

코폴리에테르에스테르 고무 탄성체의 물성에 미치는 가교제의 효과

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Effect of cross-linking agents on the properties of copolyetherester elastomer

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1. Introduction

Copolyetheresters are used as an engineering thermoplastic elastomer due to their excellent mechanical properties, thermooxidative stability up to high temperatures and a good resistance against many chemicals. However, fibers made from the copolyetheresters exhibited elastic recovery of about 80-85% after being stretched 200%, while spandex fibers usually showed 90-95% recovery. This is due to permanent deformation of crystalline hard segment phase which acts as a physical interlocking. In order to reduce the permanent deformation, several chemical cross-linking agents are introduced. However, there are many probabilities that the cross-linking agents react with diacid or diol parts which would become hard segment. This means that cross-linking agents will interfere with crystal growth. So it is important that cross-linking agents should be excluded from hardsegment.

In this study, the properties of copolyetheresters having cross-linking agent were observed according to the amount and the type of crosslink agents.

2. Experimental section

The copolymer used was prepared from dimethyl terephthalate(DMT), 1,4-butanediol(BD) and poly(tetramethylene ether)glycol(PTMG) with average molecular weight 2000. All hard segment content was fixed as 35 wt%. The two-stage polymerization was performed on a lab scale polymerization reactor in the melt[1]. 1,2,4,5-benzentetracarboxylic-dianhydride(PyAn) and glycerol were

used as cross-linking agents. The cross-linking agents were added to reactor after finishing ester interchange reaction. The samples codes are given in *Table 1*.

DSC measurement was performed on DSC (TA DSC 2910). The cooling and heating rates were 10 °C/min respectively.

Stress-strain curves were measured by Instron 4467. The testing conditions used for tensile testing were as follows: maximum capacity of load cell 5 kg, cross-head speed 20 mm/min; gauge length 9 mm. The tensile testings were done using dumb-bell specimens at room temperature.

Table 1. Nomenclature of copolyetherester samples having cross-linking agents

sample code	crosslink agent	crosslink agent content(%)*
PA1	1,2,4,5-benzenetetracarboxylic -dianhydride(PyAn)	1
PA2		2
PA3		3
p-PA1**	1,2,4,5-benzenetetracarboxylic -dianhydride(PyAn)	1
p-PA3		3
Gly1	glycerol	1
2000-35	no agent	0

* mol% of DMT

** p-PA : Before PA was added, it had reacted with PTMG.

3. Result and discussion

Figure 1 shows heat of fusion(ΔH_f) and heat of crystallization(ΔH_c) of the copolyetheresters having PyAn. ΔH_f and ΔH_c decrease with increasing the amount of cross-linking agents. It is thought that the cross-linking agents interfere with crystal growth. ΔH_f and ΔH_c of p-PA are less than those of PA. In case of p-PA, it is supposed that the probability that BD reacted with PyAn is relatively low as compared with PA because PyAn already reacted with PTMG.

Figure 2 shows stress-strain curves of the copolymers. Tensile moduli show a tendency to decrease as increasing the contents of cross-linking agents. The tensile modulus of PA is lower than that of p-PA. This can be explained by crystallinity as mentioned above. *Figure 3* shows stress-strain curves of various samples. It is observed that the tensile moduli of samples show dependence on the functionality of cross-linking agents. Strain at breaking decreases with the amount of cross-linking agent. Since the chemical interlocking parts couldn't be deformed like crystalline phase, the sample which has a large amount of cross-linking agent would be broken in the chemical interlocking parts during the stretch.

4. Conclusion

Chemical cross-linking agents which were introduced to reduce the permanent deformation would interfere with crystal growth. The cross-linking agents reduced tensile modulus and strain at breaking. So, the copolyetherster having cross-linking agent should be used within low strain region to avoid breaking.

5. References

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- 2) G. Holden, N. R. Legge, R. P. Quirk, *Thermoplastic Elastomers*, p.194, 1996.
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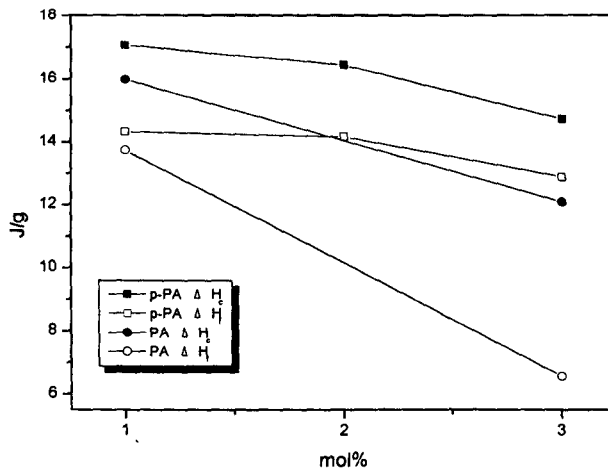


Figure 1. Heat of fusion (ΔH_f) and crystallization (ΔH_c) of sample PA and p-PA

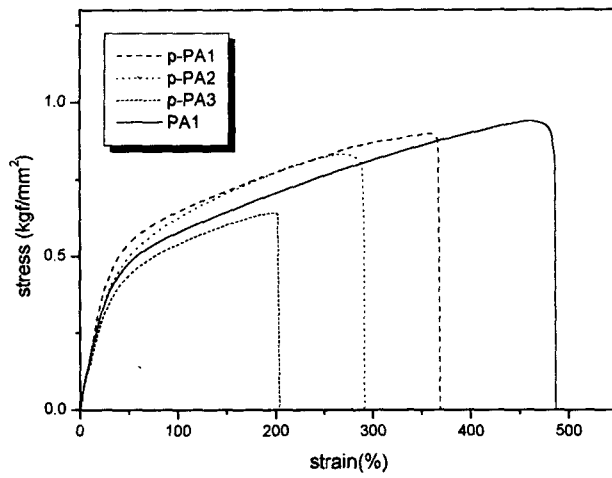


Figure 2. Stress-strain curves of sample P-PA 1, 2, 3 and PA 1

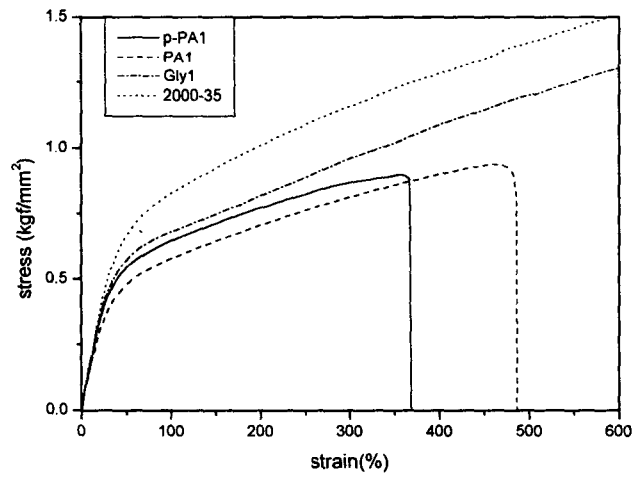


Figure 3. Stress-strain curves of sample p-PA1, PA1, Gly1 and 2000-35