Fabrication of environmentally friendly water absorbing material using clay

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Abstract

An NC (Nanocomposites) gel was synthesized as an environment-friendly and reusable water absorbing sheet which is used commonly within the shipping industry. Clay that does not adversely affect the environment was used as a cross-linking agent to the NC gels. We prepared various kinds of NC gels. Samples were prepared using 10 types of concentrated SA aqueous solutions. Many samples did not gel, but a few samples did gel. They gelled only when the concentration of the SA aqueous solution was 1.20 and 1.25 [wt%].

From these results, it was found to be possible to use the NC gel as a countermeasure sheet.

1. Introduction

Recently a lot of ships using diesel engine as their power source which produces an exhaust gas that contained a hazardous substances such as NOx(nitrogen oxides) and SOx(sulfur oxides). All of these hazardous substances are the notable contributors to environmental pollutions such as acid rain and photochemical smog. Furthermore, these pollutions also generate adverse effect on the human body. Because of that IMO (International Maritime Organization) recently strengthen the regulation of hazardous substances [1]. Regulation on SOx and NOx by IMO as according to Annex VI "Regulations for the Prevention of Air Pollution from Ships". Annex VI sets limits on NOx and SOx emissions from ship exhausts, and prohibits deliberate emissions of ozone depleting substances. Fig. 1 shows the graph of NOx emission limit [2].

MARPOL Annex VI of NOx emission limits is applied to any diesel engine that has the output power of more than 130 kW. Different levels (Tiers) of control applied is based on the ship construction date. Tier I standard was being applied to both vessels that were created on and after 1st January 2000 and vessels that are equipped with the diesel engine that created before 1st January 2011. The regulation value is dependent on the rated engine speed. Table 1 shows the allowable amount of NOx emission.

Similarly, Tier II standard is also being applied on vessels that are equipped with diesel engine that was created on and after 1st January 2011. The regulation value is also shown in Table 1. Tier II standard is expected to be met by combustion process optimization. The parameters examined by engine manufacturers include fuel injection timing, fuel injection pressure, fuel nozzle flow area, exhaust valve timing, and cylinder compression volume. Then, Tier III standard is applied on vessels that were created on or after 2016 that operating in the ECA (Emission Control Areas). The regulation value is also shown in Table 1.

Tier III standard is required to reduce 80% of NOx emission from the Tier I regulation. In Tier III, it is said that there are difficulties in reducing the NOx emission using the technology inside the diesel engine. For that reason, exhaust gas with purification technology also known as urea SCR (Selective

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Catalytic Reduction) method was used [3]. This technology is based on the fact that urea water is sprayed into the exhaust gas and the NOx that contained in the exhaust gas is decomposed to water and nitrogen by the ammonia in the urea water. In this urea SCR method, it is essential to treat the moisture that is produced.

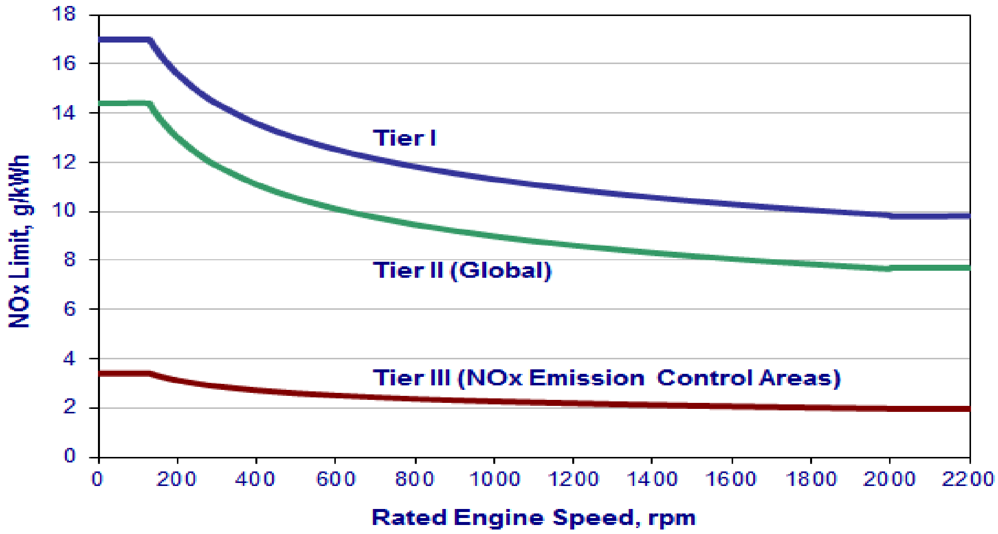

Fig.1　MARPOL Annex VI of NOx emission limits

So in our laboratory, we worked on the material of reusable water absorbing sheet in order to treat the moisture. Generally, water absorbing material is often referred to as SAP (Super Absorbent Polymers) that is used in disposable diapers [4]. However, SAP has a disadvantage in which it cannot be used once it adsorbs water. It is appears to be suitable for disposable uses such as disposable diapers but not as a water absorbing sheet which is supposed to be used repeatedly.

Table 1　NO_x emission limits by IMO

Tier I　(2000)	
Rated engine speed [rpm]	NOx emission limit [g/kWh]
● n<130	17.0[g/kWh]
● 130≦n<2000	$45.0 \cdot n^{(-0\ 2)}$ [g/kWh]
● n≧2000	9.8[g/kWh]
Tier II　(2011)	
Rated engine speed [rpm]	NOx emission limit [g/kWh]
● n<130	14.4[g/kWh]
● 130≦n<2000	$44.0 \cdot n^{(-0\ 23)}$ [g/kWh]
● n≧2000	7.7[g/kWh]
Tier III　(2016)T	
Rated engine speed [rpm]	NOx emission limit [g/kWh]
● n<130	14.4[g/kWh]
● 130≦n<2000	$45.0 \cdot n^{(-0\ 2)}$ [g/kWh]
● n≧2000	9.8[g/kWh]
T: In NOx Emission Control Areas (Tier II standards apply outside ECAs)	

2.　Polymer gel and Clay

The PNIPA gel used in this experiment is a temperature-responsive polymer and it has been studied in various fields since it has excellent characteristics such as volume phase transition that correspond to the temperature. The Society of Polymer defined polymer gel as a polymer that is cross linked and has become a three dimensional network structure, produces swelling but does not dissolve and takes the state between solid and liquid.

The volume phase transition of polymer gel is the transition between swelling phase and contraction phase of the gel was discovered by Mr. Toyoichi Tanaka [5,6]. Solvent composition, temperature, pressure, pH, electric field, and light are examples of factors that cause this volume phase transition to occur. All these external factors can change the volume of polymer gel by 10 to 1000 times.

Volume phase transition of PNIPA gel occurs due to the temperature change, which is swells at low temperature and shrinks at high temperature. This volume change is reversible and can be repeated many times. Because of that characteristic, it is possible to create a water absorbing sheet that can be used repeatedly [7].

Clay is a material that is made by removing and purifying impurities in the layered clay mineral [8]. There are various types of clay but in our research, we are using two types of clay which is Kunipia and Sumecton from Kunimine Industries. Kunipia is a purified type of clay called Bentonite. Bentonite is a layered silicate mineral containing montmorillonite as a main component and other minerals such as quartz, mica, feldspar, and zeolite. Kunipia is a natural clay, so it is difficult to completely control it´s properties. The solution to this problem is using synthetic clay called Sumecton. Sumecton is a clay formed by chemically synthesizing by removing impurities and treatment with hot water [9].

Recently, research on new soft materials combining this polymer gel and clay materials are being actively conducted. Professor Takuzo Aida from Tokyo University has succeeded in developing new soft materials that have a high strength and self-repairing performance which can contain more than 95% of moisture just by mixing clay and an organic polymer compound. It can be said to be environmentally friendly because it´s mostly made from naturally derived materials such as water and clay.

From this, we can expect a high performance and high functionality of new organic/inorganic hybrid materials to be formed if inorganic structure such as clay combined well with organic structure such as polymer gel. Representative of this organic/inorganic hybrid material is FRP (Fiber Reinforced Plastic). Moreover, there are also others materials that have been researched and developed. Consequently, our laboratory has also made a new water absorbing materials that environmentally friendly by using PNIPA gel and clay.

3. Experiment

The composition of PNIPA gel which act as a water absorbing agent was prepared as follows. Distilled water and SA(Sodium Acrylate) which is act as an ionizing agent were used to make 10 concentration(0.5, 0.8, 1.0,1.1, 1.15, 1.2, 1.25, 1.3, 1.4, 1.5 [wt%]) of an aqueous solution.1 g of clay was gradually put into the aqueous solution, stirred and dissolved. Two types of clay were used which is Kunipia and Sumecton. Next, 3.88 g of NIPA(N-isopropylarylamide) is dissolved.

After that, 120 μl of N-N,N`,N`-tetramethylethylenediamine was used as a polymerization accelerator and 20 mg of Ammonium Peroxodisulfate as a polymerization initiator was added before being left in a thermostatic chamber at 20 °C for 24 hours for gelling to occur.

4. Results and discussion

Fig.2 and Fig.3 shows the state of gelling of the samples using all the composition mention above. The horizontal axis shows the concentration [wt%] of the SA aqueous solution used and the vertical axis shows the mass ratio of the main chain NIPA when SA is 1. A sample which gelled was evaluated as O, a sample which is not gelled was evaluated as X, and a sample in a sol state was indicated by Δ in the table. The result of the experiment using Kunipia is shown in Fig.2 after being left in a thermostatic chamber at 20 °C for 24 hours, the samples using Kunipia did not gelled but remained in liquid state in all concentration of SA. The result of the experiment using Sumecton is shown in Fig.3. The sample using Sumecton only gelled in the SA aqueous solution which has the concentration of 1.15 and 1.2 [wt%] only. The remaining samples only remained in a liquid or sol state.

From the above result, we can conclude that clay also can cross-link NIPA which is the main chain in the specific condition. Originally, clay is in a state in which layers are piled up as shown in Fig. 8. In this state, it is not possible to crosslink the polymer. The SA aqueous solution can disperse the clay with the force of electric charge in the solution. In other words, SA can disperse the clay and crosslink the NIPA.

Based on the experimental results, it can be considered that sample using Sumecton could be gelled only when the concentration of SA aqueous solution was 1.15 and 1.2 [wt%] and clay could be dispersed by the force of the electric charge that working in the SA aqueous solution. During the refining process, Sumecton undergoes a hot water treatment after removing impurities while Kunipa does not undergo hot water treatment after the removal of impurities.

From that, we can conclude that Kunipia did not gel and cannot crosslink PNIPA as the clay did not disperse by the electric force that is working in SA aqueous solution due to the properties of the clay used. From above, we can distinctly see that gel can be formed only when the concentration of SA aqueous solution was 1.15 and 1.2 [wt%] by using Sumecton as a crosslinking agent.

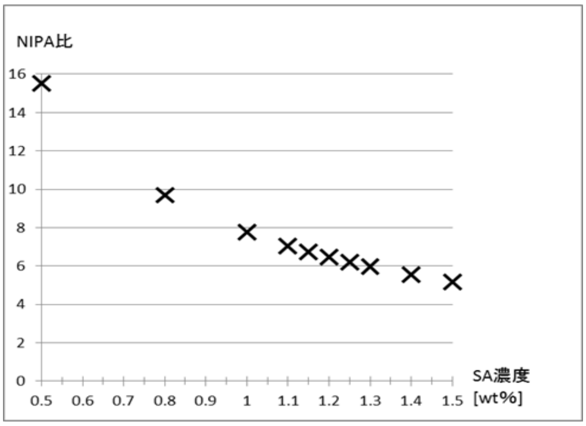

Fig.2 Gelation of sample using Kunipia

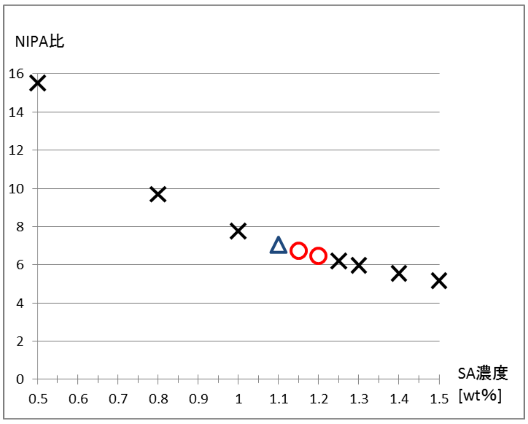

Fig.3 Gelation of sample using Sumecton

5. Conclusions

In this laboratory, we tried to use clay as a crosslinking agent for PNIPA gels in order to create an environment friendly water absorbing material. As a result, the following conclusion can be made:

1. All samples using Kunipia could not be gelled in this experiment.
2. Samples using Sumecton can gelled only at the concentration of SA aqueous solution is 1.15 and 1.2 [wt%] only.

From these conclusions, it can be said that SA can crosslink NIPA by dispersing clay in aqueous solution, but it is also found that there are specific conditions for cross-linking PNIPA in this experiment. In this experiment, it is possible for Sumecton to be gelled only when the concentration of SA aqueous solution is 1.15 and 1.2 [wt%] as the clay was dispersed by the electric charge that working in the SA aqueous solution then cross-linking PNIPA gels. In addition, Sumecton was treated with hot water during refining while Kunipia did not undergo hot water treatment after refining

process [10]. This difference can be said to influence ion exchange between clay layers and the crosslinking of PNIPA.
From this experiment, by using clay as a crosslinking agent for PNIPA gel, we were able to create a new non-toxic and environmentally friendly water absorbing material.

References

[1] Tomohiro Matsumoto : Journal of The Japan Institute of Marine Engineering,Vol.49, No.6,2014.
[2] NOx emission standard: https://www.dieselnet.com/standards/inter/imo.php, 2017.10.30.
[3] Kouichi Hirata, Masahide Takagi, Nobuyuki Kishi, Youichi Niki, Satoshi Kawauchi, Yasuhisa Ichikawa, Tetsugo Fukuda, Toshiharu Inaba, Takeo Nagai, Izumi Iwamoto, Shota Ohashi, Kazuhiro Tabuchi, Junnzou Kaneko, Eichi Muraoka : National Maritime Research Institute : NMRI, Vol.11,No.2,2011.
[4] KISHIDA CHEMICAL Co.,Ltd.,Safety data sheet, 4393,2016.
[5] T.Tanaka: Phys.Rev.Lett. , 40,820, 1978.
[6] T.Tanaka: Sci.Am. , 244, 110, 1981.
[7] Tomohiro Murakami, Wataru Akase: Memories of National Institute of Technology, Yuge College,Vol30, 2008.
[8] Kazutoshi Haraguchi ; networkpolymer, Vol33, No.6, 2012.
[9] KUNIMINE INDUSTRIES CO., LTD., SUMECTON,P2,2013.
[10] Japan Science & Technology Agency (JST), Vol.707, 2010.