DEVELOPMENT OF HIGH-PRESSURE HYDROGEN GAS BARRIER MATERIALS

Mitsuo SHIBUTANI[1], Taiji KANDA[2], Akinobu INAKUMA[3,] Fumimasa MAKI[4]
[1] Central Research Laboratory, The Nippon Synthetic Chemical Industry Co., Ltd, 13-1, Muroyama 2-chome, Ibaraki, Osaka 567-0052, Japan, shibutani.mitsuo@mf.nichigo.co.jp
[2] Central Research Laboratory, The Nippon Synthetic Chemical Industry Co., Ltd, kanda.taiji@mp.nichigo.co.jp
[3] Central Research Laboratory, The Nippon Synthetic Chemical Industry Co., Ltd, inakuma.akinobu@me.nichigo.co.jp
[4] Central Research Laboratory, The Nippon Synthetic Chemical Industry Co., Ltd, maki.fumimasa@ma.nichigo.co.jp

ABSTRACT

We prepared several gas barrier resins based on amorphous PVA derivative that has the T1C (13C spin-lattice relaxation time) of a long time component in amorphous phase. We confirmed it was important to control state in amorphous phase of gas barrier resin in order to achieve both moldability and good gas barrier property. Polymer alloy was designed to improve flexibility. Polymer alloy made of amorphous PVA and elastomer resin showed good hydrogen resistance. Even after its polymer alloy were repeatedly exposed to 70MPa hydrogen gas, the influence on higher-order structure in amorphous phase was in negligible level.

1.1 Introduction

Our theme was adopted in New Energy and Industrial Technology Development Organization (NEDO) through fiscal 2012 from fiscal 2010. In order to safely use the hose and container under high- pressure hydrogen for a long time, we have worked on the elucidation of the basic principles related to hydrogen embrittlement of the material properties. Its research was conducted based on amorphous polyvinyl alcohol resin derivative that has the best barrier property in polymer.

2.1 Preparation of the hydrogen gas barrier resin

We prepared several gas barrier resins based on PVA derivative that has the best barrier property in polymer (Figure1). We prepared amorphous polyvinyl alcohol, which has the T1C (13C spin-lattice relaxation time) of a long time component in amorphous phase. Crystallinity degree is controlled by quantity of T1c relaxation time of a long time component in amorphous phase. As a result, moldability and good gas barrier property of amorphous polyvinyl alcohol was found to be compatible. In addition, we prepared the gas barrier resin by blending a soft component to improve the flexibility.

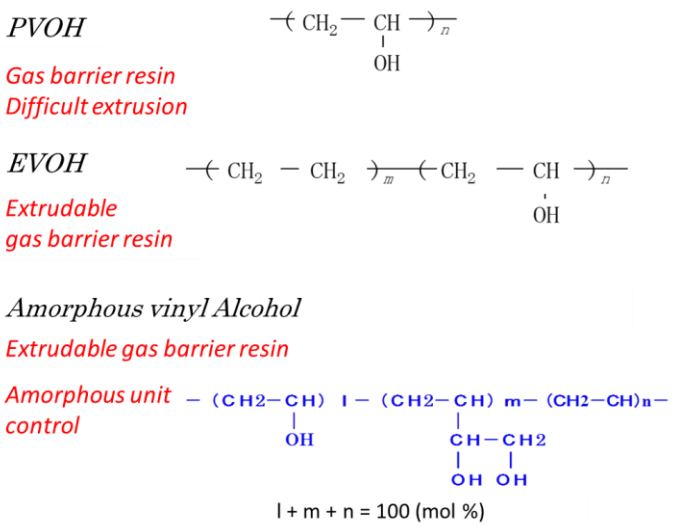
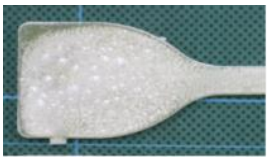


Figure 1. Polymer structural diagram

2.2 Design of polymer alloy with good hydrogen resistance

The polymer alloy which consists of amorphous polyvinyl alcohol and fluorocarbon resin was designed. The hydrogen dissolution amount into fluorocarbon resin is far less than conventional resin by using this resin as soft domain, the polymer alloy that has the upper hand in blister resistance property, hydrogen barrier property and flexibility was designed. Even after the polymer alloy was repeatedly exposed to 70MPa high-pressure hydrogen gas, we did not confirm any mechanical change.

Table 1. Picture of appearance of dumbbell after exposure test under 70MPa hydrogen pressure

	Amorphous PVA derivative	Amorphous PVA derivative / Fluorocarbon	Amorphous PVA derivative / Polyamide 11
Dumbbell 20 times of 70MPa hydrogen exposure			
Apparent condition	No blister	No blister	Blister occurs

The polymer alloy which consists of amorphous PVA derivative / fluorocarbon alloy was able to suppress the change of molecular mobility, it was confirmed by solid-state NMR analysis (Figure 2, Figure 3).

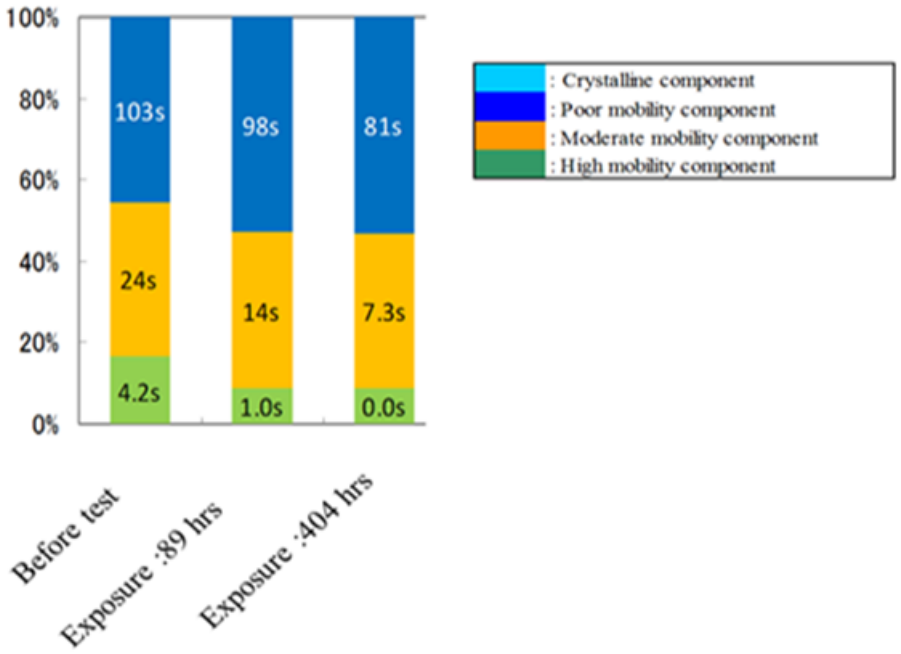


Figure 2. Relationship between duration of 70 MPa hydrogen exposure and higher-order structure in amorphous phase. *Evaluation of molecular mobility by the T_{1c} (13C spin-lattice relaxation time)

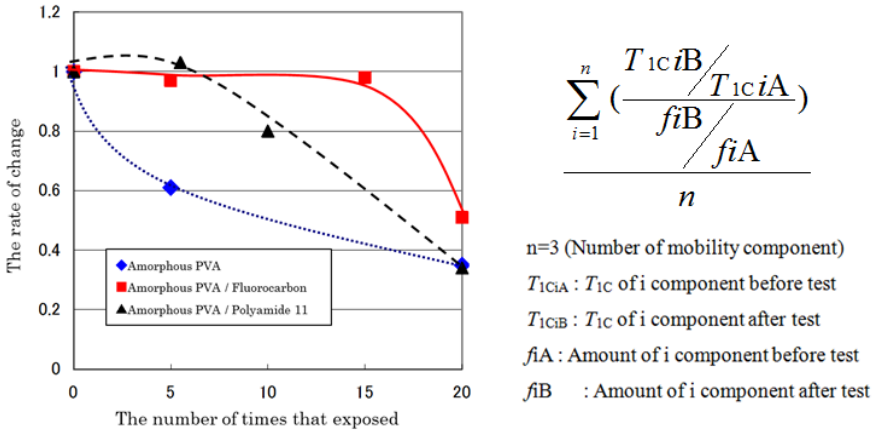


Figure 3. The influence on molecular mobility of polymer alloy after hydrogen exposer test

3.1 Conclusion

We confirmed that Gas barrier resins based on amorphous PVA derivative and its polymer alloy has unique properties in resistant to hydrogen gas under 70MPa high-pressure such as a hydrogen gas barrier and a blister resistance. We have expected that our resin material can contribute to the era of FCV.

Acknowledgments

This study is a summary of the results from the ‘‘Fundamental Research Project on Advanced Hydrogen Science’’ commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

References

1. M.Shibutani., plastics, 2009, Vol. 60, No. 1, p. 56