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〈Research Paper〉

Comparison of Oil Sorption Capacity and Biodegradability of PP, PP/kapok(10/90wt%) Blend and Commercial(T2COM) Oil Sorbent Pads

Young-Hee Lee, Eun-Jin Lee, Gap-Shik Chang[1], Dong-Jin Lee[2], Young-Jin Jung[3] and Han-Do Kim†

Department of Organic Material Science and Engineering, Pusan National University, Busan, Korea
[1]Reliability Assessment Center, FITI, Seoul, Korea
[2]Korea Institute of Footwear and Leather Technology, Busan, Korea
[3]Department of Biomaterial Science, Pusan National University, Miryang, Korea

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Abstract: The oil sorption capacities and biodegradability of nonwoven fabrics(pads) of PP and PP/kapok(10/90wt%) blend prepared in this study and commercial pad(T2COM: 100% PP) were compared. The biodegradability(58.5%) of PP/kapok(10/90wt%) blend pad was about 5times higher than those(11%) of PP and T2COM pads after 45days. The oil sorption rates of oil sorbent pads for various oils(diesel, lubricant and Bunker C oils) were markedly increased with increasing dipping time up to about 5min and then levelled off. The oil sorption rate and oil sorption capacity were found to increase in the order of PP/kapok(10/90wt%) blend>PP>commercial(T2COM) and Bunker C>lubricant>diesel.

Keywords: *kapok, oil sorbents, oil sorption capacity, PP/kapok blend pad, biodegradability*

1. Introduction

Oils are one of the most important sources of energy and also could be used for raw materials of many chemicals and synthetic polymers worldwide[1-3]. During production, transportation, storage, and usage of oil there is always a risk of oil spillage.

Oil spill occurs over the seas, water bodies and land surfaces due to tanker disasters, wars, operation failures, equipment breaking down, accidents, and natural disasters. Oil spills into land, river or ocean impose a major problem on the environment[2,4-9]. When oil comes in contact with water, it forms oil-in-water emulsion or floating film that needs to be removed before it is discharged into the environment. Even a small amount of oil in sea/river water can be toxic to microorganisms responsible for biodegradation in conventional sewage processes[10]. It is therefore necessary to clean the water or land immediately after the oil spill. The removal of crude oil and petroleum products that are spilled at sea is serious problem of the last few decades.

There are some oil spill remediation products available including but not limiting to dispersants, sorbents, bioremediation agents and other miscellaneous products like surface cleaners, gelling agents, emulsifiers, solidifiers, etc. that can be used to clean up oil spill. Some properties of good absorbent materials include hydrophobicity and oleophilicity, high uptake capacity, high rate of uptake, retention over time, oil recovery from absorbent, and the reusability and biodegradability of sorbents[11,12].

Of them, the polypropylene fiber based oil sorbent products has been found to be mostly used to clean up oil spill[11]. They have good hydrophobic and oleophilic properties, but their non-biodegradability is a major disadvantage, hence possess environmental problems[13,14]. Instead the natural fiber based oil sorbents could be an interesting alternative to the synthetic oil sorbents. Among of those natural materials, kapok has the advantages over traditional oil-sorbing materials: low cost, biodegradability, intrinsic hydrophobic characteristics and high sorption capacity[8,11], and accordingly they are preferable as an oil-sorbing

† Corresponding author: Han-Do Kim (kimhd@pusan.ac.kr)
Tel.: +82-51-510-2410 Fax.: +82-51-512-8175

material.

Generally, it was found that kapok consisted of short fiber(fiber length: 20mm) has a hollow structure, low density, high bulkiness, good oil absorptivity and a water-repellent nature[15-17]. The kapok fibers are composed of about 65% cellulose with the balance being mainly lignins and hemicellulose. Besides all those mentioned chemical compositions, they also contain a waxy cutin on the fiber surface which makes them water repellent and oil absorbent[18,19].

In our previous study, the nonwoven fabrics(pads) of PP/kapok blends with various blend ratio were prepared by needle punching, and their oil(kerosene and soybean oil) and water sorption capacities and durability were investigated[20]. But there are only a few researches on the oil sorption capacity of blends including kapok.

In this study, the oil sorption capacities(for oil only/oil in artificial seawater) of PP and PP/kapok (10/90wt%) blend pads prepared here and commercial (T2COM) pad for various oils(diesel, lubricant and Bunker C oils) were investigated, and their biodegradability also examined.

2. Experimental

2.1 Materials

Kapok(Mae Sai in Thailand), polypropylene(PP) staple fiber(Kolonglotech), PP and PP/kapok(10/90) blend nonwoven fabrics(pads), and commercial (T2COM) pad (100% PP pad, Technology Tells Company, Korea) were used as sorbent materials. The characteristics of PP and kapok are shown in Table 1. Three kinds of oils, namely No.2 fuel oil(diesel, S-oil Co., Korea), lubricant(S-oil Dragon gear EP90, Korea) and No.6 fuel oil(Bunker C, HANARO MELODY, Korea) were used to investigate the oil sorption capacity of PP, PP/kapok(10/90wt%) blend and commercial(T2COM) pads as oil sorbents in this study. The measured physical properties of these oils were listed in Table 2.

2.2 Preparation of nonwoven fabrics(pads)

As described in our earlier paper, PP and PP/kapok (10/90) blends nonwoven fabrics(pads) were prepared by needle punching process at the fixed condition (punch density: 50 punches/cm^2 and depth: 4mm)[20]. PP and PP/kapok(10/90) blends nonwoven fabrics were prepared from PP/kapok blends using needle punching machine(SAMWHA CO. Ltd, Korea).

2.3 Characterization

Viscosity of oils was measured at 25℃ using a Brookfield digital viscometer(Brookfield LVDVⅡ$^+$, USA). Surface tension of oils was measured at 25℃ using a Tensiometer(KSV sigma 7001, Finland) following the KSM 1071-4: 2007(Guide for determination of the surface tension of chemical substances).

The oil sorption capacity of the oil sorbents was determined by the KS K1600: 2010. The testing of sorption behavior of the PP/kapok blend nonwoven

Table 1. Characteristics of PP and Kapok used in this study

	Fineness (denier)	Staple length (mm)	Wall thickness (μm)	Hollowness (%)	Crystallinity (%)	Cellulose type
PP	7.00	76	-	-	55.00	-
Kapok	0.82	20	1.04	77.10	44.95	Cellulose I

Table 2. The physical properties of oils used in this study

Oil	Viscosity/cP (spindle number)	Specific gravity	Surface tension (mN/m)
No.2 fuel oil(diesel)	8.25(S5)	0.82	27.28
Lubricant	411.50(S6)	0.94	31.73
No.6 fuel oil(Bunker C)	2414(S7)	0.98	33.59

fabrics were done using oil alone and a mixture of oil and artificial seawater. The procedure for oil sorption capacity is detailed below.

Oil sorption capacities of oil bath: 100mL of oil was placed in a 150mL glass beaker. PP/kapok blend nonwoven fabrics were immersed in the system for 5min. The wetted sorbents were weighted after being drained for 2min in the sustainer.

Oil sorption capacities of a mixture of oil and artificial seawater. The beaker containing oils(6g) and artificial seawater(60mL) were mounted in a shaking apparatus, which were shaken for 10min. PP/kapok blend nonwoven fabrics were added in the systems, which were shaken for 5min at 98cycles/min. The wetted sorbent materials were weighted after being drained for 2min in the sustainer.

The contact angles of water and oils were measured at 25℃ using a contact angle goniometer (Phoenix 300, SEO, Korea). The reported results are the mean values of five measurements. The contact angle, which is a measure of the surface wettability, was used to determine the hydrophobicity and hydrophilicity. The adhesion of liquid drops on the slide and the corresponding contact angles were observed through a microscope equipped with a CCD camera.

The Biodegradability was determined according to the standards of the KS M ISO 14855-1: 2013. The KS M ISO 14855-1 test method evaluates the ultimate aerobic biodegradability of plastic materials under controlled composting conditions. Controlled compositing conditions are maintained throughout the test, including oxygen and moisture content, temperature, and pH. Biodegradability is measured as the percentage of organic carbon converted to CO_2. The test duration is 45days. Calculate the theoretical amount of carbon dioxide $ThCO_2$, in grams per vessel, which can be produced by the test material using Equation(1):

$$ThCO_2 = M_{TOT} \times C_{TOT} \times \frac{44}{12} \quad \cdots\cdots (1)$$

Where, M_{TOT} is the total dry solids, in grams, in the test material introduced into the composting vessels at the start of the test; C_{TOT} is the proportion of total organic carbon in the total dry solids in the test material, in grams per gram; 44 and 12 are the molecular mass of carbon dioxide and the atomic mass of carbon, respectively.

From the cumulative amounts of carbon dioxide released, the percentage biodegradation D_t of the test material for each measurement interval was calculate by using Equation(2):

$$D_t = \frac{(CO_2)_T - (CO_2)_B}{ThCO_2} \times 100 \quad \cdots\cdots (2)$$

Where, $(CO_2)_T$ is the cumulative amount of carbon dioxide evolved in each composting vessel containing test material, in grams per vessel; $(CO_2)_B$ is the mean cumulative amount of carbon dioxide evolved in the blank vessels, in grams per vessel; $ThCO_2$ is the theoretical amount of carbon dioxide which can be produced by the test material, in grams per vessel.

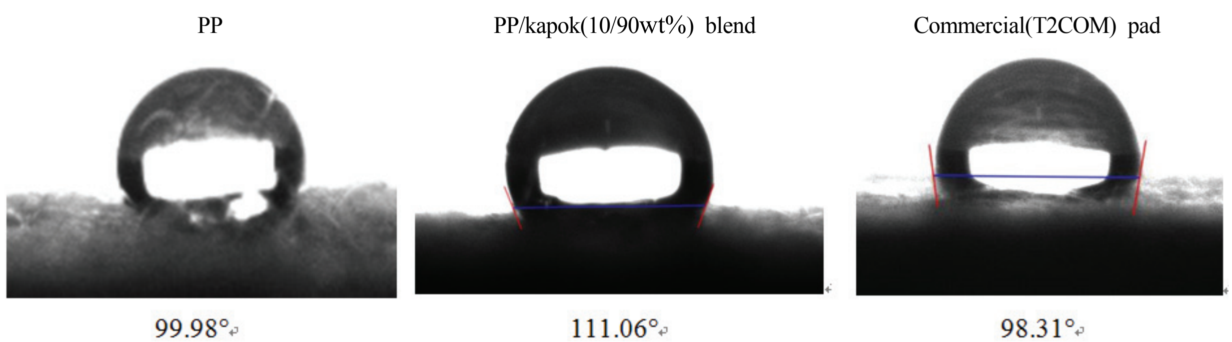

Figure 1. The water contact angles of PP, PP/kapok(10/90wt%) blend and commercial(T2COM) oil sorbent pads.

3. Results and discussion

3.1 Hydrophobicity and oil sorption capacity of oil sorbent pads

Generally, it was known that individual bundles, assemblies and simple blends of kapok, cotton and PP fibers had greater oil sorption than needle punched nonwoven fabrics(pads) prepared from the respective fibers. However, these bundles, assemblies and simple blends are not reusable and are difficult to control[21].

Therefore, reusable/easily handling PP and PP/kapok blend(10/90wt%) nonwoven fabrics (pads) were prepared in this study. However, it was found that the 100% kapok fibers could not be prepared into pads by using needle punching machine probably due to their low fineness(0.82denier) and short length(20mm)(Table 1). Therefore, the pads of PP/kapok(10/90wt%) blend and PP(100% PP fiber) were prepared here by needle punching process[20].

The water contact angles of PP, PP/kapok(10/90) blend and commercial(T2COM: 100% PP) pads as oil sorbents are shown in Figure 1. The water contact angles of PP, PP/kapok(10/90) blend and commercial (T2COM) pads were found to be 99.98, 111.06 and 98.31°, respectively, indicating that the water contact angle(hydrophobicity) increased in the order of PP/kapok (10/90) blend > PP > commercial (T2COM). This indicated that PP/kapok(10/90) blend pad has the highest hydrophobicity. This might be due to not only the wax component in kapok fiber[18,19] but also the lower bulk density of PP/kapok (10/90) blend pad than that of PP pad[20]. The water contact angle of PP pad prepared here was higher than that of commercial (T2COM) pad. This might be attributable to the difference of textures(bulk density and morphology, etc) between two samples.

The oil sorption capacities of PP, PP/kapok(10/90) blend and commercial(T2COM) pads for various oils(diesel, lubricant and Bunker C oils) are shown in Figure 2. The oil sorption capacities for diesel, lubricant and Bunker C were in the order of PP/kapok(10/90) blend > PP > commercial(T2COM) pads.

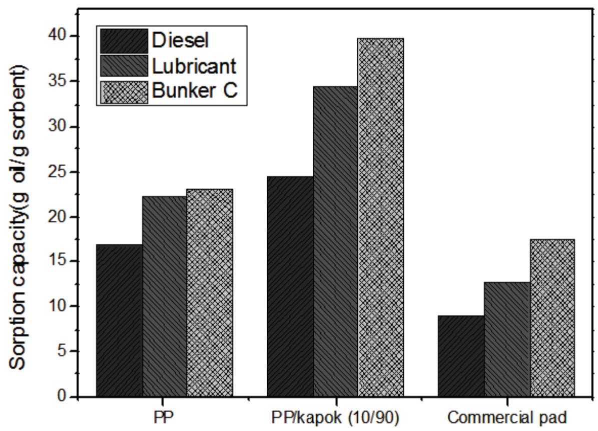

Figure 2. Oil sorption capacities of PP, PP/kapok(10/90) blend and commercial(T2COM) oil sorbent pads for various oils(diesel, lubricant and Bunker C oils).

The oil sorption capacity of PP/kapok(10/90) blend pad were 1.5-1.7times higher than that of PP pad and 2.3-2.7times higher than that of commercial(T2COM) pad. The highest oil sorption capacity of PP/kapok (10/90) blend pad was also attributable to not only the wax component in kapok fiber[18,19] but also the lower bulk density of PP/kapok(10/90) blend pad than that of PP pad[20], as described above.

The oil types are important factor which influences the oil sorption capacities of the sorbents. The properties of oil which are of prime importance in oil clean-up are its viscosity and specific gravity. Table 2 lists the viscosity, specific gravity and surface tension of the three kind of oils(diesel, lubricant and Bunker C oils) used in this study. Since most oils are lighter than water, they lie flat on top of water. However, the specific gravity of an oil spill can increase if the lighter substances within the oil evaporate. Viscosity is the measure of a liquid`s resistance to flow. The higher the viscosity of the oil, the greater the tendency for it to stay on one place. Surface tension is the measure of attraction between the surface molecules of a liquid. The higher the oil`s surface tension, the more likely a spill will remain in place. If the surface tension of oil is low, the oil will spread even without help from wind and water currents. The specific gravity, viscosity and surface tension of oils was increased in the order of Bunker C > lubricant > diesel.

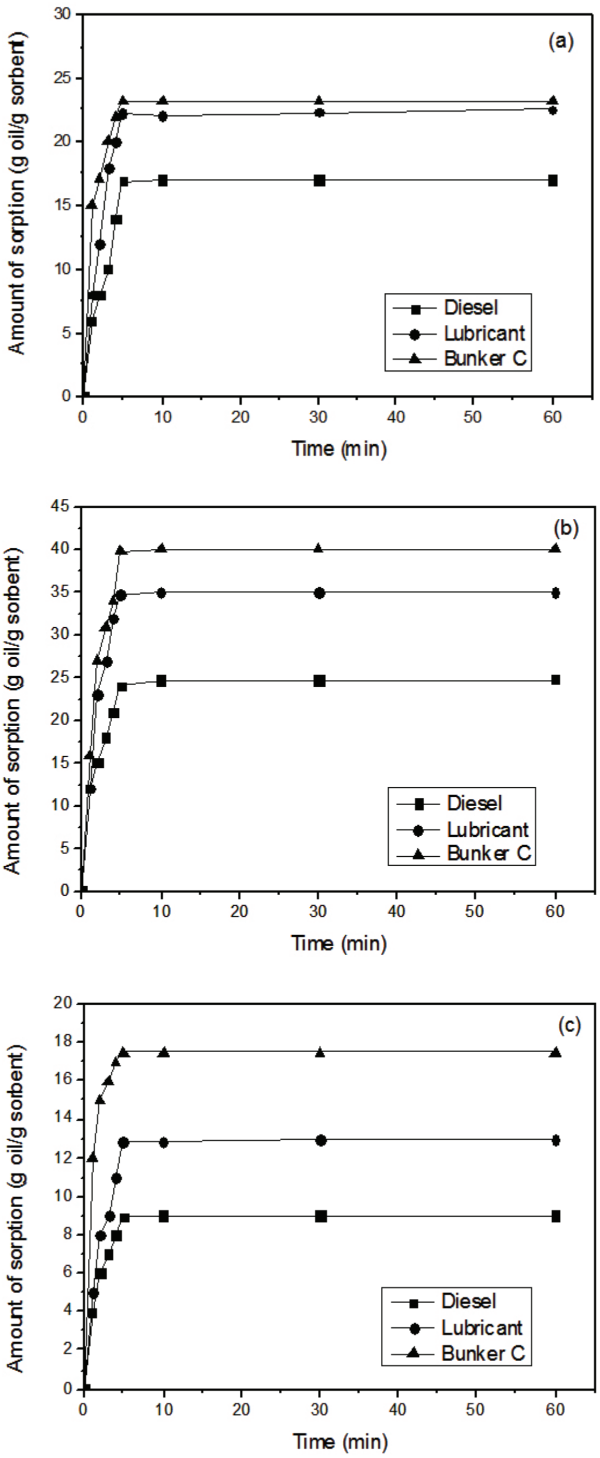

Figure 3. Oil sorption rate of (a) PP, (b) PP/kapok(10/90) blend and (c) commercial(T2COM) oil sorbent pads for various oils(diesel, lubricant and Bunker C oils).

The oil sorption rates of PP, PP/kapok(10/90) blend and commercial(T2COM) pads for various oils(diesel, lubricant and Bunker C oils) are shown in Figure 3.

The oil sorption rates(the slope in Figure 3) of PP, PP/kapok(10/90) blend and commercial(T2COM) pads for various oils(diesel, lubricant and Bunker C oils) were markedly increased with increasing dipping time up to about 5min and then levelled off. From the results of oil sorption rates, it was found that the amount of oil sorption after 5min and 1hr were not significantly different because of its ability to sorb oil up until its maximum limits within a very short time. The initial oil sorption rates of all pads increased in the order of Bunker C > lubricant >diesel. The increase order of oil sorption rates of PP, PP/kapok (10/90) blend and commercial(T2COM) pads for three kinds of oils was found to be coincident with the increase order of the viscosity of oils, indicating that the viscosity(the measure of a liquid`s resistance to flow) of oils is the crucial factor for the oil sorption of oil sorbent pads.

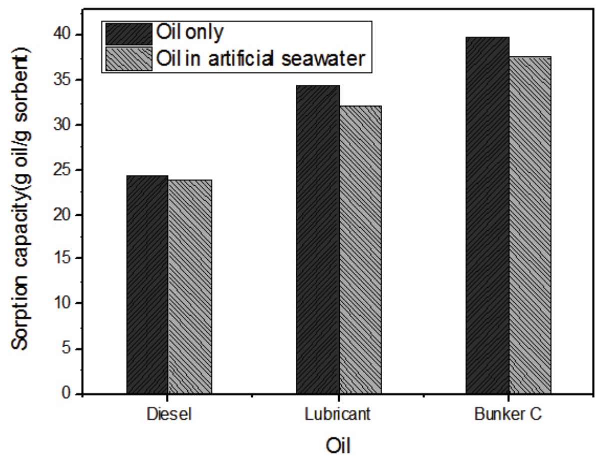

Figure 4. Oil sorption capacities of PP/kapok(10/90) blend pad for various oils under different conditions(oil only and oil in artificial seawater).

Figure 4 shows the oil sorption capacities of PP/kapok(10/90) blend pad for various oils under different conditions(oil only and oil in artificial seawater). The oil sorption capacities of oil only condition were a little higher than those of oil in artificial seawater condition. The oil sorption capacities of PP/kapok(10/90) blend pad for various oils were found to be increased with increasing the oil(diesel, lubricant and Bunker C) viscosity (Figure 4, Table 2). Wei et al. reported that oil with higher viscosity tends to have a higher initial sorption ratio[22].

As predicted, therefore, Bunker C, which has the highest viscosity among the test oils, showed greater oil sorption by PP/kapok(10/90) blend pad. One of the possible reasons for this higher sorption capacity may be that the fibers have greater absorption capacity to adsorb and hold the oil of higher viscosities. More viscose oils were highly absorbed by sorbent. Since the oil is more viscous as well as heavy, having a higher specific gravity, it goes on to the fiber, moves into the interior of the fibrous mass which remains floating on the surface of the water. In the case of low viscosity oil with low specific gravity, the oil quickly moves into the fibrous mass as well as on to the surface but desorbs easily during the drainage period. Therefore, the oil sorption capacities of PP/kapok(10/90) blend pad for various oils were understandably increased in the order of Bunker C > lubricant > diesel.

3.2 Biodegradability

The biodegradation ratio of polymeric materials is determined by several abiotic and biotic factors such as climatic conditions, microbial diversity, and composition of the materials[23,24]. The biodegradability is generally determined by the measurement of evolved carbon dioxide, when the polymeric matrix is exposed to controlled environmental conditions(eg., soil, sludge compost, or waste water). The respirometric method is testing method for confirming the total biodegradability of a material[25].

Figures 5, 6 show the cumulated CO_2 production curve (a) and biodegradability (b) estimated from relative amount of CO_2 evolved during the test for

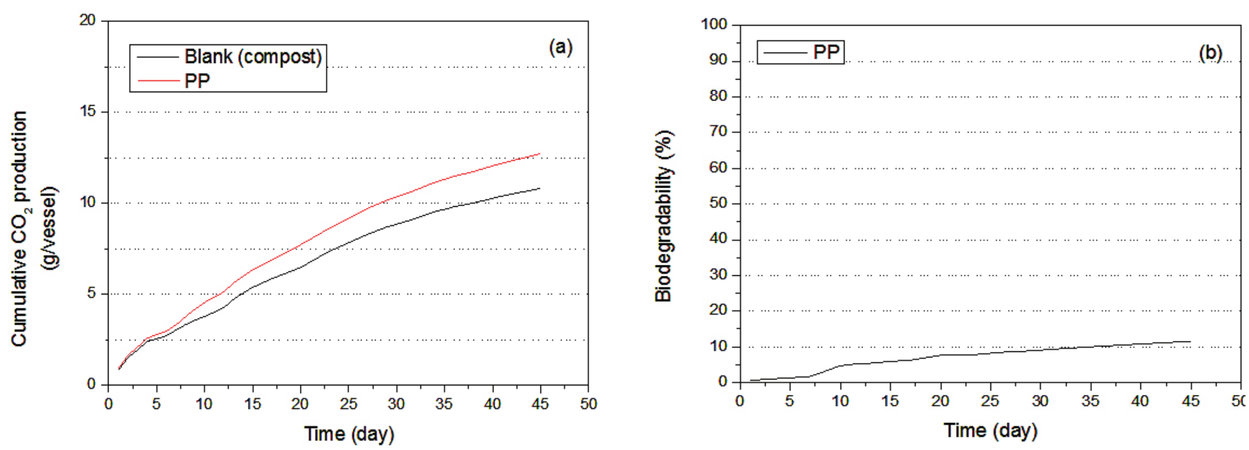

Figure 5. The cumulative CO_2 production(g/vessel) (a) and biodegradability (b) of PP pad as function of time.

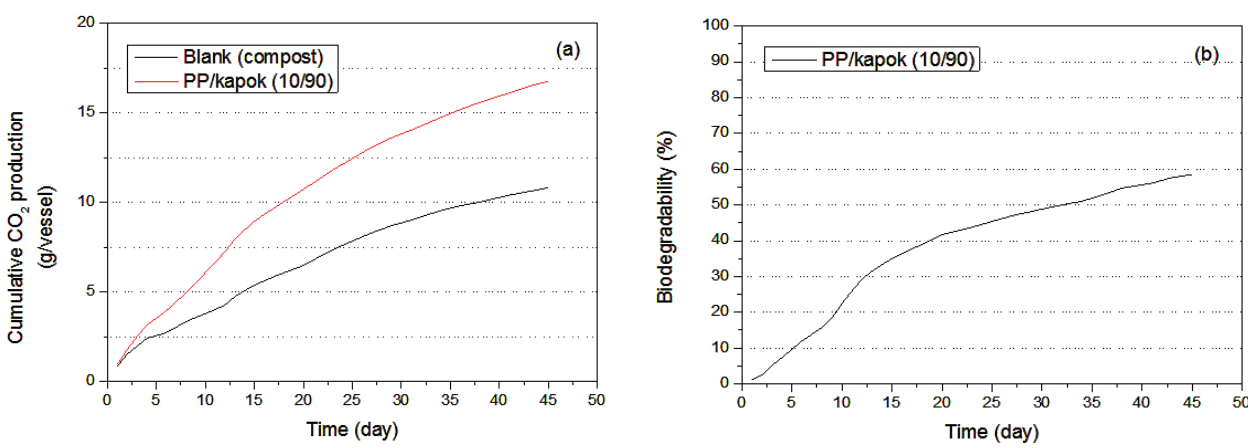

Figure 6. The cumulative CO_2 production(g/vessel) (a) and biodegradability (b) of PP/kapok blend(10/90) pad as function of time.

PP and PP/kapok(10/90) blend pads. On biodegradability test, there should be no change of color, odor, and the water content of inoculum for test materials and reference material(cellulose) during and at the end of the test(45days). We found that there were no changes on our biodegradability test. Biodegradability (58.5%) of PP/kapok(10/90) blend pad was 5times higher than that(11%) of PP pad after 45days. The higher biodegradability of PP/kapok(10/90) blend pad is obviously related to the high contents of biodegradable kapok fibers.

These results suggest that the PP/kapok(10/90) blend pad has high potential as a biodegradable high performance oil sorbent component.

4. Conclusions

The non-biodegradability of oil sorbent component PP is a major disadvantage. We compared the oil sorption capacities and biodegradability of PP and PP/kapok(10/90wt%) blend oil sorbent pads prepared here by needle punching process at the fixed (optimized) condition(punch density: 50punches/cm^2 and depth: 4mm) and commercial(T2COM: 100% PP) oil sorbent pad in this study.

The biodegradabilities of PP/kapok(10/90wt%) blend pad and PP pad after 45days were found to be 58.5% and 11.0%, respectively, indicating that PP/kapok (10/90wt%) blend pad was about 5 times higher than PP/T2COM pads. The oil sorption rates of PP, PP/kapok(10/90wt%) blend and commercial (T2COM) oil sorbent pads for various oils(diesel, lubricant and Bunker C oils) were markedly increased with increasing dipping time up to about 5min and then levelled off. The oil sorption rate and oil sorption capacity were found to be in the order of Bunker C > lubricant > diesel.

The increase orders of oil sorption rate and oil sorption capacity of PP, PP/kapok(10/90wt%) blend and commercial(T2COM) pads for three kinds of oils were found to be coincident with the increase order of the viscosity of oils(Bunker C > lubricant > diesel), indicating that the viscosity(the measure of a liquid`s resistance to flow) of oils is the crucial factor for the oil sorption of oil sorbent pads. The oil sorption capacities for various oils(diesel, lubricant and Bunker C oils) were in the order of PP/kapok blend > PP > commercial(T2COM). The oil sorption capacity of PP/kapok(10/90wt%) blend pad was 1.5-1.7 times higher than PP pad and 2.3-2.7 times higher than commercial(T2COM) pad. These results demonstrate significant potential of PP/kapok(10/90wt%) blend pad as a high performance biodegradable oil-sorbent material.

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