유기티타늄을 촉매로 한 폴리트리메틸렌테레프탈레이트 합성에 관한 연구

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Synthesis of Poly(trimethylene terephthalate) Using an Organic Titanium Compound as a Catalyst

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1. INTRODUCTION

The synthesis of poly(trimethylene terephthalate) (PTT), whose application is being expanded very rapidly to new apparel and carpet materials, was investigated by melt condensation polymerization using 1,3-propanediol (PDO) and terephthalic acid (TPA). No catalyst was used in the 1st step reaction (esterification), but tetrabutyl titanate(TBT) was used as a polyesterification catalyst ranging from 25 to 75 ppm based on the weight of TPA used in the 2nd step reaction (polyesterification). The molar ratio of PDO to TPA was set as 2.2:1. The effect of reaction conditions on the color and intrinsic viscosity of the final product was investigated.

2. EXPERIMENTAL

2.1. Synthesis of Poly(trimethylene terephthalate)

PDO (1.99 mol) and TPA (0.90 mol) were charged into the autoclave with a 2.2 molar ratio. This reaction mixture was stirred and heated under nitrogen atmosphere (esterification step). During this step the water was collected in a graduated cylinder under pressure in a closed system, until more than 95 % of theoretical amount was obtained. At the beginning of the polycondensation step, the catalyst TBT was added and the reaction was continued under vacuum (ca. lower than 0.5 Torr) in order to remove the by-product PDO. After the polycondensation step was completed, PTT was extruded in iced water. Temperature and pressure profiles in the course of polymerization is seen in Fig.1.

2.2. Measurements

PTT samples were dissolved in a mixture of phenol/tetrachloroethane (50 w/w%) in order to determine the intrinsic viscosity, using a Ubbelohde viscometer at 25°C. L*, a*, and b* values of PTT pellets were measured according to a CIE Lab color system using a spectrophotometer (10° standard observer and D65 illumination source).

3. RESULTS AND DISCUSION

Fig.2 shows the amount of water removed as a function of time during the 1st step reaction based on the self-catalyzed TPA process. As seen in Fig.2, since one hour passed, it has increased with a proportion to time and the water was removed to the extent of about 99 % after 3.1 hour. Intrinsic viscosity was increased a little bit with the catalyst content, whereas the L* value indicating the lightness of the sample was not improved. It needs the addition of a thermal

stabilizer such as trimethyl phosphate or triphenyl phosphate. Considering all factors, the best results can be thought to be obtained at the temperature of 260-265°C. This temperature was also most appropriate to exclude thermal degradation in the course of the polymerization. The highest motor speed showed the highest intrinsic viscosity because of easier and faster extraction of PDO.

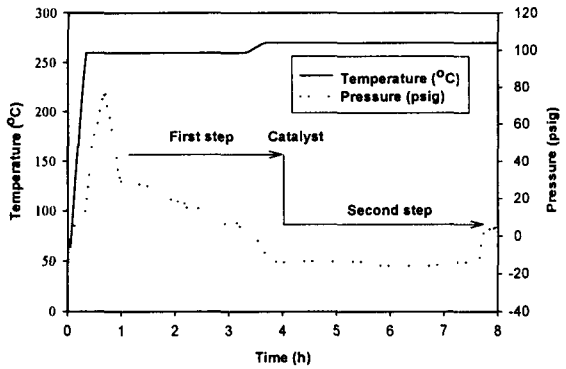

Figure 1. Temperature and pressure profiles in the course of polymerization.

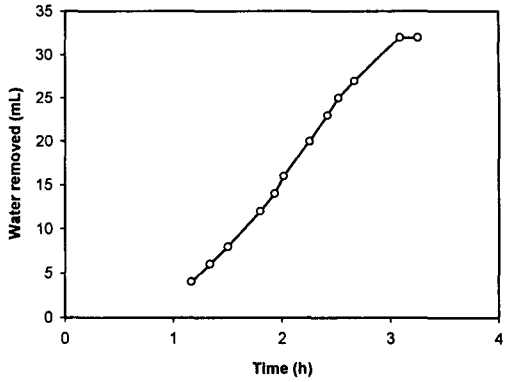

Figure 2. The amount of water removed as a function of time during the 1st step reaction.

Table I. Intrinsic viscosity and color values of the PTT samples obtained under different conditions.

Conc. of TBT (ppm) (250 rpm, 265 °C)	I.V. (dl/g)	L*	a*	b*
25	0.88	73.92	-2.02	6.71
50	0.89	61.20	-1.80	6.40
75	0.91	66.17	-1.20	6.25
Temperature of polyesterification (°C) (TBT 25 ppm, 200 rpm)				
250	0.27	79.56	-0.16	8.69
260-265	0.88	73.92	-2.02	6.71
270	0.78	74.95	-2.26	7.92
Rotation speed of a stirrer (rpm) (TBT 25 ppm, 270 °C)				
200	0.78	74.95	-2.26	7.92
250	0.78	87.98	4.38	-13.20
300	0.85	73.15	-0.93	9.48

4. CONCLUSIONS

PTT was synthesized via a TPA process using different conditions. The catalyst TBT was not used during the first esterification step, but the catalyst was added in the second step. The best polymerization conditions were 260-265°C at 300 rpm. The catalyst content increased the intrinsic viscosity, whereas it made the color quality worse.

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