J. Korean Wood Sci. Technol. 2016, 44(2): 231~240 pISSN: 1017-0715 eISSN: 2233-7180
http://dx.doi.org/DOI : 10.5658/WOOD.2016.44.2.231

Original Article

Change in Chemical Compositions of Leachate and Medium Density Fiberboard from a Laboratory-scale Simulated Landfill[1]

Min Lee[2,4] · Lynn Prewitt[3] · Sung Phil Mun[4,†]

ABSTRACT

The change in chemical compositions of leachate and medium density fiberboard (MDF) from a laboratory-scale simulated landfill which constructed in a plastic container containing alternating layers of soil and MDF was investigated to evaluate decomposing of MDF in soil. Four treatments were conducted: 1) MDF in soil, 2) MDF only, 3) cured UF resin in soil, and 4) soil only. Molecular weight (MW) distribution of compounds in leachate from soil only treatment did not change over time. In UF resin in soil treatment, the MW distribution shifted to a lower MW distribution over time, while the peak shifted to the left indicated changing to higher MW distribution in leachate from treatment 1 and 2 contained MDF. Higher percent nitrogen in leachate was observed in MDF containing treatments due to the UF resin in the MDF. The percent carbon slightly increased in MDF only while that greatly decreased in MDF in soil treatment maybe due to bacterial activity. The percent of extractable materials from the MDF decreased greatly on day 35 compare to day 0, and subsequently did not change much on day 77. In contrast, percent holocellulose and lignin did not change much over time. No structural change of the wood fiber in MDF occurs during the study. Water-soluble materials from MDF in soil contributed the change in chemical composition of leachate.

Keywords : simulated landfill, leachate, medium density fiberboard, urea-formaldehyde resin, chemical analysis, elemental analysis

1. INTRODUCTION

Medium density fiberboard (MDF) use in worldwide has been increasing due to the development of new technologies which is adding functionalities to MDF (Thomas *et al*., 2008). MDF is made by bonding wood fiber in or with an adhesive under pressure and a non-structural panel product developed in the 1970s (Maloney, 1996). MDF, in addition, can be manufactured with different densities depending on it use. For example, low density MDF is used for the indoor applications and high density MDF are used where high stiffness

[1] Date Received February 3, 2016, Date Accepted March 2, 2016
[2] Department of Forest Products, National Institute of Forest Science, Seoul 02455, Republic of Korea
[3] Former professor, Department of Forest Products, Mississippi State Univ., Mississippi State, Mississippi 39759, USA
[4] Department of Wood Science & Technology, Chonbuk National University, Jeonju, Jeonbuk 54896, Republic of Korea
[†] Corresponding author: Sung Phil Mun (e-mail: msp@jbnu.ac.kr)

is needed such as in a door or siding. After MDF become wood waste, MDF was previously sent to landfill to dispose of them as waste material or burned.

MDF is susceptible to decay by microorganisms, and urea-formaldehyde (UF) resin also can be degraded by bacteria into urea, formaldehyde, ammonia, and carbon dioxide (Chung *et al*., 1999; Jahns *et al*., 1998). However, to our knowledge, no studies have been directly conducted to analyze change in chemical components of leachate and buried MDF from a landfill. In our previous studies, formaldehyde released in leachate and environmental impacts of leachate from MDF disposed in a simulated landfill were investigated (Lee *et al*., 2014; Lee *et al*., 2015). Most formaldehyde from MDF in soil was released in leachate by 28 days and toxicity of leachate required 56 days to decrease to the level of soil while BOD and COD remained above permissible discharge levels. Lee *et al*. (2015) reported formaldehyde concentration, toxicity, COD, and BOD of leachate were negatively affected by MDF in soil. Regardless of these results, effects of leachate and MDF from a simulated landfill to environment are still ambiguity that is correlation between leachate and MDF or soil. In order to understand effects of waste MDF to environment when it buried, degrading pattern of MDF and extracting chemicals in water from MDF should be analyzed. In this study, therefore, what chemical components leached out in water from MDF disposed in a simulated landfill, and change in chemical components of MDF during the test period were determined by means of fourier transform infrared (FTIR) spectroscopy, gel permeation chromatography (GPC), elemental analysis, and chemical component analysis.

2. MATERIALS and METHODS

2.1. Materials

Unknown grade MDF (100 cm × 100 cm × 1.27 cm, Georgia-Pacific, NC, USA) manufactured at 2001 was provided by the Forest Products Department at Mississippi State University and cut into 3 cm × 1.5 cm × 0.5 cm. Silty clay soil and cured UF resin were used as described in pervious study (Lee *et al*., 2015). The dried MDFs (disposed and non-disposed) were ground approximately to fiber with a Hi-Mixer (HM-2500, Hyundai electronics Co., Ltd., South Korea). Potassium bromide (KBr) was purchased from Shimadzu (Kyoto, Japan). Dichloromethane (Fisher Scientific, Pittsburgh, PA, USA), acetic acid (Sigma-Aldrich Co., St. Louis, MO, USA), sodium hydroxide (NaOH, Mallinckrodt, Hazelwood, MO, USA), and hydrochloric acid solution (HACH Co. Loveland, CO, USA) were used.

2.2. Methods

2.2.1. Simulated landfill design

Laboratory-scale simulated landfills (simulated landfills) were constructed as described in our previous study (Lee *et al*., 2014). There were four treatments with three replicates per treatment: 1) cut pieces of MDF wrapped in

polyethylene fabric and covered in soil, 2) cut pieces of MDF only, 3) cured UF resin wrapped in polyethylene fabric and covered in soil and 4) soil only.

2.2.2. Leachate, MDF, and UF resin sampling

Leachate was collected as same as previous study (Lee *et al*., 2014) and was sampled weekly for 56 days. For the leachate analysis, days 0, 28, and 56 leachates were used. Each leachate sample was filtered through a GH Polypro 0.45 μm filter (Pall Corporation, Port Washington, NY, USA). The filtered leachate was first frozen with liquid nitrogen and then lyophilized using a freeze dryer (model 4.5, Labconco Corporation, Kansas City, MO, USA). The dried leachate powder was further dried in a vacuum oven (SACO-38, San Cheon Tech-Ind. Co, LTD, South Korea) over P_2O_5 and then was kept in a refrigerator until use. Simulated landfills were dismantled on day 0, 28, and 56 for MDF and UF resin sampling in order to determine chemical analysis.

2.2.3. Gel permeation chromatography (GPC)

The dried leachate (70 mg) was dissolved in 1 mℓ of deionized (DI) water and filtered through a 0.2 μm GH Polypro membrane filter (Acrodisc®, Pall Corporation, Port Washington, NY, USA). The filtered sample was stored in a refrigerator at 4℃. The filtered leachate was analyzed using a GPC system with RI detector (Shodex RI SE-61, Showa Denko America, Inc., USA). The GPC system consisted of a pump (Shimadzu LC-10AD, Japan), a column heater and controller (CH-30 and TC-50, Flatron, UK) and an Autochro data module (Young Lin, South Korea). The analytical column was an 8 × 300 mm GPC column (Shodex® OHpak KB-804, Showa Denko America, Inc., USA). Standards used for estimating molecular weights were Dextran T2000 (Mw 2000000), T70 (Mw 70000), T40 (Mw 39100), T10 (Mw 10000), glucose (Mw 180.16), and ethylene glycol (Mw 62.07). The filtered sample was injected into the pump through a sample loop (20 μℓ) and analyzed with GPC conditions as follows: eluent: water for 35 min; column temperature: 30℃; flow rate: 0.5 mℓ/min; injection volume: 20 μℓ.

2.2.4. Fourier transform infrared (FTIR) spectroscopy

The dried leachate was ground with KBr and then pelletized into 13 mm diameter discs using a hydraulic press (SSP-10A, Shimadzu, Japan). FTIR spectra were recorded in the wave number range from 4000 to 400 cm^{-1} using a FTIR-8201 PC spectrophotometer (Shimadzu, Kyoto, Japan), in the percentage transmittance mode at a resolution of 4 cm^{-1}.

2.2.5. Elemental analysis

Elemental analysis (C, N, S, and H) of the dried leachate and MDF were analyzed using an Elementar Vario EL analyzer (Elementar Analysensysteme GmbH, Germany) by the Center for University - Wide Research Facilities at Chonbuk National University, South Korea, for elemental compositions.

Table 1. The percent nitrogen, carbon, sulfur, and hydrogen changes of MDF disposed in soil and MDF only for 56 days

Unit: %

Element	Sample	Landfill (Day)			
		0	7	28	56
N	1	3.43	2.89	2.30	2.03
	2	3.43	2.44	3.05	2.70
C	1	50.05	49.88	49.12	48.55
	2	50.05	49.09	48.92	48.87
S	1	4.16	3.89	0.39	0.30
	2	4.16	0.46	0.40	0.69
H	1	5.83	5.89	6.52	6.44
	2	5.83	6.49	6.48	6.47

1: MDF in soil, 2: MDF only.

2.2.6. Chemical composition of MDF disposed in soil

Ground MDFs (disposed and non-disposed) were used to determine chemical composition. Chemical composition was determined according to Technical Association of the Pulp and Paper Industry (TAPPI) Standard Methods; hot- and cold-water extracts (T-207 cm-99), 1 percent NaOH extract (T-212 om-02), dichloromethane extracts (T-204 cm-97), ash content (T-211), and Klason lignin (T 222 om-06). Acid soluble lignin was determined by a spectrophotometric method with UV absorbance at 208 nm (Ehrman, 1996) using UV-VIS spectrophotometer (Cary 100 Bio, USA).

3. RESULTS and DISCUSSION

3.1. Analysis of MDF

3.1.1. Elemental analysis

The elemental content (N and C) values in MDF may show the UF resin degradation by changes in the total nitrogen content and MDF degradation by changes in the total carbon content. Table 1 shows the percent nitrogen, carbon, sulfur, and hydrogen changes of MDF disposed in soil and MDF only for 56 days. The percent nitrogen in MDF, which mainly come from UF resin, slowly decreased from 3.43% to 2.03% at the end of study while nitrogen also decreased from 3.43% to 2.70% in MDF only on day 56. The percent carbon in MDF from treatment 1 and 2 slowly decreased 50.05 to 48.55 and 48.87, respectively, over time. Although both MDF disposed in soil and MDF only showed decreasing trends in percent nitrogen and carbon over time, the MDF in soil or MDF only were not significantly decomposed. MDF alone in the ambient environment may decompose by aerobic bacteria or fungi, but the decomposing process may be different from environmental condition as disposed in soil. In addition, difference between MDF in

Table 2. The results of chemical composition of MDF from the treatments during 77 days

	Landfill (Day)		
	0	35	77
Extractives (%)			
Cold water	11.92	3.54	3.96
Hot water	16.84	7.73	7.60
1% NaOH	30.02	19.78	18.19
Dichloromethane	1.85	0.44	0.32
Holocellulose (%)	63.46	66.26	65.49
Lignin (%)			
Klason lignin	21.63	22.44	22.66
Acid-soluble	0.48	0.50	0.51
Total	22.11	22.94	23.17
Ash (%)	0.76	1.74	1.71

soil and MDF only may be caused by present of soil which may block the leaching of elements originated from the MDF.

3.1.2. Chemical composition

MDF had 16.84% of hot-water extract on day 0 (original condition) and then 7.60% on day 77 (Table 2). According to Pettersen (1984), the normal range of hot-water extract from natural wood samples is 2.0% to 14%. More than 70% of cold-water extract and 54% of the hot-water extract were reduced on day 35 and then remained at that level through the 77 day study. During the 35 days, it appears that most of water soluble materials were removed by adding water weekly.

One percent NaOH extract can indicate the degree of fungal decay or of degradation by heat, light, and oxidation which indicate an decrease in the 1% NaOH extract may represent an increase in wood decay or degradation (Morgan, 1931; Procter *et. al*., 1973). During the 35 days, 34% of 1% NaOH extract was reduced, and then a 5% additional reduction occurred from day 35 to the end of study. Under our experimental conditions, approximately 78% of the dichloromethane extract was removed on day 35 and another 25% were removed on day 77 (Table 2). Therefore, approximately 83% of dichloromethane extract was removed over time.

Initially, MDF contained 63.46% of holocellulose and then slightly increased by 2 - 3% over time, as shown in Table 2. This indication during the 77 day experiment, degrading of cellulose and hemicelluloses was minimal. Based on these results, Klason lignin and acid-soluble lignin increased slightly but did not significantly change over time. Lignin is difficult to degrade under natural environmental conditions due to its aromatic structure. Therefore, 77 days may not have been sufficient time to degrade lignin.

On day 35, the ash content doubled compared to day 0 more than likely because of the removal of water and solvent soluble materials which caused increase in the ash content. Ash is usually less than 1% in wood (Pettersen, 1984). In summary, through the first 35 days, most of the water- (hot and cold), 1% NaOH-, and dichloromethane-soluble materials from MDF disposed in a simulated landfill were rinsed out by watering. However, holocellulose, Klason and acid soluble lignin, and ash content increased or constant while water and solvent soluble materials decreased over time.

In addition, no fungal hyphae and signs of

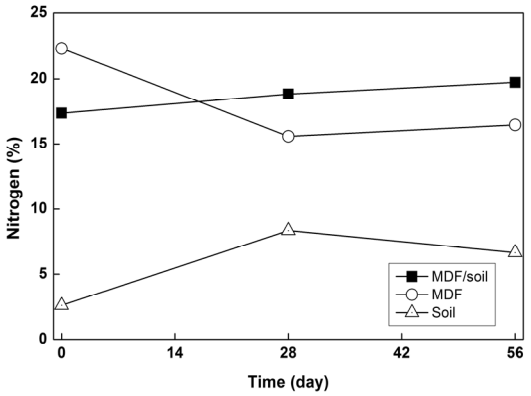

Fig. 1. Percentage of nitrogen in the leachate from MDF in soil (■), MDF only (○), and soil only (△) on days 0, 28, and 56.

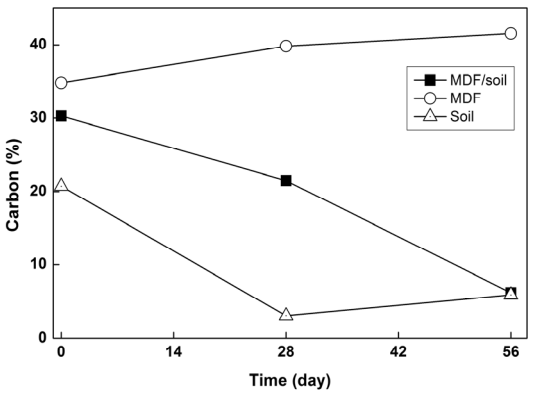

Fig. 2. Percentage of carbon in the leachate from MDF in soil (■), MDF only (○), and soil only (△) on days 0, 28, and 56.

decay by fungi were observed on MDF disposed in soil and MDF only at any sampling times according to SEM, damage may have come from mechanical processes or manufacture processes. Throughout the analysis of chemical compositions of MDF, extractives from MDF might affect the leachate quality in negatively as increasing COD and BOD by feeding bacterial or fungi. Moreover, 77 day was not enough time to degrade holocellulose and lignin, but MDF got on in years, these components will be degraded and affect on leachate quality in either ways.

3.2. Analysis of leachate

3.2.1. Elemental analysis

Fig. 1 indicated the percentage of nitrogen in the leachate on day 0, 28, and 56. Higher percentage of nitrogen was analyzed in leachate from treatments containing MDF (treatment 1 and 2) than soil only at all sampling times. Soil only treatment contained nitrogen which exists naturally or come from small woody debris. The percent nitrogen in the leachate from MDF only caused mainly by UF resin in MDF due to generally wood dose not contains nitrogen. Excess amount of percent nitrogen in leachate from MDF in soil may be contributed by organisms in soil and continuously broken down of the UF resin in MDF disposed in soil.

Higher percentage of carbon was found in MDF only than MDF in soil or soil only at all sampling times (Fig. 2). At 56 days, the percent carbon in leachate from the MDF in soil reduced at same level of soil only treatment, while a percent carbon increased in leachate from MDF only. The leachate from MDF only treatment may contain more water-soluble carbon materials than MDF in soil due to no interference of releasing carbon materials into leachate, so a higher percentage of carbon may be observed. This indicates (Fig. 2) that the percent carbon reduction in leachate was mainly

caused by soil in way that emission of carbon through air, which may have resulted in methane formation by anaerobic digestion of carbon sources leaching from MDF. Another hypothesis can be possible that wood fiber as carbon source from MDF may be blocked to come out through soil by physically or chemically hold.

Soil only treatment contained more sulfur content than MDF in soil and MDF only which indicated sulfur may be adsorbed to MDF or digested by soil microorganisms (Date not shown).

3.2.2. GPC

Six MW standards were used to investigate the molecular weight distribution of the leachates. The retention time (RT) for the highest MW standard (MW = 2,000,000) was 13.6 minutes, which indicated the void volume in this GPC column, while the RT for the smallest, glycol, (MW = 62.07) was 21.3 minutes (Date not shown). The leachate from all treatments (MDF in soil, MDF only, UF resin in soil, and soil only) contained compounds which were analyzed within an improper range of MW distribution based on the 6 standards in our chromatogram condition. Therefore, determination of the water-soluble materials' MW in the leachate sample was not successful. Nevertheless, the GPC chromatogram does indicate change in MW distribution of compounds in leachate over time by shifting.

Fig. 3 shows GPC results of leachates from MDF in soil, MDF only, UF resin in soil, and soil only with respect to RT on day 0. Based on chromatogram, soil only and UF resin in soil treatments had similar MW distribution and peak at 19.5 minutes, while treatments containing MDF (treatments 1 and 2) had similar MW distribution and peak at 23.5 minutes. However, MDF in soil treatment contained shoulder peak around 19.5 minutes which may be contributed by soil.

The MW distribution of compounds from soil only leachate did not changed over time. The compounds' MW distribution changed from lower to higher in MDF in soil and MDF only treatments based on the peak shifted to the left slowly over time which means higher MW compounds leaching on day 28 and 56 than the first sampling time. In leachate from UF resin in soil treatment, the peak was observed at 19.5 minutes on day 0 which was the same as soil only treatment and then the peak was detected at 21 and 23 minutes on days 28 and 56, respectively. In comparison to MDF amended treatments 1 and 2, the peak shifted to the right which means MW shifted from higher to lower (Fig. 3).

Based on GPC results of leachates, MDF may contribute to producing a lower MW compounds in leachates from the initial period due to the leachate containing water-soluble materials that originated from MDF. On the other hand, UF resin may not contribute to the change in MW distribution from the initial period, but over time, it may affect the MW distribution of compounds in the leachates.

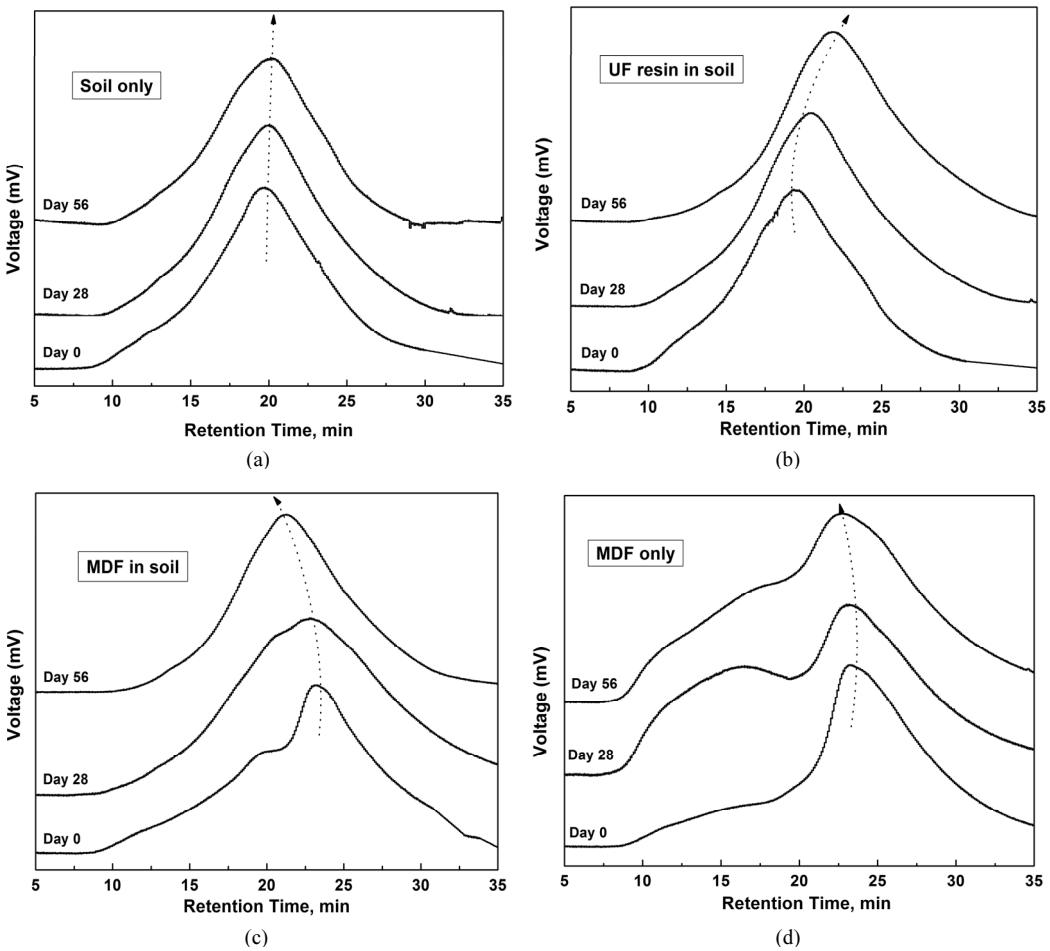

Fig. 3. GPC results of leachates from (a) soil only, (b) UF resin in soil, (c) MDF in soil, and (d) MDF only on days 0, 28, and 56.

3.2.3. FT-IR spectroscopy

Fig. 4 shows FT-IR spectra of cured UF resin and leachates from MDF in soil, MDF only, UF resin in soil, and soil only treatments on day 56. Following comparison analysis between each spectrum of leachate from treatments was considered with total amount of sample. UF resin in soil and soil only treatments had similar IR spectrum which contain O-H stretch at 3336 cm^{-1}, aromatic skeletal vibration plus C=O stretch at 1593 cm^{-1}, CH deformation in cellulose and hemicellulose at 1372 cm^{-1}, C-O-C vibration in cellulose and hemicellulose at 1150 cm^{-1}, and N-CH_2-N stretch at 1130 cm^{-1}, and C-O of ether at 1060 cm^{-1} (Jada, 1988; Müller *et al*., 2009). These results indicate cured UF resin did not much affect on chemical composition of leachate.

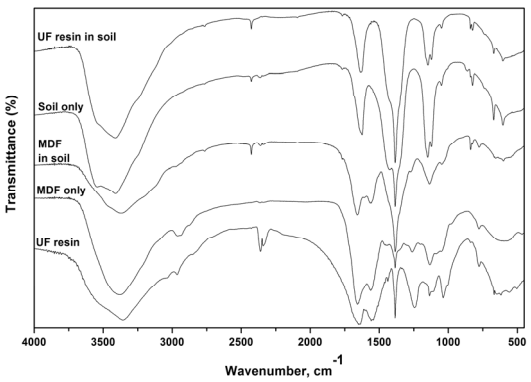

Fig. 4. FT-IR spectra of cured UF resin and leachates from MDF in soil, MDF only, UF resin in soil, and soil only treatments on day 56.

The spectrum of leachate from MDF in soil had additionally amide II, mixture of C-N and NH deformation at 1550 cm^{-1} which may be contributed by MDF, and CH deformation in cellulose and hemicellulose was stronger compare to MDF only treatment (Fig. 4). It was probably caused by soil not MDF because cellulose and hemicellulose of MDF did not decrease over time according to chemical analysis of MDF. Therefore, C-O-C vibration in cellulose and hemicellulose was contributed by compound releasing from soil.

The leachate from MDF only treatment and UF resin had similar IR spectrum but MDF only treatment has strong C-O-C vibration in cellulose and hemicellulose at 1150 cm^{-1} compare to UF resin due to wood fiber from MDF. These results indicate the chemical compound of leachate from MDF only treatment may be originally contributed by UF resin in MDF.

4. CONCLUSION

Each leachate contains different chemical compounds based on FT-IR and GPC data. From our GPC experimental conditions, even MW of compounds could not be calculated, but changes in MW distribution of compounds in leachates with respect to time were observed. Based on GPC results, MDF probably contributed to producing a lower MW of compounds in the leachate. These compounds in leachate may consist of nitrogen and carbon which were released from MDF. UF resin was slowly degraded by microorganism then produced formaldehyde, urea, ammonia, and sulfur over time.

The chemical analysis of MDF disposed in a simulated landfill for 77 days provides useful information for wood decomposing in a landfill. The results showed a significant reduction in water-, 1% NaOH-, and dichloromethane-soluble materials during the first 35 days. In formaldehyde leaching experiments, the leachate data indicated that after 28 days, formaldehyde emission level in leachate was close to the soil control (Lee *et al*., 2014; 2015). Therefore, most of the free formaldehyde probably was rinsed out with water-soluble components by watering. However, holocellulose, Klason and acid-soluble lignin, and ash contents increased which means hemicellulose, cellulose, and lignin were not degraded over 77 days which indicated main structural compounds of MDF were not decomposed in soil during the test period. Therefore, in leachate, extractives

from MDF may affect significantly in compositions and environment impacts but not by other components as holocellulose and Klason.

For future studies, longer sampling times are needed in order to determine if decomposed wood components or resin, will increase in leachates and the determination of methane and hydrogen emission will be needed for better understanding of MDF decomposition in soil.

REFERENCES

Chung, W.Y., Wi, S.G., Bae, H.J. 1999. Microscopic observation of wood-based composites exposed to fungal deterioration. Journal of Wood Science 45: 64～68.

Jada, S.S. 1988. The structure of urea formaldehyde resins. Journal of Applied Polymer Science. 35(6): 1573～1592.

Jahns, T., Schepp, R., Siersdorfer, C., Kaltwasser, H. 1998. Microbial urea-formaldehdye degradation involves a new enzyme, methylenediurease. Acta Biologica Hungarica 49(2-4): 449～454.

Lee, M., Mun, S.P., Prewitt, L. 2014. Formaldehyde Release from Medium Density Fiberboard in Simulated Landfills for Recycling. Journal of The Korean Wood Science and Technology 42(5): 597～604.

Lee, M., Mun, S.P., Prewitt, L. 2015. Environmental Assessments of Leachate from Medium Density Fiberboard in a Simulated Landfill Journal of The Korean Wood Science and Technology. 43(5): 548～557.

Maloney, T.M. 1996. The family of wood composite materials. Forest Products Journal. 46(2): 19～26.

Morgan, H.W. 1931. Wood evaluation for soda pulp manufacture. Paper Trade Journal. 92(15): 51.

Müller, G., Schöpper, C., Vos, H., Kharazipour, A., Polle, A. 2009. FTIR-ATR spectroscopic analyses of changes in wood properties during particle and fibreboard production of hard and softwood trees. BioResources 4(1): 49～71.

Pettersen, R.C., 1984. The Chemical Composition of Wood, American Chemical Society 2: 57～125.

Procter, A.R., Chow, W.M. 1973. A chip quality index for rot. Pulp Paper Magazine of Canada 74(7): 97～100.

TAPPI (Technical Association of the Pulp and Paper Industry) Method T-452. 2002a. Brightness of Pulp, Paper, and Paperboard (Directional Reflectance at 457 nm).

TAPPI (Technical Association of the Pulp and Paper Industry) Method T-212 om-02. 2002b. One percent sodium hydroxide solubility of wood and pulp.

TAPPI (Technical Association of the Pulp and Paper Industry) Method T-211. 2002c. Ash in Wood, Pulp, Paper, and Paperboard.

TAPPI (Technical Association of the Pulp and Paper Industry) Method T-204. 2007. Solvent Extractives of Wood and Pulp.

TAPPI (Technical Association of the Pulp and Paper Industry) Method T-207 cm-99. 2008. Water solubility of Wood and Pulp.

Thomas N., David, W.T., Timothy, M., William, C.P., Barry, M. 2008. Medium density fiberboard. United States Patent Application 0032147 A1.