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Material Properties

Preparation of anionic polymerized polyamide 6 using internal mixer: The effect of styrene maleic anhydride as a macroactivator

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ABSTRACT

The effect of styrene maleic anhydride (SMA) on the anionic polymerization of ε-caprolactam was investigated. Poly-caprolactam (PA6) was prepared at three levels of hexamethylene diisocyanate (HDI) as the microactivator and three levels of SMA in an internal mixer at 200 °C. Then, the polymerization characteristics obtained from the mixing torque curves were compared. With increasing HDI content, reaction time decreased and the reaction rate increased. Final torque, which is attributed to the molecular weight of the synthesized polymer, showed a peak in the average level of HDI. In the presence of SMA, final torque had the same trend, but reaction time increased and reaction rate decreased. Monomer conversion increased by raising both the HDI and SMA contents. In solvent separation by formic acid, samples were found to behave differently. Anionic polymerized polyamides with no SMA formed a uniform and transparent solution, while SMA-containing samples turned into a canescent solution having a colloidal suspension part. The remaining small amount of SMA after solvent separation proved the attribution of SMA in the reaction.

FTIR spectra of samples indicated that SMA acts as a macroactivator in the anionic polymerization of ε-caprolactam. Also, samples containing SMA showed only one glass transition temperature which was higher than that of samples without SMA, suggesting the existence of a copolymer of SMA and PA6, which raises the Tg.

1. Introduction

There are two routes available to manufacture polyamide 6 (PA6) from caprolactam. The first and predominant method is via hydrolytic polymerization, and the second route, anionic polymerization, is used for special products. It is well known that the activated anionic ring opening polymerization of caprolactam takes place in the presence of an alkaline catalyst and can be accelerated using co-catalysts (initiators or activators). In this method, the polymerization kinetic is extremely dependent on the specific initiators (activators) and accelerators (catalysts). Conversion to high molecular mass polymer can be almost instantaneous [1,2].

Use of various catalysts has been reported in the literature: alkali metal salt of 2-pyrrolidone [3], sodium *n*-butoxide, sodium isoamylate, sodium cyclohexylate, sodium isobutoxide [4], caprolactam magnesium halide [5], alkali metal caprolactam [6], caprolactam magnesium bromide [7–11] and sodium lactamates [12]. The most common used catalyst is sodium caprolactamate [13–23], which gains industrial and scientific importance due to its high reactivity.

In addition, some of the activators which have been reported are: ε-caprolactam blocked hexamethylene diisosyanate [6]; diphenyl methan diisosyanate [16]; *N*-acetyl caprolactam [17,7–9,21]; bis-acyllactam hexamethylene diamine [18,19]; isophtaloyl-bis-caprolactam [7–9]; HDI [20,24]; tolulene diisosyanate [20,25]; hexamethylene

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dicarbamyl dicaprolactam [10–12,19]; and cyclohexyl carbamoyl caprolactam [22].

The anionic polymerization can be controlled by changes in the catalyst and activator contents, which would be faster in the presence of higher concentration of reactants. In contrast to the hydrolytic polymerization of PA6 which requires several hours, activated anionic method generally takes place in only a few minutes. Considering the short time required for the activated anionic polymerization, in recent years attempts have been made to use this polymerization technique to prepare compatibilized blends of PA6 with other polymers using a macroactivator, the method being termed in situ polymerization and in situ compatibilization [26–33]. In this way, isocyanate bearing polymers have mostly been utilized as the macroactivator, such as isocyanate bearing PP [26,28–30] and isocyanate bearing PS [33]. The main role of isocyanate groups on the macroactivator is to act as growing centers for the polymerization of caprolactam to form the graft copolymer in the interface (as the compatibilizer). To generate the compatibilized blends of PA6 and styrenic polymers, which are naturally immiscible, styrenic macroactivators can be used.

The work described here deals with the study of activated anionic polymerization of caprolactam in the presence of styrene maleic anhydride (SMA). We have investigated the effects of SMA as a macroactivator on the anionic polymerization of caprolactam which is useful for production of compatibilized blends of PA6/styrenic polymers. Anionic polymerized polyamides have been prepared in an internal mixer, at various concentrations of hexamethylene diisocyanate (microactivator) and SMA, with sodium caprolactamate as the catalyst. The effects of SMA have been evaluated considering mixing torque curve characteristics, monomer conversion, solvent separation and FTIR spectroscopy. Also, glass transition temperatures and melting behavior of samples have been studied as a function of molecular structure of synthesized PA6.

2. Experimental

2.1. Materials

Three main components of the reaction consist of monomer (ε-caprolactam), catalyst (Na- caprolactamate) and microactivator (Hexamethylene diisocyanate, HDI). High pure caprolactam and HDI were purchased from Merck and Fluka, respectively. Sodium caprolactamate was kindly supplied by Pacast AG Co., Switzerland. SMA with M_w of 224,000 and 7 wt% maleic anhydride was obtained from Aldrich.

2.2. Polymerization

Prior to experimental work, all the solid materials were dried for at least 12 h at 40 °C in a vacuum oven. Table 1 gives the concentration of ingredients in each sample. HDI and SMA were taken at levels of 2, 4, 6 phc and 0, 3, 6 phc, respectively. Catalyst concentration was chosen with regard to the activators content, taking the molar equivalent to the HDI and maleic anhydride contents. Before polymerization, a premix of the formulation was prepared to ensure adequate dispersion and uniformity of the compound. Firstly, caprolactam was melted in a heated vessel at a temperature of 70 °C, then catalyst was added and after the caprolactam and Na-caprolactam were well mixed, about 20 s, HDI was added. Addition of SMA to the mixture was done after all other components. Then, the mixture was put in a dry place to solidify. This premix was polymerized in an internal mixer (70 cm^3, Haake, SYS90) at a temperature of 200 °C, with two contra-rotating rotors at a speed of 60 rpm. The variation of the torque in the mixer was monitored as an indication of the polymerization reaction.

Table 1
Formulation of samples.

Sample code	Caprolactam (phc)	HDI (phc)	SMA (phc)	Na-caprolactam (phc)
H20	100	2	0	3
H40	100	4	0	6
H60	100	6	0	8
C23	100	2	3	4
C43	100	4	3	7
C63	100	6	3	9
C26	100	2	6	5
C46	100	4	6	8
C66	100	6	6	10

phc, part per hundred caprolactam.

2.3. Measurements

Residual monomers were extracted in ethanol and then to further purify the samples they were placed in a vacuum oven at 50 °C for a week. To separate the different products of anionic polymerization, 0.3 g of a thin film of each sample was immersed in formic acid for a week.

After removing residual monomers and unreacted SMA, samples were analyzed by FTIR spectroscopy, using an Equinox 55 model from Bruker Corp. (Germany).

Using a PL Differential Scanning Calorimeter (DSC), glass transition temperature, melting and crystallization behavior of samples were determined. 9–10 mg of each sample was heated from 0 to 250 °C, held for 5 min, cooled to room temperature and reheated up to 250 °C at a rate of 10 °C min^{-1}.

3. Results and discussion

3.1. Chemistry of activated anionic polymerization of caprolactam

The reaction mechanism of activated anionic polymerization of caprolactam is presented in Scheme 1. The role of Na-caprolactam and diisocyanate, as the catalyst and activator (microactivator), respectively, is clear in the reactions. This mechanism is the most likely that has been proposed in the literature [1,2] and can be summarised as follows: in a first step, acyl caprolactam is formed as a product of reaction between isocyanate and caprolactam (reaction 1). This then reacts with catalyst to form a new reactive sodium salt (reaction 2), which initiates the polymerization