

REACTIVE POLYMERISATION OF POLYAMIDE 6 IN A TWIN-SCREW EXTRUDER

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RINGKASAN: Proses pempolimeran anionik ϵ -caprolactam dalam mesin pengestrud skrew-kembar dibincangkan berdasarkan kepada struktur poliamid 6 (nylon 6) yang dihasilkan. Hasil daripada penggunaan berbagai jenis teknik pencirian analitik dan mikrostruktur adalah didapati bahawa berat molikul, baki kandungan monomer, dan morfologi hablur poliamid 6 adalah sensitif terhadap keadaan pemprosesan reaktif, rejim lebur-sejuk dan kehadiran bahan additif seperti pengukuh gentian kaca. Implikasi praktik kajian ini juga dipertimbangkan dengan merujuk kepada ciri-ciri mekanikal varian poliamid 6 yang disediakan secara fasa tunggal dan fasa ganda.

ABSTRACT: The anionic polymerisation of ϵ -caprolactam in a co-rotating intermeshing twin-screw extruder is discussed in terms of the structural forms of polyamide 6 (nylon 6) produced. Using a variety of analytical and microstructural characterization techniques, it is demonstrated that molecular weight, residual monomer content and crystalline morphology of the polyamide 6 are sensitive to reactive processing condition, the melt cooling regime and to the presence of additives, such as glass fibre reinforcement. Practical implications of the study is also considered with reference to the mechanical properties of single and multiphase polyamide 6 variants prepared here.

KEYWORDS: Polyamide 6, nylon 6, ϵ -caprolactam, reactive extrusion, polymerisation, twin-screw extruder, glass-reinforced polyamide 6, structural form.

INTRODUCTION

Polyamide 6 (PA 6) can be prepared by activated anionic polymerisation of ϵ caprolactam in the presence of alkaline catalysts, such as alkali carbonates, hydrides or organo-metallic compounds (Joyce and Ritter, 1941). This method of polymerisation enables the synthesis of high molecular weight PA 6 at a rapid reaction rate compared to the prolonged reaction time when an alternative hydrolytic polymerisation process is employed (Kircher, 1987). Continuous anionic polymerisation of ϵ caprolactam may be undertaken in a twin-screw extruder through appropriate control of the process parameters - the screw geometry and necessary functional characteristics of the machinery, such as the natures of feeding, melting, mixing, reacting and devolatilization zones (Menges and Bartilla, 1987). Procedures with claimed economic and technical benefits have been reported for combined polymerisation of ϵ -caprolactam in a twin-screw extruder together with die forming of the resulting PA 6 into a semi-finished product (Berghaus and Michaeli, 1990). Polymerisation of ϵ -caprolactam in the presence of glass fibre reinforcement has also been considered previously using both the reactive injection moulding and twin-screw extrusion melt impregnation technologies (Bartilla *et al.*, 1986), with the aim of enhancing fibre-wet-out by the PA 6 and interfacial adhesion.

Very limited attention has been given, however, to the influence of polymerisation conditions, or the presence of fibre reinforcement on the molecular mass, residual monomer content and crystalline morphology of the PA 6. These factors have a critical bearing on the physical property of PA 6.

This paper will address these issues through detailed characterization of PA 6, made using different processing conditions on a co-rotating intermeshing twin-screw extruder.

EXPERIMENTAL

Polymerisation of ϵ -Caprolactam

Samples of PA 6 were prepared on a 40 mm screw diameter co-rotating twin-screw extruder (BTS 40-Betol Machinery) by anionic polymerisation of ϵ caprolactam monomer (DSM Chemicals Ltd) containing 3% by weight of sodium caprolactamate catalyst and 2% by weight of an accelerator (V-5 DSM Chemicals and Fertilizers). The extruder configuration and barrel temperature profiles (Figure 1) were chosen to accommodate the changing characteristics of the material from melting the ϵ -caprolactam feedstock, monomer polymerisation in the reaction zone and melt conveying of the PA 6 reaction

product. Screw speeds were varied between 50 and 150 rpm, thereby altering material residence time within the barrel, whilst maintaining constant conditions of both material feed rate to the extruder and barrel temperature profile. PA 6 extrudate, die formed as a 4 mm diameter rod, was either water-quenched or allowed to cool slowly to room temperature.

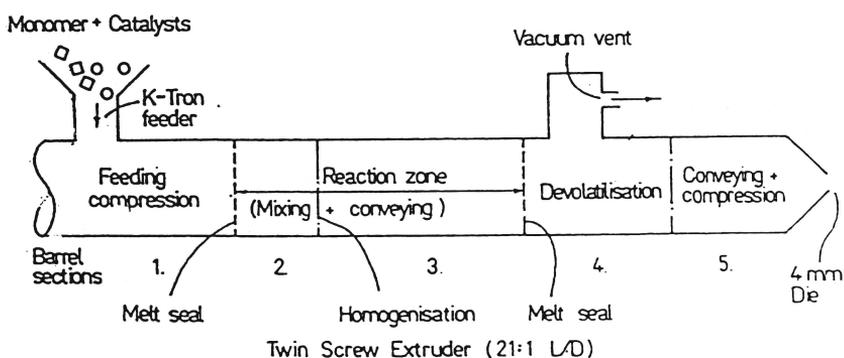


Figure 1. Schematic diagram of twin-screw extruder (21:1 L/D) for polymerisation of PA 6

Some samples of PA 6 containing short glass fibre reinforcement were made by combining 10% by weight of sized, chopped glass strand (with 6 mm nominal fibre length) into the monomer/catalyst/accelerator system as a premix. The pelletized samples were subsequently extracted with boiling distilled water overnight to remove residue monomer before drying in vacuo at 90°C for 6 h. The dried samples were then stored in dessicators maintained in an atmosphere of 50% humidity prior to determining its properties.

Structural Characterization

Representative samples of PA 6 with different processing history were analysed on a Perkin-Elmer DSC (differential scanning calorimeter)-2B, by thermal cycling under specified conditions of heating and cooling to assess melting and crystallization phenomena. During the first heating cycle (Stage I), between 6 and 8 mg of sample was heated from 40°C to 250°C at a rate of 10°C min⁻¹, to monitor the melting behaviour. The sample was then maintained at 250°C for 15 min before cooling to 40°C at a rate of 5°C min⁻¹ to determine the onset of crystallization. A second melting thermogram was then obtained (Stage II), using the same conditions as the first run. Some samples were annealed at temperatures up to 180°C for 90 min, prior to analysis on DSC.

Wide angle X-ray diffraction (WAXD) profiles were also obtained on a Philips PW1050 Goniometer to further elucidate the influence of processing, compositional and annealing variables on the crystalline order produced.

Determination of Mechanical Properties

Tensile and impact test specimens were prepared by the injection moulding technique in accordance to ISO 1887. For comparison purposes, samples from a commercial PA 6 resin (CAPRON 8202C - Allied Signal Inc.) were also prepared. Tensile testing was performed on a Lloyd L1000S tensometer at a strain rate of 50 mm min⁻¹ in accordance to ASTM D638 procedures. Izod impact testing was conducted on a notched specimen at 25°C in accordance to ASTM D256 procedures.

Determination of Molecular Weight and Residual Monomer Residue Content

Molecular weight and molecular weight distribution were determined using gel permeation chromatography. The ϵ -caprolactam monomer residue content of the as-processed samples prepared from different processing conditions were evaluated using a modified gas chromatography technique (Tung, J.F., 1993).

RESULTS AND DISCUSSION

DSC Analysis

Peak melting and crystallization temperatures are listed in Table 1. These values are representatives of transition temperatures for the different PA 6 samples prepared using extruder speeds of 50, 70, 90, 120 and 150 rpm where little variation in transition temperatures were seen as a function of screw speed. It was observed that all the samples yielded consistent stage II peak melting temperatures of between 213°C and 215°C, which is comparable to the commercial grade PA 6 resins prepared by the hydrolytic polymerisation process (Allied Signal Technologies-Trade literature, 1992). However, a noticeable increase in maximum crystallization temperature (T_c) was recorded for the short glass fibre reinforced samples as compared to the unfilled PA 6. This observation suggests that the glass fibre nucleates PA 6 during melt crystallization. Differences in endothermic melting temperatures obtained between stage I and stage II heatings were also recorded for the reinforced samples.

Table 1. Peak melting and crystallization temperatures of PA 6

Sample type	Peak melting temperature (°C)		Peak crystallization temperature (°C)
	Stage I	Stage II	
Water-quenched	214.2	213.5	180.1
Water-quenched annealed	214.9	213.0	179.5
Air-cooled	216.2	215.0	181.2
Air-cooled annealed	216.1	214.5	181.0
Water-quenched glass	218.0	214.1	183.0
Water-quenched glass annealed	217.6	213.0	183.7

Figure 2 shows DSC thermograms of the samples obtained from stage I and stage II heating cycles. During stage I, both the water-quenched and glass-reinforced samples exhibited broader melting peaks [2 (a) and (e)], which can be attributed to the melting of the smaller, less perfectly organized crystals at lower temperatures. After annealing these samples at 180°C for 90 min followed by slow cooling to room temperature, a narrower melting peak with only a slight shoulder at the lower temperature slope was obtained [2(b) and (f)]. The shoulder is more pronounced however, for the annealed, reinforced samples [2(f)]. Similar but more obvious shoulder peaks were also observed for the air-cooled samples [2(c) and (d)]. These lower temperature melting peaks are tentatively attributed to the melting of the γ crystalline phase of PA 6. During stage II heating, all samples regardless of previous thermal history showed rather similar DSC thermograms, with bimodal melting peaks possibly due to melting of α and γ crystalline phases of PA 6 resulting from slow cooling and subsequent reheating of the samples during the second DSC scan. The heats of fusion and crystallization for all the PA 6 samples including the commercial grade were observed to be about 60-65 J g⁻¹ which is equivalent to about 31-34% crystallinity.

WAXD Analysis

WAXD reflection profiles of water-quenched PA 6 samples are shown in Figure 3 (a). Two sharp peaks are observed, characteristic of α crystalline phases with interplanar spacings of $d_{200} = 4.44 \text{ \AA}$ and $d_{002} = 3.82 \text{ \AA}$, corresponding to Bragg angles (2θ) of $\sim 20^\circ$ and 23° respectively. All air-cooled samples except for that extruded at 150 rpm showed similar WAXD pattern to the water-quenched materials. The WAXD profile

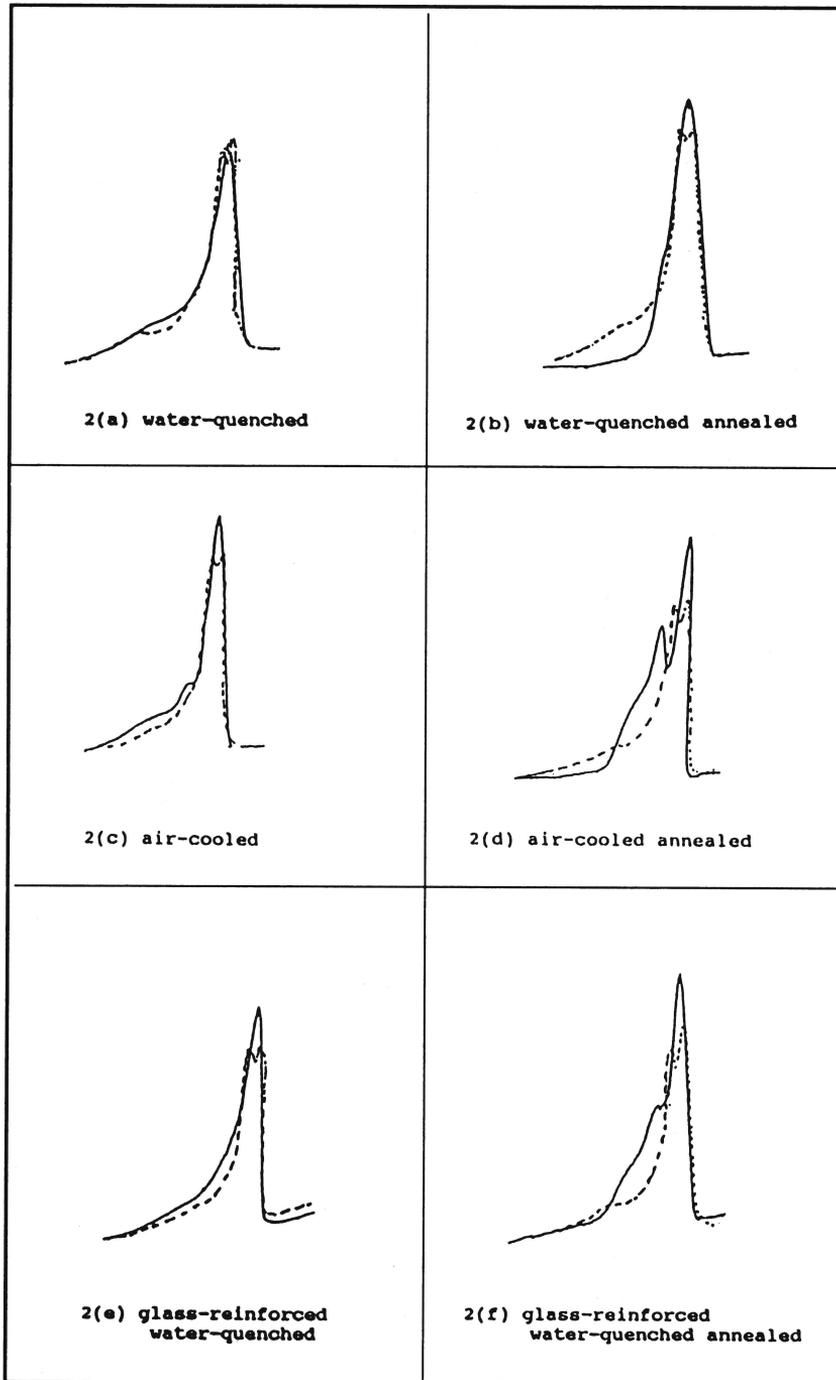


Figure 2. DSC thermograms of PA 6

———— Stage I heating
----- Stage II heating

of the sample made at 150 rpm has an additional reflection peak at Bragg angle (2θ) of 21° , which is characteristic of a PA 6 γ peak [Figure 3(c)]. However, all the water-quenched and air-cooled samples upon annealing yielded only two peaks on the WAXD profiles indicating the presence of only the α crystalline phase [Figures 3(b) and (d)]. The disappearance of the γ peak for the 150 rpm air-cooled sample upon annealing agrees well with the finding of Kyotani (1975), who stated that γ crystalline phase of PA 6 is unstable at temperatures above 160°C and could possibly transform into either the amorphous or the more stable α form.

The WAXD profiles for glass fibre reinforced samples prepared at various extruder screw speeds are as shown in Figures 3(e) and (f). In addition to the two sharp α peak reflections, another reflection peak with lower intensity was observed at a Bragg angle (2θ) of 21° , corresponding to a crystal inter-planar spacing of $d_{100}=4.24\text{\AA}$ which is again consistent with the presence of γ crystalline form of PA 6 [Figure 3(e)]. This observation supports the view that the presence of glass fibre during polymerisation of ϵ -caprolactam nucleates the polymer, leading to the formation of an additional γ phase in PA 6. This finding is in agreement with the DSC analysis discussed earlier. Furthermore, it was observed that on annealing the PA 6 composite sample at 180°C for 90 min, both the α and γ peaks remained but with increased intensity [Figure 3(f)]. This finding is in contrast with the WAXD profile for the sample extruded at 150 rpm which also had an additional γ peak but disappeared on annealing as mentioned earlier [Figures 3(c) and (d)].

Determination of Mechanical Properties

Figure 4 compares the mechanical properties of PA 6 samples produced at different extruder screw speeds and that of a commercial polymer. The unreinforced sample, obtained at 90 rpm, has the highest tensile strength, but is still about 30% lower than the commercial sample [Figure 4(a)]. Incorporation of 10% by weight of short glass fibre has the effect of raising the tensile strength to a level comparable to that of the commercial material. By contrast, all the unreinforced samples recorded much higher elongation at break than either the short fibre reinforced variant or commercial grade [Figure 4(b)]. An improvement in toughness was also evident from the Izod impact resistance values depicted in Figure 4(c). PA 6 samples prepared at screw speeds of 150 rpm yielded the highest impact properties, about 30% greater than that of the commercial resin.

Molecular Weight and Residual Monomer Content

The molecular weight (MW) and molecular weight distribution (MWD) (expressed as a polydispersity index) of the samples prepared at different extruder screw speeds

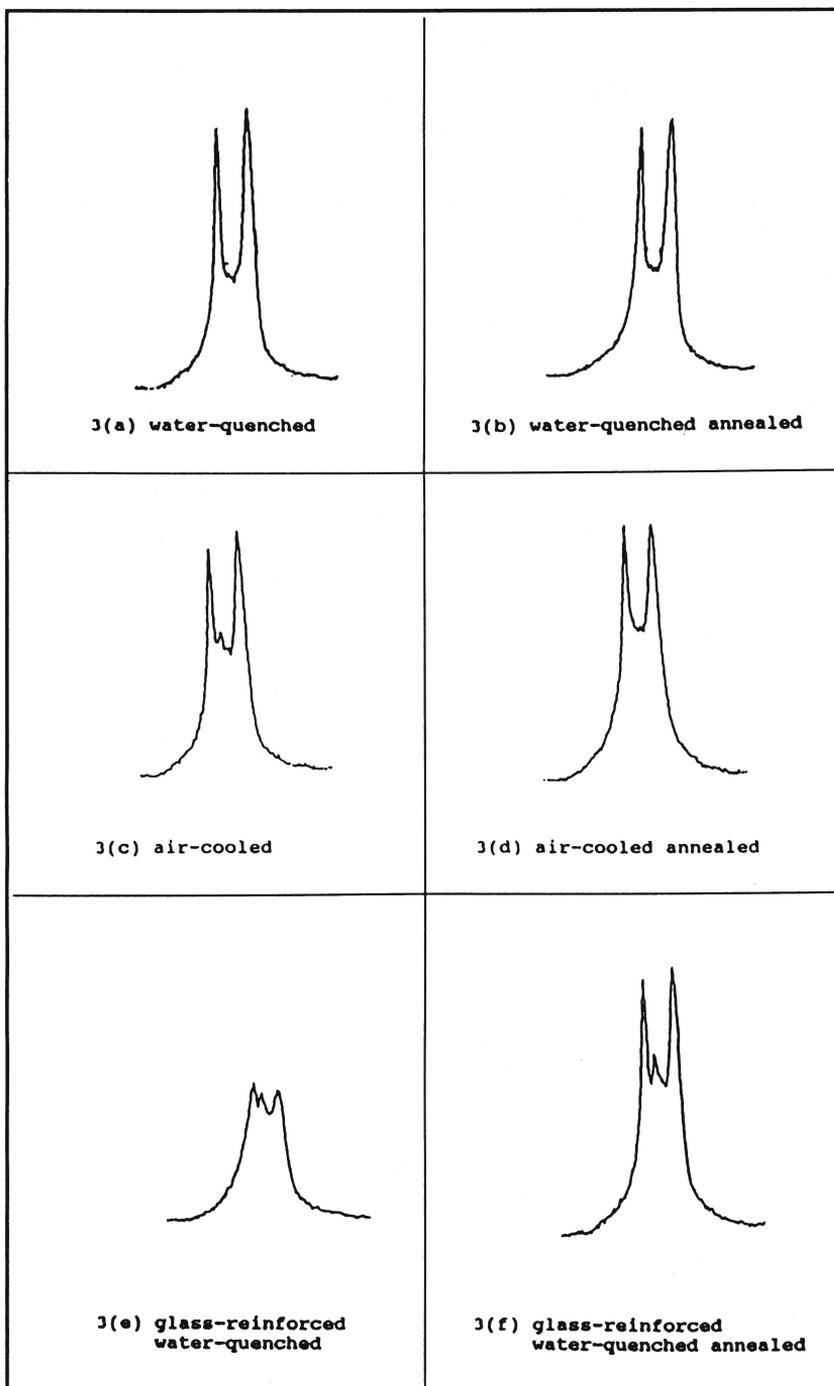


Figure 3. WAXD profiles of PA 6

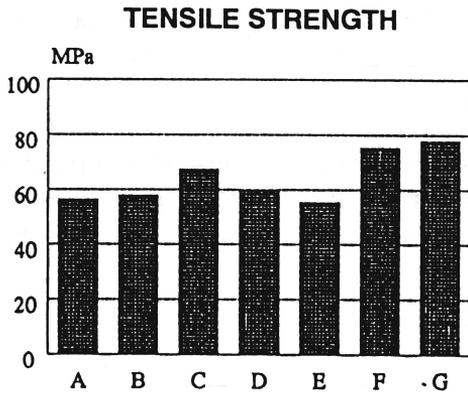


Figure 4 (a)

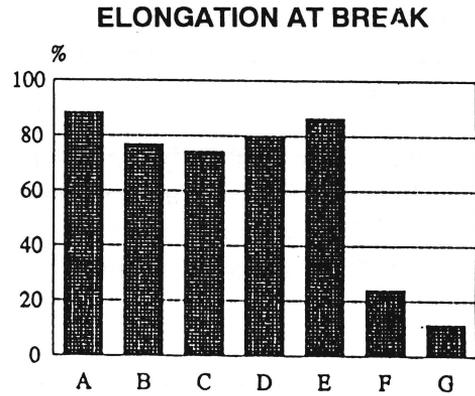


Figure 4 (b)

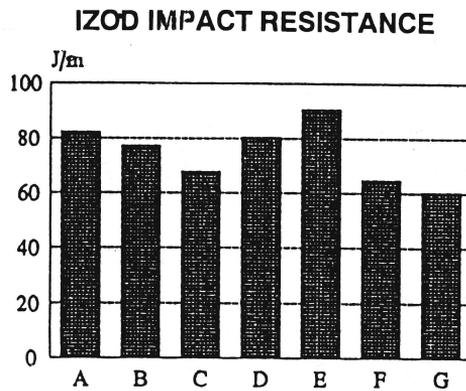


Figure 4 (c)

Figure 4(a) - (c). Comparing the mechanical properties of PA 6 produced at different extruder screw speeds and a commercial PA 6
 A-E : PA 6 made at 50, 70, 90, 120 and 150 rpm
 F : 10% glass-filled PA 6 made at 90 rpm
 G : Commercial grade PA 6

were measured (Figures 5 and 6). Samples prepared at screw speeds of 70 and 90 rpm exhibited the highest molecular weights in the region of 100 kg mol^{-1} and a high MWD of about 6. Samples obtained at other speeds yielded a MW of 54 to 62 kg mol^{-1} which is about 80% higher than those obtained from commercial PA 6 materials.

Figure 7 shows that the unreinforced PA 6 samples prepared at lowest and highest extruder speeds possess the highest monomer residue contents (6%). It is however, interesting that much lower monomer residue contents (3%) are associated with the glass fibre reinforced samples.

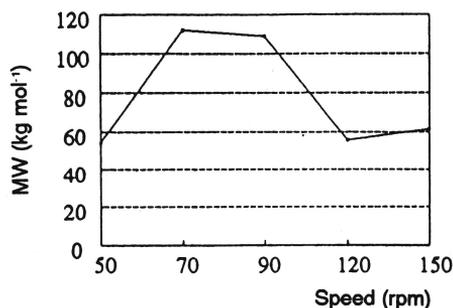


Figure 5. MW of samples prepared at different extruder screw speeds

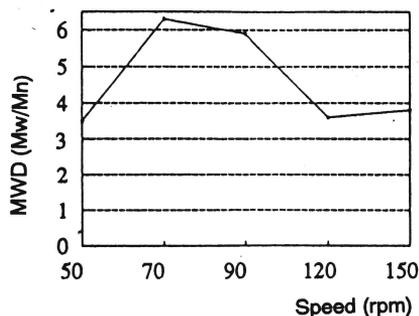


Figure 6. MWD (Polydispersity Index) of samples prepared at different extruder screw speed

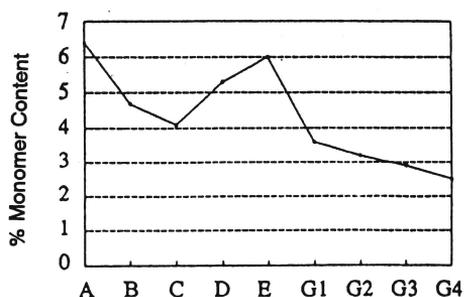


Figure 7. Residue Monomer Content of PA 6 and glass-reinforced PA 6 made at different extruder screw speeds

A - E : PA 6 made at extruder speeds of 50, 70, 90, 120, and 150 rpm respectively

G1 - G4 : Glass-reinforced PA 6 made at extruder speeds of 70, 90, 120 and 150 rpm respectively

CONCLUSIONS

PA 6 materials prepared by reactive polymerisation of ϵ -caprolactam, using various extruder screw speeds yielded different MW, MWD and residual monomer contents. The molecular weights obtained are generally much higher than commercial PA 6 materials formed by hydrolytic polymerisation. Reactive polymerised PA 6 materials also exhibit superior impact and elongation properties but have lower tensile strength. DSC and WAXD results indicate possible formation of a meta-stable γ crystalline phase structure obtained at a screw speed of 150 rpm and slow melt cooling conditions, in addition to the α crystalline forms. It is suggested that this thermally unstable γ crystalline state transforms into the more stable α phase upon annealing at a temperature of 180°C. On the other hand, incorporating short glass fibres into the monomer during polymerisation can also induce the formation of the γ phase in addition to the α crystalline forms. This γ phase is however, observed to be very stable and apparently not affected by subsequent annealing conditions. The glass fibres present in the PA 6 samples may act as possible nucleating agents during melt crystallisation, as evident from an increase in crystallisation temperature of the cooling PA 6 melt.

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REFERENCES

- Allied Signal Technologies-Trade literature (1992) Form No. (L-200-785).
- Bartilla, T., Kirch, D., Nordmeier, J., Promper, E., and Strauch, Th. (1986). Physical and chemical changes during the extrusion process. *Advances in Polym. Techn.*, **6** (3), 339-387.
- Berghaus, U. and Michaeli, W. (1990). Reactive extrusion of nylon 6-Aspects of industrial use. *ANTEC 1990*, 1929-33.
- ISO 1874-2 (1987). Preparation of PA test specimens and determination of properties.
- Joyce, R.M. and Ritter, D.M. (1941). U.S. Patent 2,251,519.

- Kircher, K. (1987). *Chemical reactions in plastic processing*. Hanser Publications, Munich, p 101-103.
- Kyotani, M. (1975). Studies on crystalline forms of nylon 6. *J. Macromol. Sci-Phys.*, **B11 (4)**, 509-525.
- Menges, G. and Bartilla, G. (1987). Polymerisation of ϵ -caprolactam in an extruder: process analysis and aspects of industrial applications. *Polym. Eng. & Sci.* **27**, 1216–1220.
- Tung, J.F. (1993). *Characterisation of polyamide 6 and blends synthesised by reactive extrusion*. Ph D Thesis, Brunel University, U.K. pp 54-56.