE matrix using Integrate coupling agent. By closely examining this micrograph, one can observe that wood is strongly bonded to PE and has to be broken in order to fracturing the WPC bar. On the other hand, Figure (11) shows the loose wood particles when zinc stearate was used with coupling agent.

The water soak data for the extruded wood/thermoplastic composites utilizing Integrate coupling agents and lubricants is given below. The results for water sorption and thickness swell are presented in Figures (12) and (13) respectively. The water soak specimens were machined to a 0.25 x 1" cross-section from the extruded 0.375 x 1.5" profile. The specimen thickness was achieved through use of a knife-edge planer by taking equal amounts off of each face. The specimens were then cut to a 1" width and 5" length. Prior to measuring, the specimens were allowed to equilibrate for seven days at 70°F and 50% relative humidity. The specimens were then weighed and measured for thickness in four separate locations utilizing a dial indicator.

Once the initial measurements were recorded, the specimens were then placed in a bath of distilled water at 70°F. Weight and thickness measurements were then taken at 2, 24, 48 hours after initial submergence. Measurements continued to be made for 1,2,3,4,6,8,10, and 12 weeks and presently at 4-week intervals.

Figure (12) clearly shows the effect of Integrate coupling agents in protecting WPC from water sorption. The fiber particles are encapsulated inside the hydrophobic HDPE and are protected from water. Thickness swell data are presented in Figure (13). The un-coupled samples swelled 400 times more than the coupled WPC samples. The same Figure also provides the results for the WPC samples containing coupling agent and zinc stearate. It is interesting to notice that the curve of the lubricated sample follows exactly the same trend of the un-coupled WPC sample indicating the loss of the coupling effect in presence of metal stearates

Figure (12): Reduction of Water Sorption by Integrate Coupled WPC

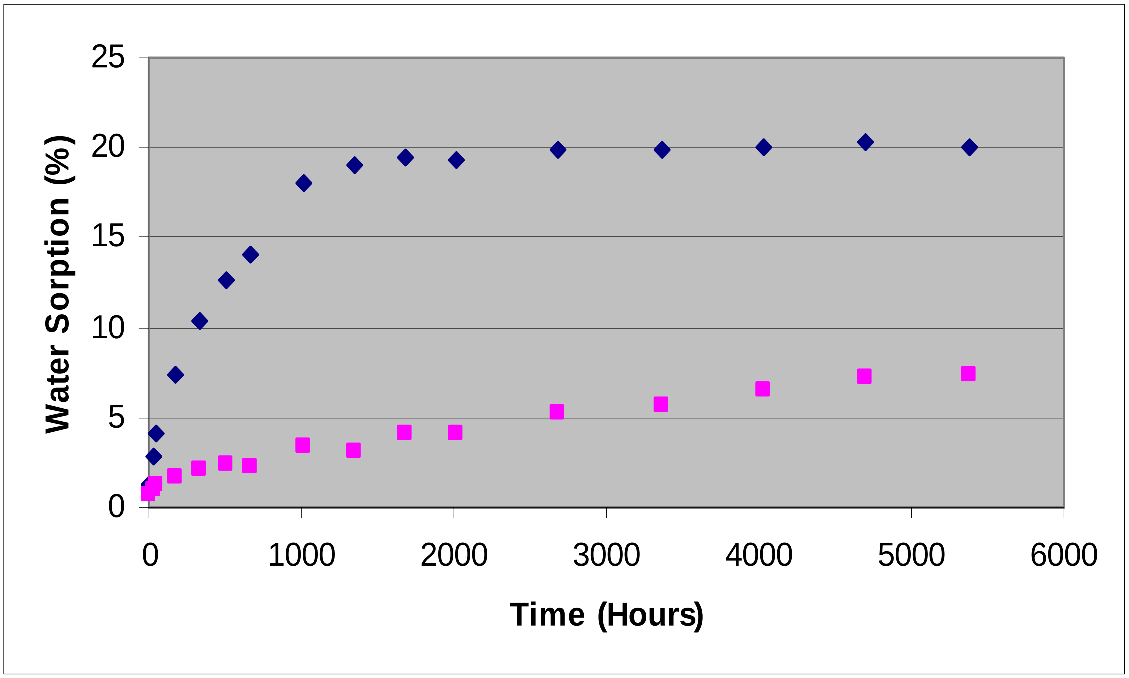
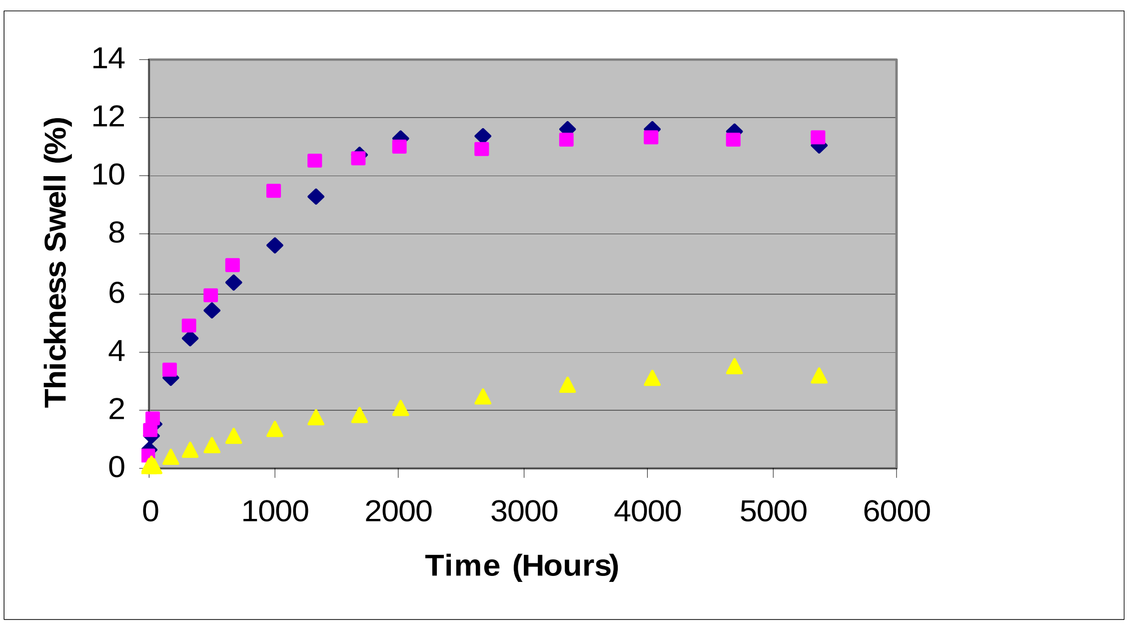
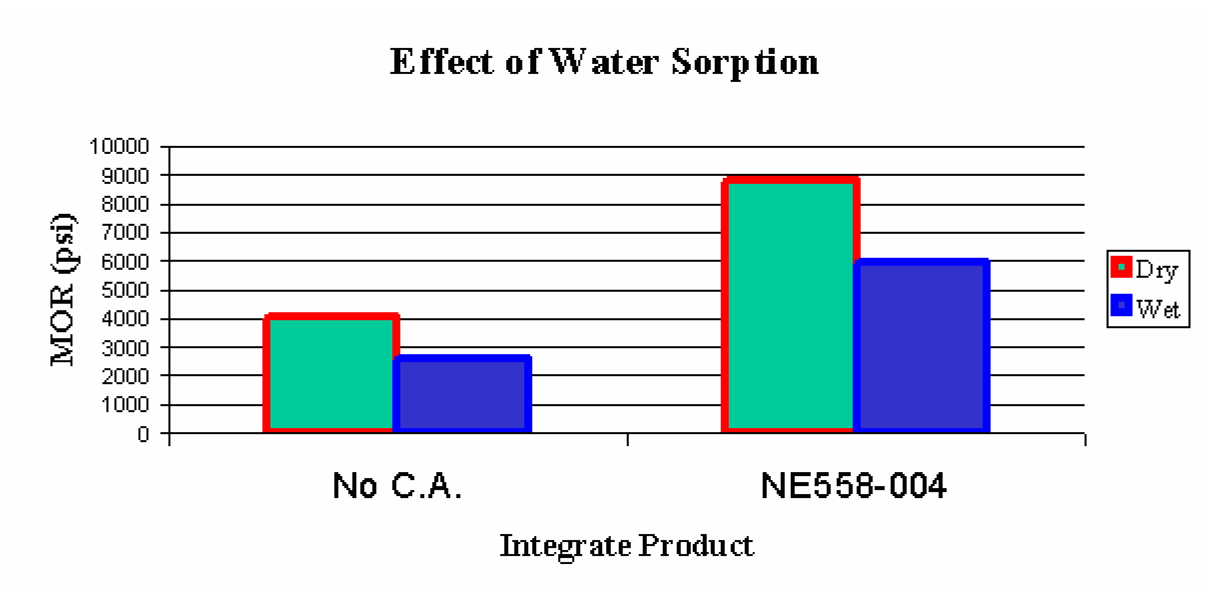


Figure (13): Coupling Agents Protect WPC from Thickness Swell



Moreover, Figure (14) shows the magnitude of loss in mechanical properties as measured by MOR upon swelling of the un-coupled WPC. It is important to notice that the performance of the water-soaked coupled sample is significantly higher than the un-coupled even before water soaking.

Figure (14): MOR of Coupled and Un-Coupled WPC before and after Water Soak



To study this phenomenon further, SEM micrographs of WPC were taken for the coupled, un-coupled and coupled with zinc stearate. Figure (15) and Figure (16) clearly show the difference in fiber swelling of the un-coupled WPC structures. Figure (16) shows the magnitude of individual fiber swelling where the water is absorbed inside the fiber. This result is very significant since absorbed water will be a lot harder to remove than adsorbed water.

Figure (15): SEM Micrograph of Un-Coupled Dry WPC

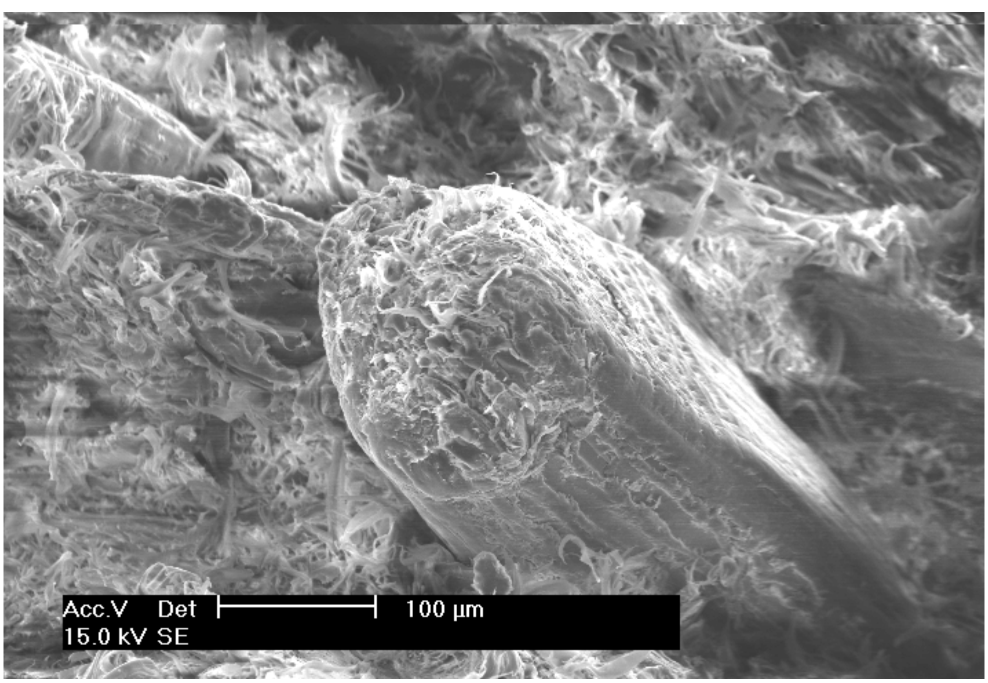
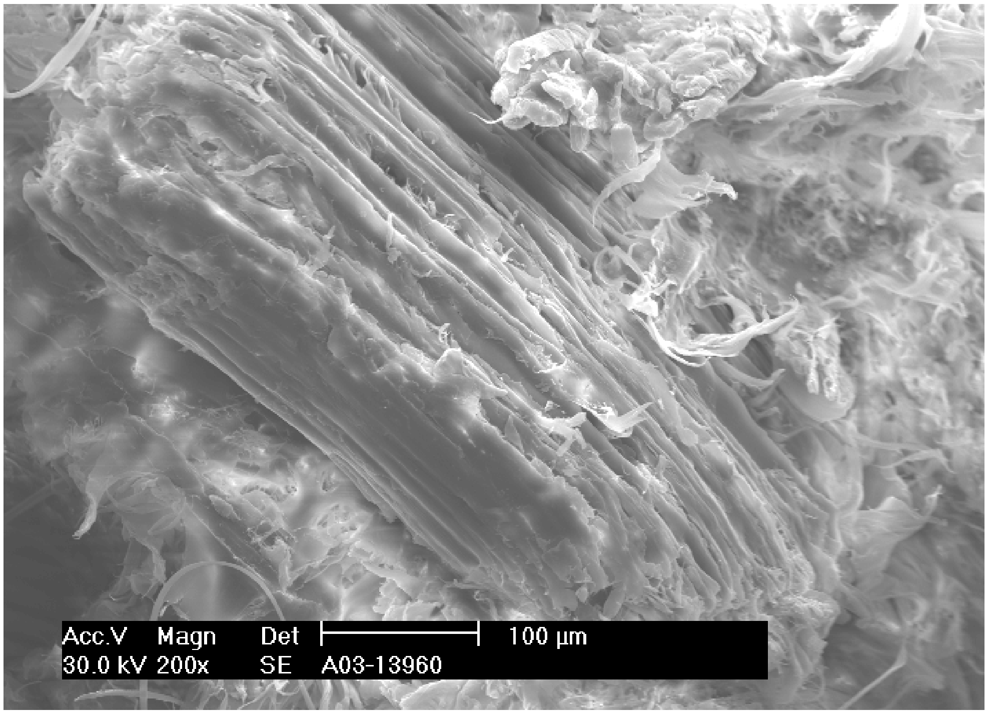
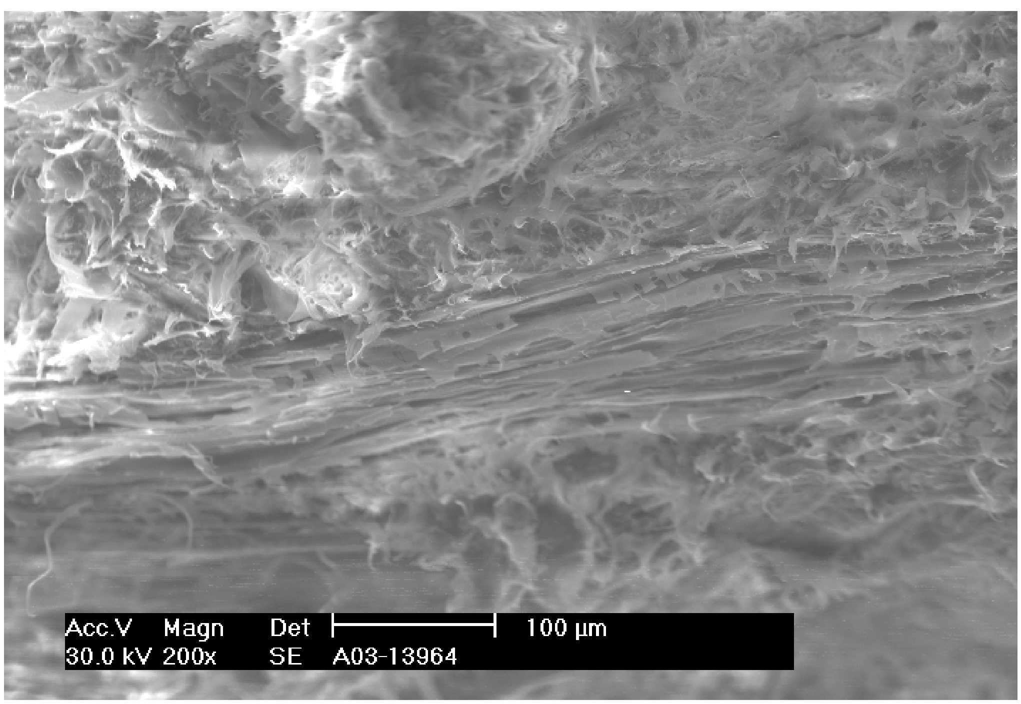


Figure (16): SEM Micrograph of Un-Coupled Water Soaked WPC



On the other hand, Figure (17) shows the significant protection of wood fibers against water absorption when Integrate was used. The broken wood show slight signs of swelling compared to the un-coupled. The efficient coupling protects wood by encapsulating it in the hydrophobic polymer matrix.

Figure (17): SEM Micrograph of WPC Containing 2% Integrate NE558-004 after Water soak



CONCLUSIONS

- Results indicate substantial enhancement of mechanical properties of injection molded and profile extruded WPC containing Integrate coupling agents
- Coupling agents protected WPC from water sorption and dimensional instability
- Investigated the mechanism of coupling of WPC using several analytical techniques and found excellent bonding at the wood-polymer interface.
- Loss in performance when zinc Stearates is used as lubricant in wood-polymer composites is attributed to a reaction of the Lubricant with maleic acid. The formation of zinc ionomer is the primary reaction. FTIR also indicates that stearic acid could be formed but to a much lesser extent.
- All available coupling agent functionality is practically consumed due to the abundance of metal stearate in the composite and the relative ease of reaction.
- Non-metal Stearates provided the best results for formulations containing lubricants

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