

A reactive rotational molding process of PP/PA6 bilayer systems: experimental investigations

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ABSTRACT: Rotational molding has been regarded as a plastic molding method with great potential. The process offers virtually stress-free products without weld lines or material wastage, and utilizes relatively inexpensive molds. Yet, its growth is hindered due to long production cycle times, which are limited by the time, required to heat and cool the mold and the product. This study concerns the fabrication of multilayer PP/PA6 parts with a reactive rotational molding process. In the past, various investigations have already been focused on rotational molding or the reactive process of monolayer parts. The aim of this work is thus to reduce the cycle time by making a layer via anionic polymerization of caprolactam, and then to compare each process. This presentation is divided into two parts: the first part deals with rheological, dielectrical and thermal analysis for investigating the effect of mixtures and the crystallization/polymerization; the second part deals with the processing of bilayer parts. First, several mixtures of catalysts and activators (i.e., 2-2 (2% of activator and 2% of catalyst), 3-3, 4-4 and 6-6) were investigated by rheology and thermal analysis in order to determine which mixture would be the most appropriate for the rotational molding process. In the second step, different processing investigations were carried out in order to study the influences of parameters such as oven time or cooling time. An experimental analysis of heat transfer in a reactive rotational molding process was also led. By using an instrumented mold, associated with a radio transmission data acquisition system, it could be demonstrated that the rotational parts of the PP/PA6 bilayer (reactive route) could be obtained with optimized conditions in correlation with the results of rheology and dielectric measurements. Moreover, the results indicated that it was possible to fabricate reactive bilayer parts with the rotational molding process with less energy and in a smaller amount time.

Key words: Rotational molding, reactive process, in situ polymerization, multilayer, PA6

1 INTRODUCTION

Rotational molding is a shear-free and pressure-free process used to manufacture hollow plastic parts with a relatively low investment [1]. Since the rotational molding industry is presently dominated by powdered plastics, in particular polyethylene with limited properties, molders are being forced to use other kinds of plastic processing. Other resins currently used by the industry, for instance polycarbonate and nylon, offer better properties, but at a higher cost.

Reactive rotational molding (RRM) is an important way to overcome these problems. T. This process

offers numerous benefits over the conventional powder processes, e.g., shorter cycle times, lower processing temperatures and improved material properties [2]. Additionally, the use of an RRM process allows to synthesize engineering thermoplastic such as high molecular weight polyamide 6 with a through anionic polymerization of caprolactam by the aid of chain initiators and a catalyst. This advantageous anionic polymerization of caprolactam has been put to use in several reactive polymerization-molding processes, namely reaction injection molding [3], rotational molding [4, 5] and centrifugal molding [6,7]. It thus permits a direct manufacturing of large and complex-shaped

plastic parts with a high degree of surface finish and control of the product characteristics. . There are numerous problems in controlling the reaction viscosity and an uneven distribution of the material which are inherent to the processing of reactive monomers that have limited the development and uptake of the process in the rotational molding industry [2,8] On the other hand, the manufacturing of multilayer objects by rotomolding is a new and relatively difficult technology; one of the difficulties is to ensure a proper adhesion between the layers. There have been several studies on the interdiffusion and reaction at polymer/polymer interfaces using rheological and morphological tools [9], and these reports have indicated that the final properties between layers depends on various parameters such as the reaction temperature, contact time, shear, etc... Therefore, to gain a fundamental understanding of the RRM of caprolactam, the means of controlling the viscosity during anionic polymerization have to be investigated.

This work deals with rheological, dielectric and thermal analysis of the polymerization kinetics of caprolactam at various temperatures and concentrations of catalyst/chain initiator. The objective was to investigate the effect of mixtures and of crystallization/polymerization mechanisms during an RRM process. Moreover, the processing of PP/PA6 bilayer parts (through a reactive route and a molten route) was investigated.

2 EXPERIMENTAL SECTION

2.1 Materials

The materials used in this study are reported in Table 1

Table 1. The characteristic of the used materials

Monomer (CL)	Caprolactam (melts at 69°C)
Activateur (C)	Bruggolen C230 (Aliphatic polyisocyanate in N-methyl-2-pyrrolene).
Catalyst (C)	Bruggolen C10 (17-19% caprolactam sodium in caprolactam), (melts at 68°C)
Capron	BASF grade 20 melts at 220°C
copolymer E-P	Borealis grade 18

The E-P copolymer was used for the first layer, and the monomer, catalyst and activator were employed for the second layer. The PA6 powder was used as reference (molten route).

2.2 Polymerization kinetics (by rheology, DSC, and

dielectric characterizations)

The in-situ monitoring of the polymerization was carried out in (i) a differential scanning calorimeter (DSC-200), and (ii) a dielectric analyzer. In addition, the measurements of the rheological properties of the material formulations were performed with both parallel and cone plate geometries using an ARES strain controlled rheometer. The premix was prepared in an oil bath at 80 °C under a nitrogen atmosphere. I. In one vessel, a monomer/activator-mixture was melted under stirring, and in a second vessel, the catalyst was melted together with caprolactam. Subsequently, the contents of both vessels were mixed together. The rheological test method was a dynamic time sweep in which a 0.5 ml sample of the reactive liquid was loaded between the rheometer plates and a strain of 5% was applied. For the dielectric study, the in-situ monitoring of the caprolactam polymerization and crystallization was done in the mold; a TMS sensor was introduced in a specifically designed mold in order to collect the dielectric signal. The experimental conditions were as follows: a C10/C230/CL, mixture (6/6/100) under a nitrogen atmosphere with mold temperatures of 140, 150, 160, 170, 180 and 190°C.

2.3 Rotational molding (description of the process and equipment)

A Rotoline pilot-scale shuttle rotational molding machine with an aluminum cube mold (volume: 25×25×10 cm³) was used to produce PP/PA6 bilayer parts. The Datapaq® Tracker Telemetry system measured, in real time, the temperatures in the oven, along the outside wall of the mold, and also of the internal air/nitrogen during the processing cycle. After loading the PP as a first layer in the mold, the mold rotation speed and the thermal cycle were started. The reactive systems for the second layer were poured in the mold throughout the *special system*. The mold rotation speeds of the two axes were 4 and 5 rpm.

3 RESULTS AND DISCUSSION

3.1 Influence of the environment

The anionic polymerization of caprolactam becomes inhibited in the presence of even small amounts of moisture, due to the anionic nature of the reaction

[10]. Figure 1 shows the effect of the environment on the reaction time and viscosity increase at 160 °C. The polymerization reaction under the effect of moisture. Therefore, the storage and processing had to be conducted in absolutely moisture-free environments.

3.2 Influence of the catalyst/activator concentration

Increasing the amount of activator resulted in additional initiation points for chain growth. Also, with the increase of the catalyst concentration, more anions were set free and more complexes could be formed. Consequently, the polymerization rate increased [11]. Figure 2 shows the effect of varying the ratio of catalyst/activator on the induction time and viscosity-time profile of the CL polymerization at a test temperature of 160°C. It can be seen that when increasing the ratio from 2 to 4 the induction time was decreased by 300 s. It can also be noted from figure 2 that the rate of polymerization increased with the composition. Moreover, figure 3 shows the connection between polymerization and crystallization as observed by rheology and DSC.

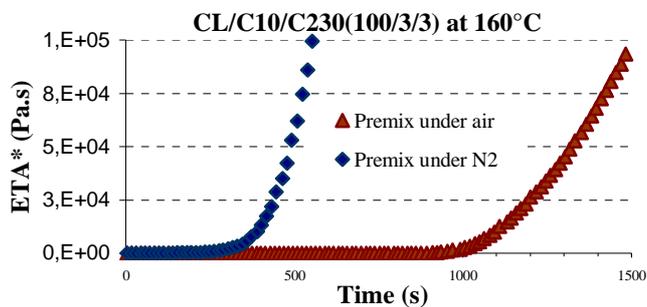


Fig. 1. The effect of the environment on the viscosity-time profile of CL/C10/C230 at 160 °C.

3.3 Influence of the polymerization temperature

The polymerization took place below the polymer melting and crystallization point (the α (the polymerization and crystallization kinetics occurred simultaneously), resulting in a solid and highly crystalline (40–50% [10]) PA-6. Figure 4 demonstrates the effect of an increasing the temperature on the induction time and viscosity profile of a 3/3 ratio formulation. It can be seen that raising the temperature reduced the induction time and increased the rate of polymerization.

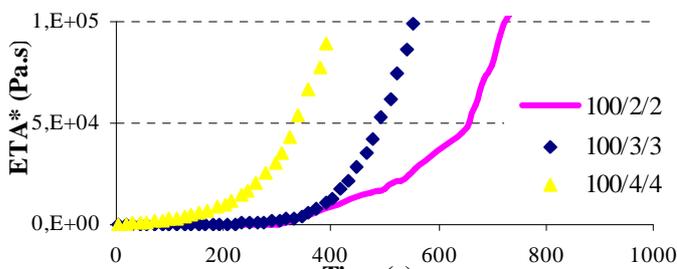


Fig. 2. The effect of the concentration of the catalyst/activator on the viscosity-time profile of CL/C10/C230 at 160 °C.

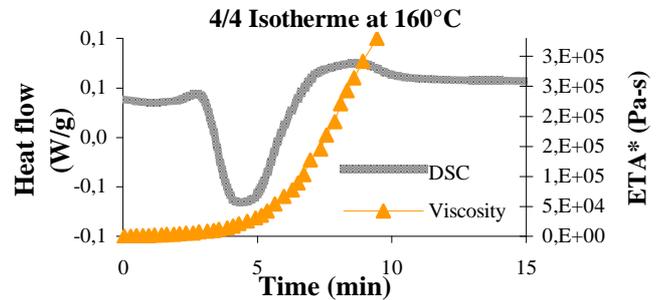


Fig. 3. A superimposing of the viscosity-time and heat flow profile.

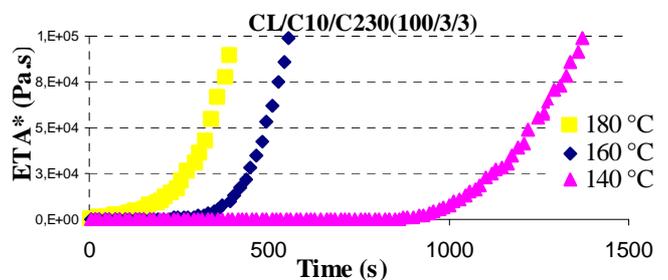


Fig. 4. The effect of the polymerization temperature on the viscosity-time profile of CL/C10/C230.

3.4 Dielectric in-situ monitoring of caprolactam polymerization and crystallization

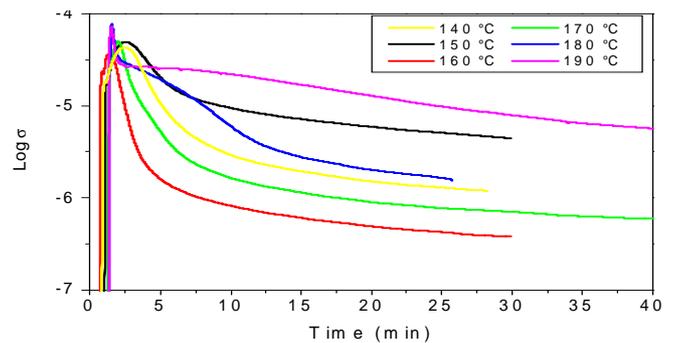


Fig. 5. The in-situ monitoring of the electrical conductivity Dielectric measurements were carried out to control the in-situ polymerization and crystallization of caprolactam at various temperatures. The results are displayed in figure 5, where, at higher temperatures (180 - 190°C), a two-step conductivity decrease can be noticed corresponding to the CL polymerizing and then crystallizing (cycle time ~ 5 – 6 min). At lower temperature (e.g., 140°C), the polymerization and crystallization occurred simultaneously.

3.5 Preparation of PA6 as a second layer by rotational molding from caprolactam

Since the viscosity is such an important parameter for rotational molding of liquid plastics, such as molten reactive systems, it was crucial to control its viscosity during rotational molding. The initial and minimum viscosity ideal for rotational molding of liquids is normally between 0.05 and 1 Pa.s [8]. From the viscosity-time profile in figure 6, the initial and minimum viscosity was 4000 Pa.s at 160 °C, a very high value for a reactive rotomolding process. Figure 6 illustrates the effects of the mold temperature and the amount of activator/catalyst on the material distribution. It can be seen that when the initial viscosity was high, the flow defects are important as a result of the liquid not having enough time to spread and this resulted in a faulty molding. The comparison of the temperature profiles of a PP/PA6 bilayer obtained by either a molten or reactive route (figure 7) indicated that it was possible to create bilayer parts with the rotational molding process by using less energy and a shorter time.

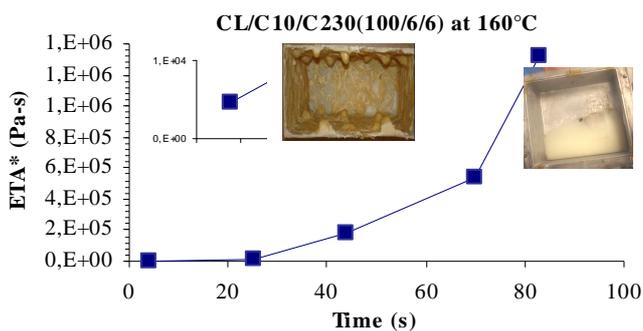


Fig. 6. The viscosity-time profile of CL/C10/C230 (100/6/6) at 160°C.

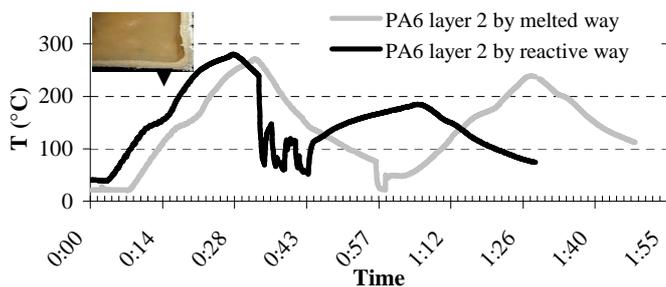


Fig. 7. The temperature profiles of a reactive system (100/3/3) and molten PA6 in a mold under air.

4 CONCLUSIONS

The objective of this work was to determine the formulation of reactive systems to be used in rotational molding. Results from rheology, DSC and dielectric measurement of samples from a rotational molding process indicated that a material

formulation with a ratio of 6% catalyst/activator could reduce cycle times as compared to non-reactive parts but had a negative effect on the material distribution. However, by correctly choosing the material formulation and molding parameters, such as the initial mold temperatures, one can expect to achieve good quality moldings with this material. Also, smaller amounts of catalyst and activator should be used in order to get enough induction time when keeping cycle times short. By using the composition 100/3/3, it was demonstrated that the rotational parts of the PP/PA6 bilayer (reactive route) could be obtained with optimized conditions in correlation with the rheology results. Moreover, the results demonstrated that it was possible to create reactive bilayer parts through a rotational molding process by using less energy and a smaller amount of time.

WORK IN PROGRESS

A slower catalyst (C1) will be used in order to increase the time available for the material to become evenly spread on the mold wall before the increase in viscosity. Rheological and morphological study will be carried out to investigate the interfacial reaction between reactive PA6/grafted polymer layers.

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