PREPARATION OF RECYCLED PLASTICS FROM DEPOLYMERISED MATERIALS OF WASTE FRPS

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The preparation of recycled plastic from the depolymerized materials is the final stage for the chemical recycled process.[1] Recently, we have developed an efficient method to depolymerize waste fiber-reinforced plastics,[2] one of the formidable plastic to treat in chemical recycling scheme, by treatment with supercritical MeOH.[3] For this process, addition of catalytic amounts of DMAP, *N*,*N*-dimethylaminopyridine,[4] was essential for the complete break down of FRP. The monomeric material made by this way, however, failed for the formation of recycled polymers due to the contamination of impurities derived from the decomposition of DMAP. This is a problem to be overcome for establishing efficient chemical recycling of FRP. Removal of the impurities and purification of the recovered materials were achieved by washing treatment with water and the purity of dimethylphthlate, DMP, was enhanced to more than 90%.[5] Although this was a satisfactory solution of the problem, the washing treatment was somewhat troublesome in the practical manipulation. As a result, much simple method for the purification was desired. In this presentation, we report the following two methodologies for the solution of the problem. One is the method in which reduced amounts of DMAP was used for the depolymerization process. This method may enable the rebuilding polymers without further purification. The second method was use of activated carbon for the removal of impurities in the recovered monomer. This method would offer a simple operation for the purification of DMP. We will also present an improved method for the formation of recycled polymer which was used for the preparation of a test product.

We firstly examined depolymerization reaction in the presence of less than 3% of DMAP. Usually the depolymerization required more than 3% of DMAP for the complete depolymerization and separation of recovered materials. Treatment of waste FRP in the presence of 1% or 2% of DMAP resulted in the depolymerization of FRP to give monomeric materials and insoluble residue. As we expected, the insoluble residue contaminated with polymeric materials that could not be solved any kind of solvent. So the separation of glass fibre and linker polymer failed. This was probably because the small amounts of DMAP decomposed too quickly to progress sufficient transesterification reaction on linker molecules. Thus, at least 3 % of DMAP should be needed to achieve the efficient separation of linkers and inorganic contents.

The monomeric material made from 1% of DMAP contained DMP, glycol and *N*-methyl-4-pyridone,[6] decomposed product of DMAP. GC analysis revealed the content of DMP was about 60%. The polymerization reaction of the material with adding new DMP in various ratios was carried out under the standard conditions. Fortunately, the polymerization took place smoothly in any ratios of new and recovered DMP. Even staring from 100% recovered materials, recycled polymer was successfully obtained. Some of the recycled polymers were shown below (Fig. 1).

Fig. 1 Obtained polymers from the monomeric material recovered from the reaction in the presence of 1% of DMAP. From left, 20%, 40%, and 60% of recovered monomer was used

We then examined hardness tests for the polymers. Fig. 2 shows the HDD hardness test. As shown in Fig. 2, the hardness of the polymer was unchanged in high level when the ratio of recovered material was less than 60%. As the ratio of recovered monomers exceeded more than 60%, HDD values were slightly lowered, but still maintained sufficient hardness. Thus, the present monomeric material was useful for the formation of recycled polymers.

We next examined to use activated carbon for the purification of the recovered monomer. For these experiments, we used monoeric material made from the decomposition reaction in the presence of 2% of DMAP. The original content of DMP was estimated to be 25% with GC analysis. The recovered monomer was dissolved in various solvent and activated carbon was added. Then the mixture was heated at refluxing temperature for 20 h. After cooling, the

mixture was filtered and the filtrate was concentrated. The contents of DMAP were examined by GC analyses. The results are summarized in Fig.3.

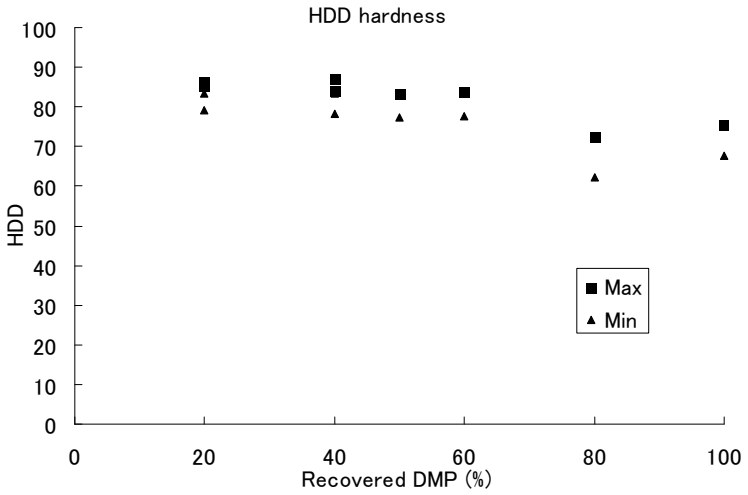

Fig. 2 HDD hardness tests for the rebuilt polymers

Use of MeOH did not change the purity and almost 100% of original DMP was recovered. This is due to strong polarity of MeOH which prevent absorption of impurities on activated carbon. As the polarity of solvent decreased, the prutity was gradually improved. For example, treatment in acetone, THF, EtOAc, and DCM resulted in slight improving the purification of DMP up to 35% and nearly 100% of DMP was recovered. Use of less polar Et_2O and toluene much effectively recovered DMP and improved the purity to about 45%. The purity increased about 70% when hexane was used as the solvent. In this case DMP recovery just decreased, but more than 80% of original DMP was recovered through the manipulation. Thus, the purification with activated carbon was effective when non polar solvent such as hexane was used for the treatment. However, the purity of DMP was improved about 70% level. Rebuilding of the polymer with these purified materials is now investigating.

In the last section we will show an improved formation of recycled plastic. Use of a modified catalyst system for the formation of unsaturated polyester resulted in the preparation of recycled plastic with better quality than before. This material was applied to the synthesis of test products to promote chemical recycling of FRP in practice.

In conclusion, recovered monomers were useful directly for the re-polymerization reaction to give recycled plastics although the depolymerization of FRP with reduced amounts of DMAP resulted in the incomplete decomposition of FRP. Treatment with activated carbon provided a convenient method to purify the monomeric materials and it purity was improved uo tp 70%.

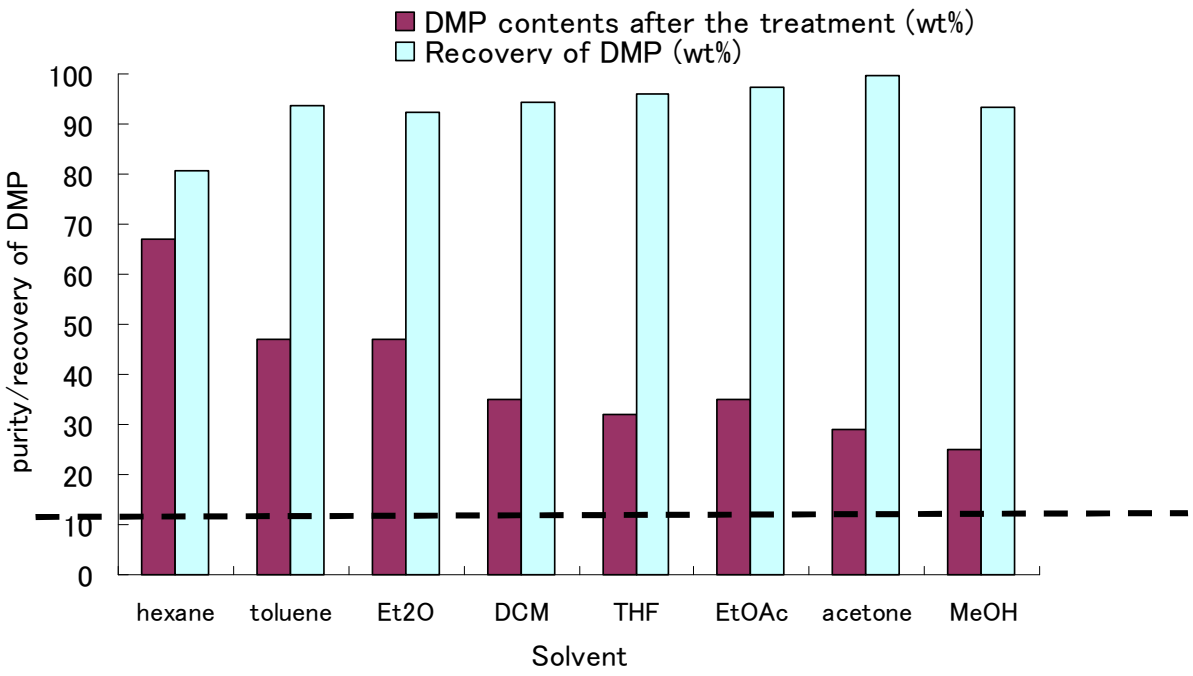

Fig. 3 Purification/recovery of DMP on treatment with activated carbon.

References

[1] Technology for Feedstock Recycling of Plastic Wastes, *Research Association of Feedstock Recycling of Plastics*, 2005.

[2] S. Kubota, H. Mori, T. Maeda. *Nettowaku Porymer* **2003**, *24*, 22.

[3] A. Kamimura, Y. Yamada, T. Kuratani, Y. Oishi, T. Watanabe, T. Yoshida, F. Tomonaga. *ChemSusChem* **2008**, *1*, 845-850.

[4] A. C. Spivey, S. Arseniyadis, *Angew. Chem. Int. Ed.* **2004**, *43*, 5436.

[5] A. Kamimura, E. Konno, S. Yamamoto, T. Watanabe, K. Yamada, F. Tomonaga. *J. Mater. Cycles Waste Manag.* **2009**, *10*, 38-41.

[6] P. Guerry, R. Neier. *Synthesis,* **1984**, 485-488.