New continuous process of the supercritical fluid using extruder for the modification of the polymer

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Here, we represent the development of the new continuous process for supercritical fluid which can treat cross-linked polymer.

In the previous study, it was revealed that silane-XLPE turned into the recycled PE which could be used as raw PE only in supercritical alcohol.

By using this reaction, we are going to recycling industrial waste come out from extrusion process of the product made from silane-XLPE. For the industrialization, we developed the new continuous process using twin screw extruder.

As a result of the investigation, the silane-XLPE could be recycled to thermoplastic recycled PE at the speed of 14kg/hour continuously. These results means that the continuous process using twin screw extruder can be applied for the chemical reaction between supercritical alcohol and silane-XLPE.

INTRODUCTION

Development of the continuous process for supercritical fluid to treat the material like solid is general problem for the supercritical fluid technology. Here, we investigated the new continuous process which used twin screw extruder as feeder, reactor and equipment for the separation between sticky material like thermoplastic polymer and supercritical fluid.

In the previous study, the condition for recycling of silane-XLPE to obtain the recycled polyethylene (recycled PE) was investigated by batch process using autoclave. As a result of the study, it was revealed that the selective decomposition of the cross-linking element was occurred in supercritical n-propanol around 10MPa and 320°C, only in the supercritical state shown in **Figure 1**.

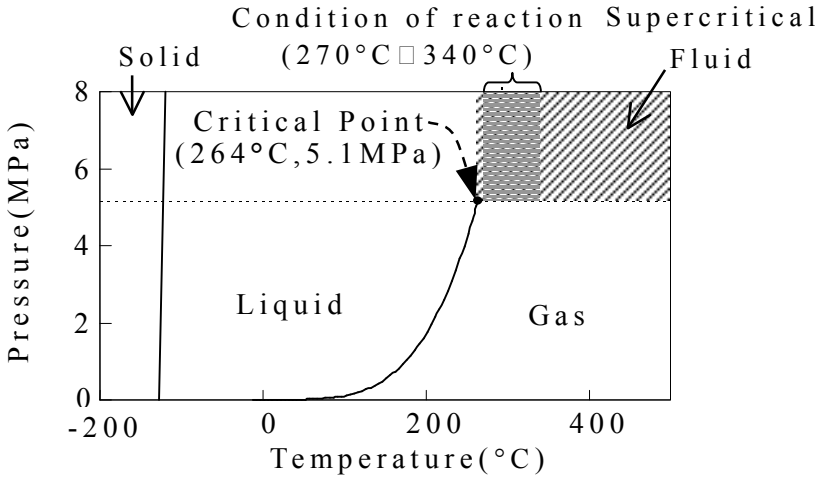

Figure Condition for the reaction to obtain the recycled PE

Moreover, we demonstrated the new continuous process which used twin screw extruder using the silane-XLPE pellet made as the imitation of the industrial waste[3)4)].

In this study, the silane-XLPE used here was the industrial waste came from the extrusion process of the product made from silane-XLPE in the factory.

MATERIALS AND METHODS

Silane-XLPE used here was the industrial waste from the extrusion process making the insulation of the 600V XLPE power cable.

The waste shown in shown in **Figure 2** was crushed into the size about 5mm pellet to be fed to the extruder. Gel fraction of the silane-XLPE pellet was about 48%.

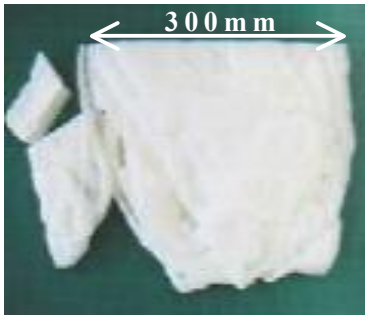

Figure 2 Appearance of waste came from the extruder

Figure 3 The crushed silane –XLPE waste.

The crushed silane-XLPE waste shown in **Figure 3** was fed to the hopper of continuous process using twin screw extruder shown in **Figure 4**. Twin screw extruder made by Japan Steel Works was used as equipment for chemical reaction (Ext-Chem) and degas(Ext-Degas). One-way valve was attached to the cylinder of the Ext-Chem to inject the supercritical n-propanol. N-propanol was fed by high pressure pump and heated to the supercritical state before it was injected to the cylinder. The tube reactor was attached to the Ext-Chem to keep the supercritical state for 30min. Pressure control valve was connected to the front of the reactor. Ext-Degas was mounted to the outlet of the intermediary pipe to separate recycled PE and n-propanol.

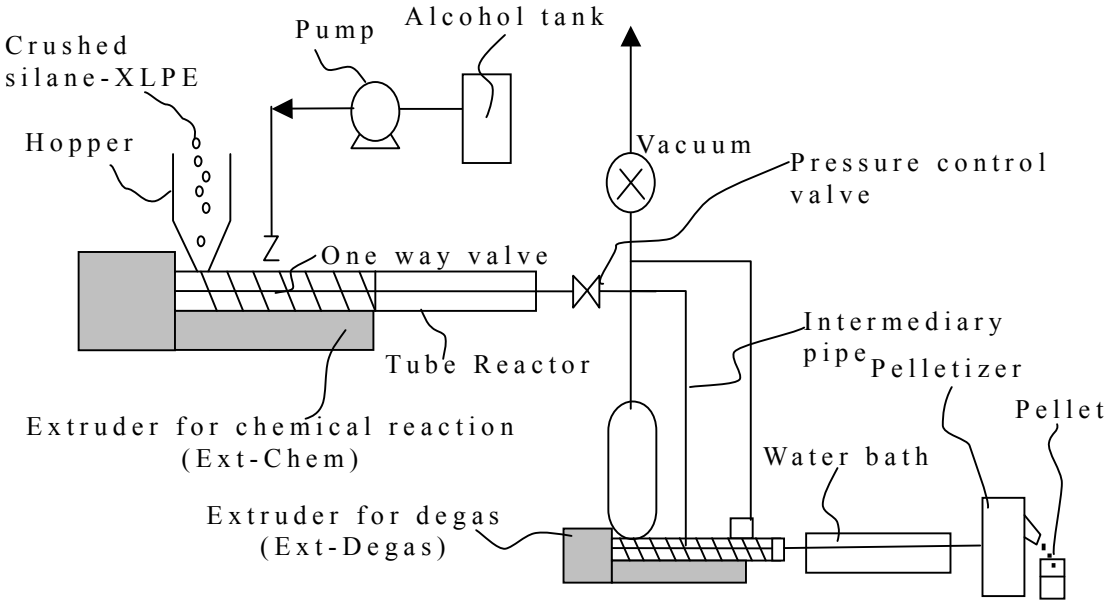

Figure 4 Scheme of the continuous process for recycling of silane-XLPE by supercritical alcohol using twin screw extruder.

The Silane-XLPE was charged to the extruder from the hopper of the Ext-Chem, then 10phr of n-propanol per 100phr of

silane-XLPE was injected to the cylinder. Supercritical n-propanol was kept over 300 ° C at 8MPa. Pressure and temperature in the reactor was kept at 330°C and 10MPa. The n-propanol was separated in Ext-Degas and recycled PE was extruded as the strand. The strand was cut into the pellet after it was cooled in the water bath.

The structure of the recycled PE was evaluated by the gel fraction(GF) for characterizing the degree of cross-linking and infrared spectrum.

Gel fraction(GF) was determined as follows. The initial weight of specimens(Wf) was measured before they were immersed in the xylene at 110°C. The residue after extraction was taken out from the xylene and dried at 80°C under vacuum aspiration for more than 4 hours. The weight of dried specimens (Wa) was also measured. The gel fraction was calculated from the weight of the specimen before and after extraction according to following equation.

$$GF(\%) = (Wa / Wf) \times 100$$

RESULT AND DISCUSSION

The recycled PE was continuously obtained from Ext-Degas at the speed of 14kg/hour as shown in **Figure 5**. The strand was automatically cut into the pellet as shown in **Figure 6**.

Figure 5 Extruded strand from the continuous process.

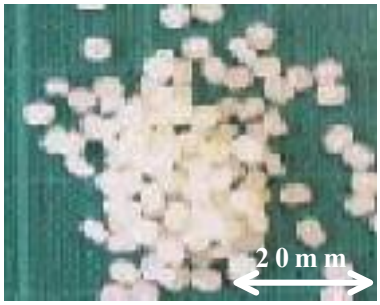

Figure 6 Recycled PE pellet

Gel fraction of the recycled PE was plotted against temperature of the reactor in **Figure 7**. The gel fraction was decrease from 48% to less than 20%. In the previous study, we got the recycled PE which gel fraction was 0% from the imitation silane-XLPE pellet. It is expected that the difference between industrial waste and

imitation silane-XLPE pellet is caused by the impurity of the waste. Further investigation is required to reveal the origin of the difference.

The infrared spectra also showed that the cross-linking element was decomposed. Assignment of the absorption is represented in **Table 1**. Peak at $1030cm^{-1}$ represent the siloxane bond which constitute the cross-linking element, that can be observed as shoulder of the peak at $1090cm^{-1}$. The peak at $1090cm^{-1}$ in the spectrum of the recycled PE is sharper than that of silane-XLPE. It is indicated that the siloxane bond is decomposed to the alcoxy silane or hydroxy silane.

These results mean that decomposition reaction which is observed in the supercritical alcohol as shown in **Figure 9** was reproduced in the new continuos process. It is also indicated that the new continuous process using twin screw extruder is the one of the solution for the problem of the process for the polymer modification using supercritical fluid.

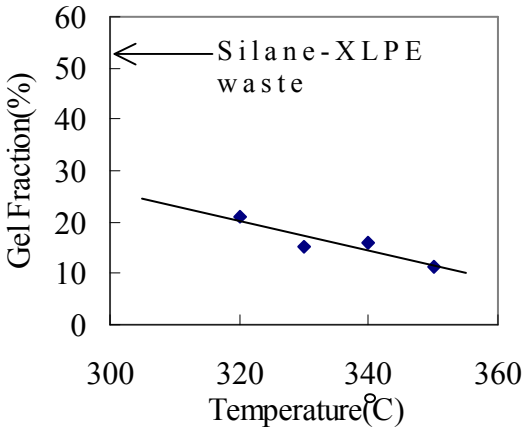

Figure 7 Gel fraction of the recycled PE.

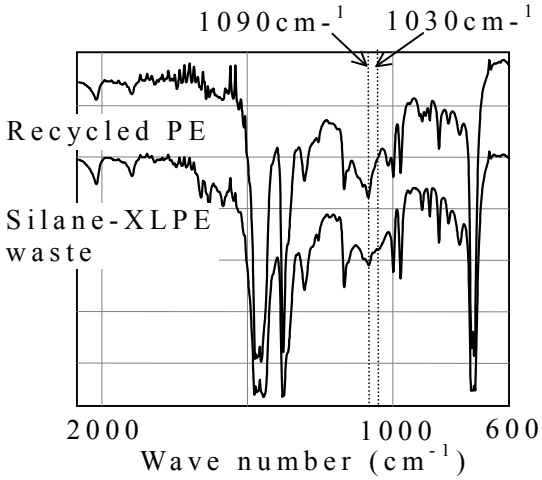

Figure 8 Infrared Spectra of the recycled PE

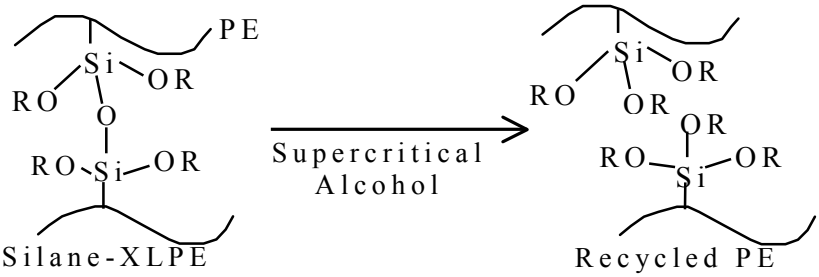

Figure 9 Reaction of the cross-liking element of silane-XLPE in Supercritical Alcohol

Table 1. IR absorption wave number related to silane-crosslinking unit[2)]

Wave number (cm^{-1})	Structure
1030	-Si-O-Si-
1090	$-SiOCH_3$ or –SiOH

CONCLUSION

The reaction for selective decomposition of silane-XLPE, which is known as the specific reaction in supercritical alcohol was occurred in continuous process using twin screw extruder.

As a results, recycled PE could be produced from the waste of the silane-XLPE. These results mean that the process using twin screw extruder is useful for recycling silane cross-linked polymer by supercritical alcohol.

Moreover, it is expected that the new continuous process represented here can be useful as other polymer modification process.

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REFERENCES

1.M.Maruyama□*JECTEC NEWS*,**39**,18(2003)

2.T.Goto, T.Yamazaki, I.Okajima, T.Sugeta, T.Miyoshi, S.Hayashi, T.Sako :*Koubunshi Ronbunsyu*,**58**,12(2001)

3.T.Goto, T.Yamazaki, M.Mukaide, Y.Iwamoto, J.Kakizaki, T.Sugeta: The 14th Japan Society of Polymer Processing, **2**, 104, 81(2003)

4. Toshiharu Goto, Shingo Ashihara, Takanori Yamazaki, Idzumi Okajima,Takeshi Sako, Yoshihiko Iwamoto, Masamichi Ishibashi, Tsutomu Sugeta: The 7th International Symposium on Supercritical Fluids,WA4(2005)