코폴리에테르에스테르 고무 탄성체의 물성에 미치는 가교제의 효과(II)

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Effect of cross-linking agents on the properties of copolyetherester elastomer(II)

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1. Introduction

In the prior work,[1] we introduced several chemical cross-linking agents in order to improve elastic recovery of copolyetheresters, but we are confronted by two difficulties. The first is that cross-linking agents interfere with crystal growth which acts as a physical interlocking. The second is that strain at breaking decreases with the amount of cross-linking agent. It is considered that the chemical interlocking parts couldn't be deformed like crystalline phase.

Low crystallinity of copolyetherester having cross-linking agents can be overcome by anealing. Anealing copolyetherester samples induces increasing crystallinity and microphase separation. These facts are important role in properties of copolyetheresters, for example, elastic recovery, modulus, tenacity, etc.

The purpose here is to investigate these phenomena and the properties of copolythertester while they are stretched or annealed.

2. Experimental

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), glycerol and Pentaerythritol were used as cross-linking agents. The cross-linking agents were added to a reactor after finishing ester interchange reaction. The sample codes are given in *Table 1*.

DSC measurement was performed on DSC (TA DSC 2910). The heating rate was 20 ℃/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. In the cyclic test, 50 mm/min cross-head speed was used.

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

sample code	crosslink agent	crosslink agent content(%)*
PA1	1,2,4,5-benzentetracarboxylic -dianhydride(PyAn)	1
PA2		2
PA3		3
p-PA1**	1,2,4,5-benzentetracarboxylic -dianhydride(PyAn)	1
p-PA2**		2
p-PA3**		3
Gly1	Glycerol	1
Gly2		2
Gly3		3
Penta1	Pentaerythritol	1
Penta2		2
Penta3		3
2000-35	no agent	0

* : mol% of DMT

** : Before PyAn was added, it had reacted with PTMG

3. Results and discussion

Figure 1 shows effect of cross-linking agents on the elastic recovery. Tensile modulus decreases with increasing cross-linking agent contents. It is thought that the cross-linking agents interfere with crystal growth. The recovery of elastomer seems to be affected by initial modulus. The moduli of elastomers having cross-linking agents are in the order ; Gly > Penta > p-PA > PA

In order that the cross-linking agents as chemical interlocking points might play an important role in copolyetherester, sufficient crystal should be created.

Figure 2 shows annealing effect on PA3 and p-PA3 samples. It is clear that overall force to deform samples increases with raising annealing temperature. It means that the higher degree of crystallization is induced as a result of annealing samples. The degree of crystallization was also estimated by DSC, and the same result was obtained. When PA3 is compared with p-PA3, increment of overall force as increasing annealing temperature is higher. Immediately after molding samples PA3 has a smaller amount of crystal, so it has higher potential ability to increase the degree of crystallization.

Figure 3 shows the change in hard segment soft segment phase according to stretching ratio. By performing DSC measurements, it is shown that PTMG crystals were obtained during stretching copolyetheresters and two crystal phases of PBT and PTMG increase while the mechanical stress is applied. It appeared that above a certain strain level crystallization of the soft segments occurs, and this transition is irrevesible.[2]

4. Conclusion

Chemical cross-linking agents which were introduced to reduce the permanent deformation would interfere crystal growth. Copolyetherester having cross-linking agents shows low tensile modulus and crystallinity, but the degree of crystallinity increased after annealing samples.

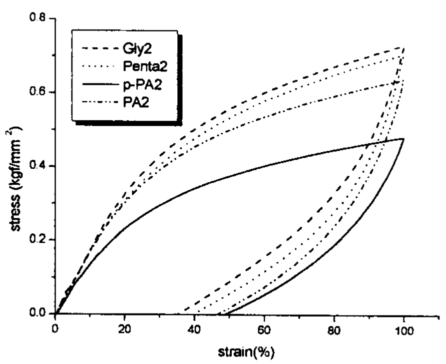
It was observed that not only PTMG phase but also PBT phase increased after stretching copolyetheresters.

5. References

1) D. H. Baik, Y. J. Jang, H. Y. Kim, *Proc. Ann. Meeting Korean Fiber Soc.*, No.2, 355 (2001).

2) W. Gabriälse, M. Soliman, and K. Dijkstra, *Macromolecules*, **34**, 1685 (2001)

3) A. Schmidt, W. S. Veeman, V. M. Litvinov, W. Gabriälse, *Macromolecules*, 5, 1652 (1998)



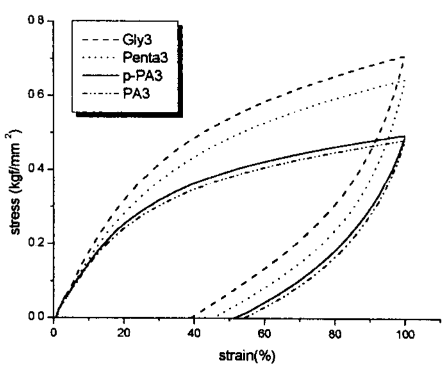


Figure 1. Effect of cross-linking agents on the elastic recovery

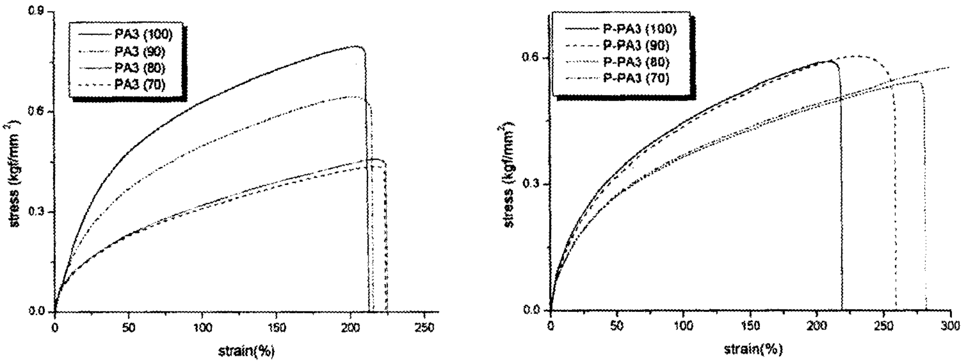


Figure 2. the stress-strain curves of PA3 and p-PA3 samples annealed at various temperature, ( ) ; annealing temperature

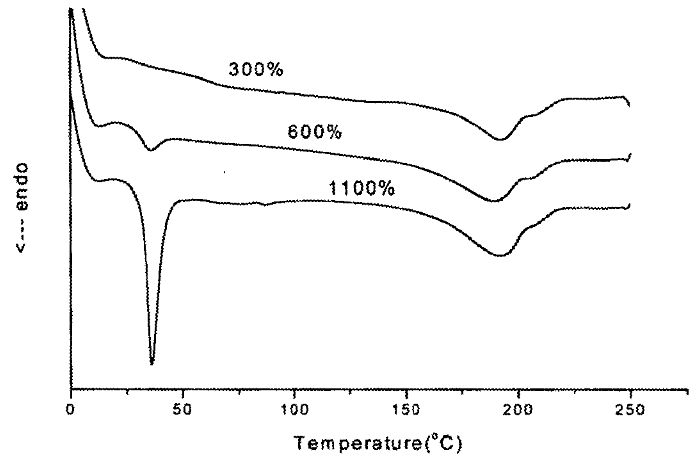


Figure 3. DSC heating scans at 20℃/min of 4GN/PTMGN2900 (35wt% of hard segment) after stretching (stretching ratio ; 300, 600, 1100%)