IN-SITU PREPARATION OF POLYAMIDE-6/POLYPROPYLENE GLYCOL COPOLYMERS WITH MINERAL FILLERS
Petko Krastev, Roza Mateva

University of Chemical Technology and Metallurgy
8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: p_krustev_eng@yahoo.co.uk

ABSTRACT

Polyamide-6/Polypropylene glycol (PPG) copolymers were synthesized via anionic polymerization of ε-caprolactam in the presence of inorganic additives - graphite and boron carbide using isophorone diisocyanate end functionalized PPG prepared in-situ as a macroactivator. Sodium caprolactam was used as an initiator. The influence of the graphite and boron carbide fillers on the degree of conversion was investigated. The copolymers obtained were characterized by $^1$H NMR and FTIR spectroscopies. The charpy impact strength of the composites was evaluated.

Keywords: polyamide-6, copolymers, graphite, boron carbide.

INTRODUCTION

The focus on the sustainable development of industry led in the recent years to the necessity of new materials able to meet the most stringent specifications for mechanical, thermal, electrical properties but reducing the environmental footprint. In many cases engineering plastics, the most common one still being Polyamide-6 (PA-6) and Polyamide 6,6 (PA-6,6) are able to match these requirements due to their high tensile strength, stiffness, high melting point, relatively good impact/chemical resistance and lower weight compared to that of metals. As different applications of these materials have different specifications, the need of modifying their properties for certain end-use is critical. This area of polymer modification is explored extensively and a broad range of commercial modifiers is presented on the market. Modifiers based on rubbers, acrylics, silicones, polyurethanes are developed to improve the impact strength of PA-6. Mineral fillers like glass fibers, carbon nanotubes [1], but also aramid types of polymers are incorporated into the polymer matrix in the course of the final stages of the injection molding process aiming at better tensile strength, temperature properties and dimensional stability. Lubricants like metal stearates or high molecular silicones are usually applied to obtain better processing-melt flow and mold release. Another aspect of properties modification refers to the development of copolymers or polymer blends, the most popular ones being PA-6 and PA-6,6 copolymer, PA-6,6/Polyphenylene oxide, PA-6 blends with polyolefins, etc. Thus the use of PA-6 in many fields like the production of automotive-under the hood appliances, etc., requiring materials able to withstand high temperatures for extended periods of time, has greatly increased. On the other hand, the continuous increase of the energy costs and the raw materials prices, the concept of light weighting (metal replacement) across the industry as well as the usage of renewable material sources drive the interest towards creating new approaches to polymer materials. One of them, the so called reaction injection molding (RIM) was developed by Monsanto in 1970s and further commercialized by DSM [2]. This process allows producing the final plastic part from ε-caprolactam (ε-CL), polyether prepolymer and in initiator by one-step process. This concept, applicable to PA-6 in particular,
allows significant energy savings. It provides also modification of the properties of the PA-6 aiming to meet certain requirements. This is achieved by introduction to the polymer chain of elastomeric segments such as polybutadiene, styrene-butadiene, polyols, etc. [3, 4]. It is worth adding that the application of the RIM concept to PA-6 copolymerization envisages the formulation of a 3-component system (ε-CL, prepolymer, filler) as PA-6 is usually modified with the introduction of mineral fillers [5, 6]. The behavior of these composite structures has to be investigated as they affect the polymerization process, while their properties depend in turn on the concentrations of the prepolymer and the filler. The present paper reports data on the copolymerization of PA-6 with polypropylene glycol (PPG) in the presence of two mineral fillers- graphite and boron carbide (B₄C) in view of their possible participation in the RIM process.

EXPERIMENTAL

Materials
The monomer ε-CL (BASF), Mᵥ=113.16 was dried for 3 days over P₂O₅ in a vacuum oven at 60°C. The initiator, sodium salt of ε-CL (Na-CL), was synthesized following the procedure described in ref. [7], Mᵥ=424. Isophorone diisocyanate (5-isocyanate-1-isocyanatomethyl-1,3,3-trimethylcyclohexane) (IF; Merck), methanol (Fluka), toluene (Fluka) were used as received. PPG (Fluka) (average molecular mass of 2000) was kept in a molecular sieve for 10 h at 25°C under vacuum. Graphite of particle size (PS) of 20 µm and B₄C (Fluka) of PS of 15-62 µm were heated at 150°C for 2 min prior to use.

Synthesis
Functionalization of PPG with isophorone diisocyanate
The PPG (1 mol dissolved in 5 ml toluene) was placed into a 250 ml flask equipped with a separating funnel, a reflux condenser, a thermometer, a stirrer and N₂ inlet. Isophorone diisocyanate (2.2 mol) was added dropwise through the separating funnel at vigorous stirring. The reaction was carried out at 50°C for 4 h. FTIR spectra showed that the NCO group absorption band reached a constant value at υ=2269.9 cm⁻¹ on the 4-th hour in correspondence with previous studies [8].

Synthesis of PA-6/PPG polymers with graphite and B₄C
The polymerization was carried out in the bulk at 180°C with the application of:

a) the ampule technique. Functionalized PPG with IF, the monomer ε-CL, additives (Graphite or B₄C) and ampules were placed into a glass flask under nitrogen atmosphere and melted for 20 min at 120°C by vigorous stirring (Macroactivator preparation in-situ). After mixture homogenization, the temperature was increased to 140°C, then the initiator (Na-CL) was added at vigorous stirring and the melt was forced into ampules by N₂.

b) the mold casting. The melt was prepared following the procedure described in (a). It was then transferred to an aluminum mold pre-heated at 180°C.

Block copolymers of different ratios of PPG:IF, graphite and B₄C were prepared. The initiator concentration was equal to 1 mol % in reference to the monomer quantity.

Analyses
Degree of conversion
The polymers obtained were placed into a Soxhlet apparatus, while the non-reacted monomers were extracted with methanol for 8 h. The residue formed was dried in vacuum at 60°C until constant weight was reached. The degree of conversion was determined gravimetrically as a ratio of the weights of the polymers prior to and after the extraction. The additives B₄C and graphite were not removed from the compound in calculating the values as they being insoluble in methanol would not affect the values of the degree of conversion.

¹H NMR
The ¹H NMR spectra were recorded on a Bruker AM400 apparatus operating at 400 MHz. The ¹H NMR analysis of the purified copolymers was performed in a mixture of HCOOH:CDCl₃ (1:1 v/v) using formic acid as an internal standard.

FTIR
The IR spectra of copolymers free from additives and monomers were recorded in the range of 4000 cm⁻¹ - 450 cm⁻¹ using a Perkin Elmer 1600 (FTIR) spectrophotometer with KBr pellets.

Charpy Impact Strength
The impact resistance was measured at room temperature by Charpy pendulum on 50 mm x 4 mm x 6 mm specimens with average notch depth of 0.5 mm.
The distance between the supports was 40 mm, while the pendulum velocity of impact was 2.9 ms\(^{-1}\).

**RESULTS AND DISCUSSION**

It is known that ε-CL polymerization is relatively slow and proceeds with a significant induction period. This problem can be overcome by using macroactivators [9]. Thus the induction period is eliminated and the polymerization occurs within several minutes leading to polymer-monomer equilibrium. Isophorone functionalized PPG was used as a macroactivator aiming the formation of PA-6/PPG/Graphite and PA-6/PPG/B\(_4\)C copolymers. The polymerization mechanism is shown in Fig. 1.

The PPG macroactivator was synthesized in two steps. The first one referred to the functionalization of PPG using isophorone diisocyanate. It was followed by in-situ synthesis of the corresponding N-carbamoilactam proceeded.

Several polymerizations of ε-CL varying the PPG-IF and graphite or B\(_4\)C content were carried out. The ratio of the components in the polymerization system was varied in order to investigate the influence of the fillers and the macroactivator on the degree of conversion. The low molecular weight activator acetyl caprolactam (Ac-CL) was used as a reference. As the copolymerization process proceeds with high polymerization rate and degree of conversion, it is attractive to obtain different composite materials of various properties.

The changes in the degree of conversion of PA-6/PPG-IF/graphite copolymers as a function of the PPG-IF and graphite content are shown in Figs. 2 - 4. It is seen that the degree of conversion is very high in most of the cases considered. A lower degree of conversion is obtained for PA-6/PPG-IF/graphite. Its PPG-IF content was the highest.

Similar results were observed for the copolymerization systems based on PA-6/PPG-IF, where B\(_4\)C was used as filler. The influence of B\(_4\)C concentration on the degree of conversion is almost negligible. In fact the macroactivator content is the main factor (Fig. 5).

The PA-6/PPG-IF/graphite as well as the PA-6/PPG-IF/B\(_4\)C copolymers obtained upon extraction of low
molecular weight products and fillers are investigated by $^1$H NMR and FTIR.

The FTIR spectra (Figs. 6 and 7) show the characteristic bands of PA-6. The absorption at 3299 cm$^{-1}$ refers to N-H Amide I, Amide II, that at 3072 cm$^{-1}$ is determined by the vibrations of N-H bond of Amid II, while those at 1637 cm$^{-1}$ and 1542 cm$^{-1}$ correspond to -C=O in Amide I and N-H + C-N in Amide II, correspondingly. The absorption at 688 cm$^{-1}$ is typical for PA-6. The absorption of the C-O-C stretching vibration at 1119 cm$^{-1}$ is due to the incorporated PPG.

The synthesized copolymers are investigated by $^1$H NMR as well. The results obtained are illustrated in Fig. 8. Peaks at 1.69 ppm, 1.60 ppm (d), 1.39 ppm (s) (-CH$_2$), 2.39 ppm (m) (-CH$_2$-CO-), 3.32 (s) (-CH$_2$-NH-) are outlined.

They are typical for PA-6. The peaks recorded at 1.24 ppm (s) (-CH$_3$) - 3.65 ppm (s), (-CH$_2$-O), 3.78 ppm (s), (-CH(CH$_3$)-) refer to the PPG block.

All results pointed above provide to conclude that copolymers of PA-6 and PPG are synthesized.

**Charpy Impact Strength**

One of the main disadvantages of PA-6 refers to its effect on the impact strength observed. It is expected that the copolymers obtained will show better mechanical properties. That is why the influence of graphite and B$_4$C additives on the impact strength of the newly prepared copolymers is followed. The results show significantly improved impact strength of the copolymers obtained when compared to that of pure PA-6/PPG ones (Figs. 9, 10). The effect is outlined.
up to 5% presence of fillers. No performance change is observed on further increase of the latter. Therefore it can be concluded that the optimal filler concentration is 5 mass% in case 3% PPG is used as a macroactivator.

CONCLUSIONS

Novel composite materials based on activated anionic polymerization of ε-CL and PPG-IF macroactivator are successfully obtained in the presence of mineral fillers - graphite and B₄C. The formation of PA-6/PPG copolymers is verified by FTIR and ¹H NMR analysis. It is found that the mineral filler incorporation results in significant improvement of the impact strength.

In case of high concentrations of the macroactivator (10%), the increase of the graphite content leads to increase of the polymerization rate and yield. This provides to consider it as an active additive, unlike B₄C which is practically inert. On the other hand, at certain levels of loading (3–5%), both fillers contribute to the improvement of the composites impact strength.

REFERENCES

1. D. Yan, G. Yang, Synthesis and properties of homogeneously dispersed polyamide 6/MWNTs nanocom-

Fig. 8. ¹H NMR spectrum of PA-6/PPG copolymer.

Fig. 9. Charpy impact strength of PA-6/PPG/Graphite copolymers.

Fig. 10. Charpy impact strength of PA-6/PPG/B₄C copolymers.


