

Preparation and Structure Study of Polypropylene/Polyamide-6 Gradient Materials

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ABSTRACT: A polymeric gradient material was prepared by a specific extruding technique in which the weight ratio of two components, polypropylene (PP) and polyamide-6 (PA6), was changed gradually with the progress of process. This columnar gradient material was formed during a combined extruding and winding operating. The gradient variation of specimens sampled along the radius of columnar gradient material was confirmed and characterized through measurements of DSC melting behavior and elemental analysis. The morphological variation was studied using SEM observation. The results indicate that the content of either polymer shows a monotonous variation along the radius direction. With increasing radius, a gradually decreased percentage of PP was observed, whereas PA6 gradually in-

creased. SEM photographs of the specimens sampled at different radii exhibit that the morphology also evolves gradually with variations in the percentage ratio of two polymers. A phase-inversion phenomenon was recognized in this polymeric gradient material and a "dual mode" of dispersed morphology was found in the sandwich zone. These results indicate that the PP/PA6 blend with gradient structure was successfully prepared by use of this unique technique. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2491–2496, 2004

Key words: polymeric gradient materials; polypropylene (PP); polyamides; extrusion; structure

INTRODUCTION

As a new kind of material, functionally gradient material (FGM), has attracted increasing attention within the past decade. The so-called FGMs are composites in which the material composition is varied spatially to optimize the performance of material for a specific application.¹ This concept was first proposed by the Japanese Space Program, and implemented successfully in preparing a new ceramic/metal composite for application of thermal-protection materials.^{2–4} Since then the concept of FGM has spread to many types of materials.^{5–13} In contrast to the ceramic/metal system and other inorganic materials, however, there have been relatively few experimental studies of polymeric gradient materials (PGMs). After the 1990s, several researchers published findings on the various preparation methods and the structural features of their products. For example, gradient refractive index materials, one category of the representative PGM, were prepared by a "closed extrusion process."¹⁴ Polymeric sheetlike FGMs were prepared by means of dissolution diffusion, cast, emulsion-blend, coating, and other

ways.^{15–18} Gradient interpenetrating polymer networks (IPNs) were synthesized where sequential IPNs composed of hydrophilic poly(2-hydroxyethyl methacrylate) and hydrophobic polystyrene were prepared by photopolymerization.¹⁹

A new method to prepare FGM by frontal polymerization has been reported in which the composition of a monomer feedstream could be varied in a programmable manner.²⁰ In the work of Jang et al.,²¹ a gradient of glass fibers (GF) was created by changing the feeding ratio of the chopped fibers in the process of GF/PMMA composite manufacture. Recently, Kikutani²² proposed a method for producing PGM where high-performance fiber, a kind of liquid crystalline polymer, is stacked up in a matrix of thermoplastics. The author expects that the gradient structure can be created by gradually changing the diameter and stacking density of the fibers. Of the previously cited articles, however, only a few of them were concerned with the investigation of an efficient melt-extruding process.¹⁴ In this study, we sought to introduce the idea of FGM into the area of polymer blend and prepare PGM with a simple processing method. The polypropylene/polyamide-6 (PP/PA6) pair was chosen to prepare the gradient materials because it combines the thermomechanical properties of polyamide and the easy processing characteristics of polypropylene. A specific extruding–winding technique was used to prepare the gradient materials.

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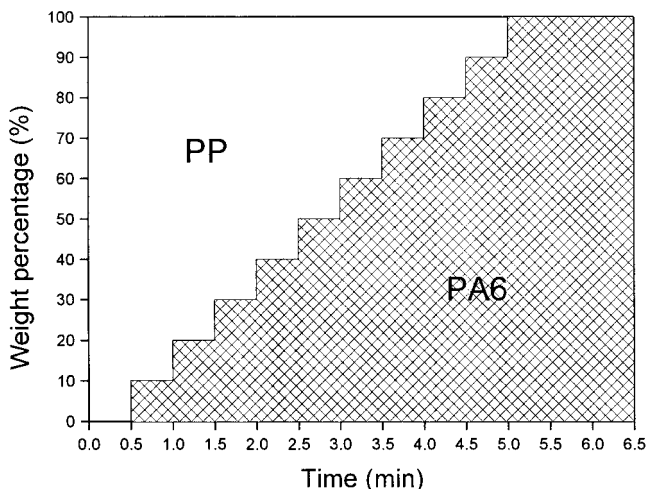


Figure 1 Composition of PP/PA6 feedstock series.

EXPERIMENTAL

Materials

Commercial polypropylene (PP) and polyamide-6 (PA6) pellets used in this study were kindly provided by Yanshan Petrochemical Inc. (China), and Yueyang Chemical Plant (China), respectively. The melt flow index (MFI) of PP as measured at 230°C and 2.16 kg was 18. MFI measured at 245°C and 2.16 kg for PA6 was 12.

To prepare the polymeric gradient materials, physical mixing of the PP and PA6 pellets was carried out before the melt-extruding process. As shown in Figure 1, PP and PA6 were mixed with different weight ratios: PP/PA6 = 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90, and 0/100. Such a feedstock series with a gradually varied weight ratio where the PA6 is gradually increased was fed into the extruder one by one in 0.5-min intervals (see Fig. 1).

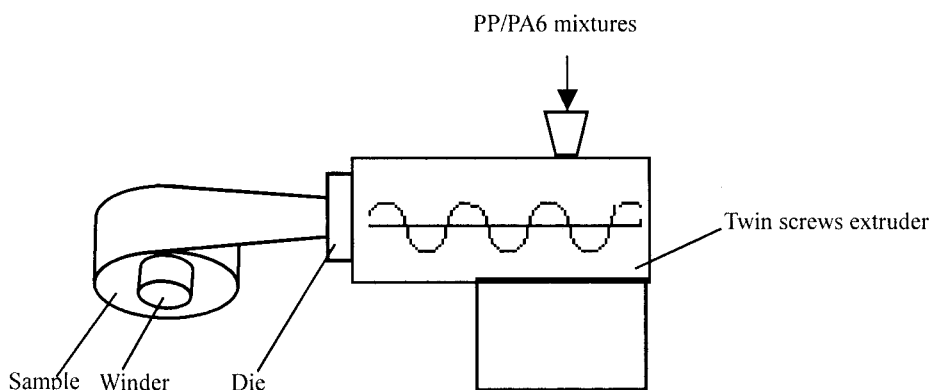


Figure 2 Experimental setup of the process for preparing PP/PA6 gradient material.

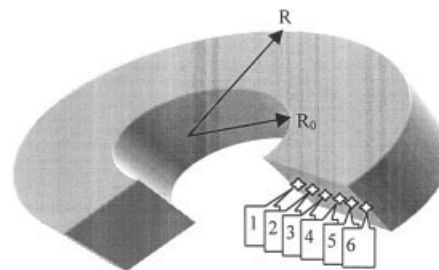


Figure 3 Sampling positions of specimens 1 to 6 in gradient material. The corresponding radii of the six specimens are 20, 26.3, 30.5, 33.9, 37.8, and 42.8 mm, respectively.

Sample preparation

A schematic diagram of the apparatus for preparing the gradient polymer sample is shown in Figure 2. A Prism TSE-16-TC twin-screw extruder with a screw diameter of 16 mm and a length to diameter ratio of 25 was used to melt and extrude the PP/PA6 blends. A melt blending temperature of 240°C was used in the experiments. The ribbonlike blended strip was molded through an extrusion die with a rectangular slot having a size of 18 × 1 mm. The obtained strip was collected and wound up immediately by a winder before it solidified, after which a columnar gradient sample was prepared. This process took about 7 min.

Characterization

Figure 3 shows an example of columnar PP/PA6 gradient materials. Its inside radius R_0 and outside radius R were 20.0 and 42.8 mm, respectively. As shown in Figure 3, the sample could be sliced into many parts and six parts were selected at different positions along the radius direction [i.e., R_0 ($0.47R$), $0.61R$, $0.71R$, $0.79R$, $0.88R$, and R , respectively]. This formed a specimen series: specimen 1 ($0.47R$) to specimen 6 (R). In addition, the melt extrudate of pure PA6 was defined

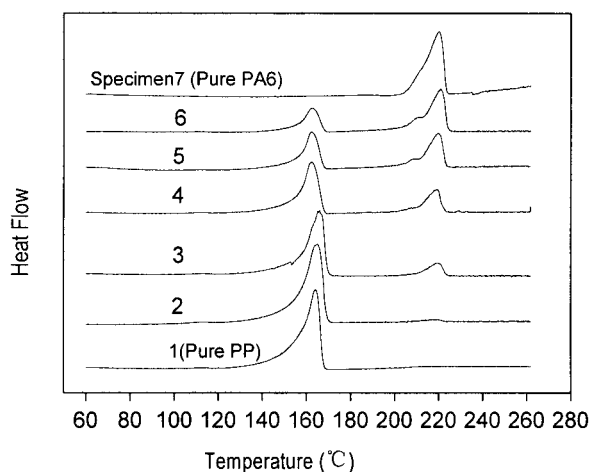


Figure 4 DSC scans of various specimens.

as specimen 7. These seven specimens were used for thermal analysis, elemental analysis, and SEM observation.

DSC measurements

Thermal analyses of PP/PA6 gradient materials were performed on a Perkin–Elmer Pyris 1 differential scanning calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT), under nitrogen atmosphere. Calibration of the apparatus for temperature and energy was made using a standard indium reference. The weight of the specimens was kept around 5 mg. The thermogram was recorded from 60 to 260°C at a thermal scan rate of 10°C/min. The melting temperature (T_m) and enthalpy value were recorded during the first heating.

Elemental analysis

A Carlo Erba 1106 elemental analyzer was used to determine the content of PA6 in PP/PA6 blend through measuring the weight percentage of the nitrogen element in the corresponding samples. The weight of each sample was about 1 mg.

Morphology observations

Morphological variation of the PP/PA6 gradient materials was studied using a Cambridge Stereoscan 250MK3 scanning electron microscope. Samples were fractured at liquid nitrogen temperature. The fragments were corroded by formic acid for 30 h, and then sputtered with gold before taking micrographs.

RESULTS AND DISCUSSIONS

Gradient variation of composition

To study the effect of composition variation on the structural features, analysis was first performed on the

various specimens with DSC measurement. DSC curves in the temperature region between 60 to 260°C for seven PP/PA6 gradient specimens are presented in Figure 4. As shown in this figure, in the cases of PP and PA6 specimens, only one endothermic peak is observed at their characteristic temperatures, respectively. For PP homopolymer, as seen at the bottom of the figure, a well-known thermal behavior is presented where a melting endotherm at about 164°C appears. In contrast to this trace is pure PA6, where the heat flow corresponding to the crystal melting is observed at about 220°C.

The respective situations between these two homopolymers exhibit a gradient change. As previously mentioned, specimens 2 to 6 were prepared with an increasing component of PA6 in the PP/PA6 blend. In contrast with the homopolymers, two endothermic peaks clearly appear for five such specimens, indicating the existence of two different polymers. The intensities of two such peaks changed significantly with blend composition. For example, the 220°C peak is relatively weak when the PA6 component is at a minor level, and exhibits a proportional increase with the increased content of PA6. Such a systematic decrease or increase in both melting peak areas of PP and PA6 indicates that the relative content of PP and PA6 is varied gradually in the radius direction.

It has been firmly established that the value of the melting peak area (i.e., the crystalline heat of fusion) is directly proportional to the crystallinity in a homopolymer material. This value, however, cannot be used to evaluate the content of either polymer in a bicomponent blend. In other words, the quantitative weight percentage of either PP or PA6 in each specimen cannot be determined with current DSC data. For clarifying the point at issue, elemental analysis is con-

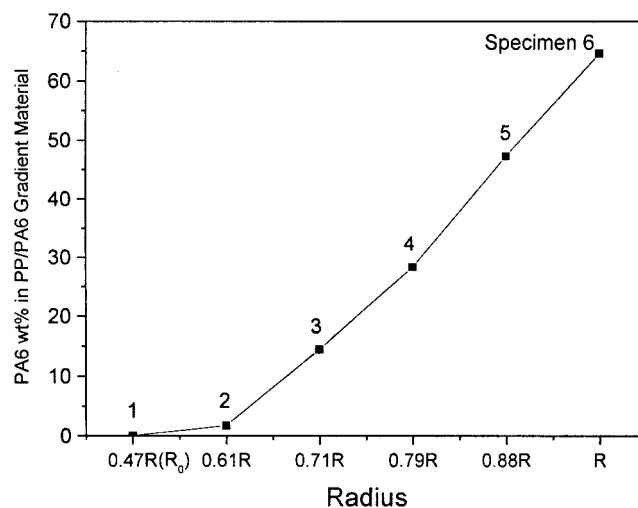
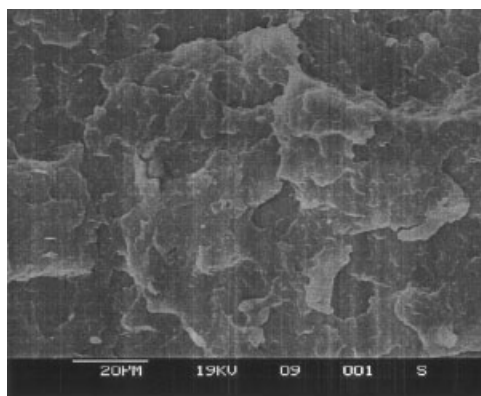
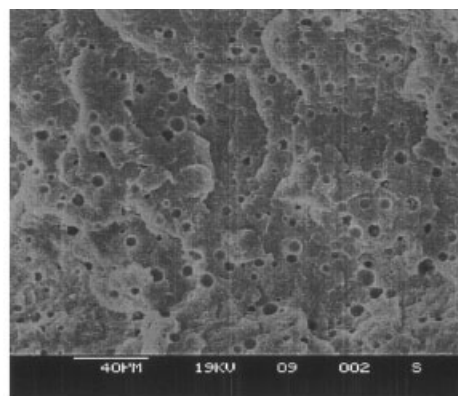


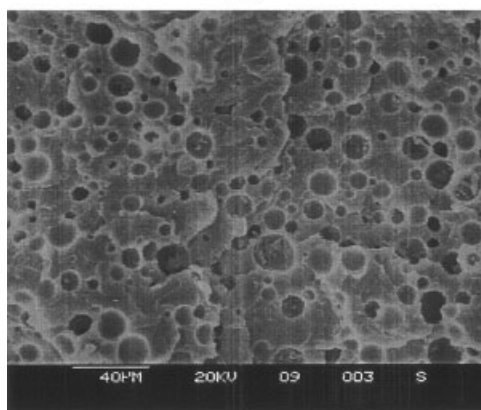
Figure 5 Content of PA6 in various specimens sampled at different radii.



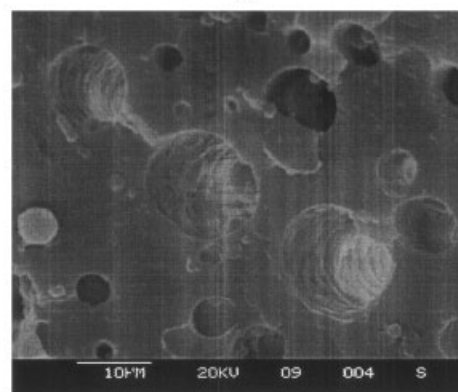
(a)



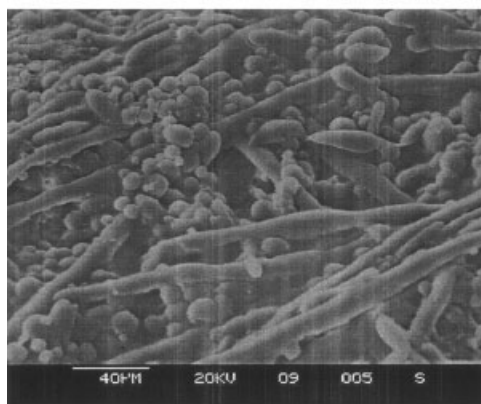
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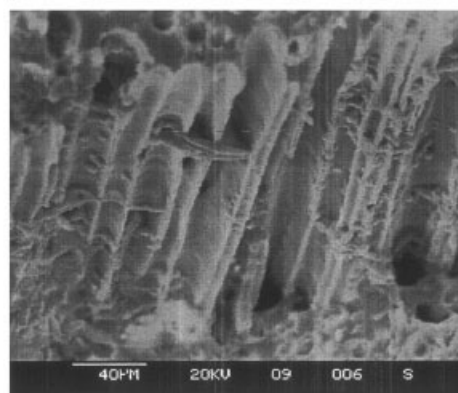
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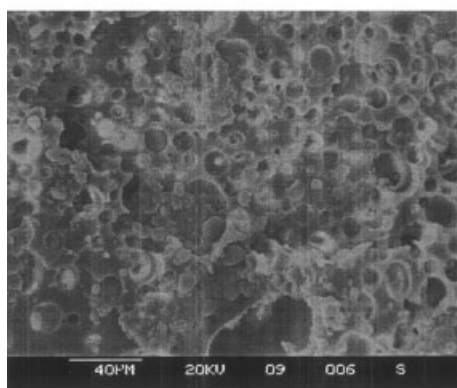
(d)



(e)



(f)



(g)

sidered to be a useful tool. Because the nitrogen (N) element exists only in the PA6 component in the whole experimental system, after the content of nitrogen element in blend has been determined, the weight percentage of PA6 in the corresponding specimen can be calculated.²³

The following equation was used to calculate the weight percentage of PA6 (PA6%) in various PP/PA6 blended specimens:

$$\text{PA6\%} = (M_0/M_N)N\%$$

where M_0 is the repeat unit chemical formula weight of the PA6, M_N is the atomic weight of nitrogen element, and $N\%$ is the percentage of nitrogen in blends that is determined by elemental analysis. The calculated results for specimens 1 to 6 are shown in Figure 5.

Figure 5 gives the relationship between the content of PA6 and sample radius. It shows that the content of PA6 gradually increased with the increased radius, indicating that the concentration gradient has formed in the PP/PA6 blended materials.

Evolution of morphology

It was previously reported that the blend of PP/PA6 is immiscible because of the obvious differences in their polarity and crystalline structure.²⁴ As a result, a multiphase structure is expected to exist in the PP/PA6 blended sample, according to the traditional blend theory.^{25–27} This morphological feature for the PP/PA6 gradient sample was examined by scanning electron microscopy. Typical SEM micrographs of the PP/PA6 gradient materials sampled at different positions along the radius are presented in Figure 6(a)–(g). Because the sliced PP/PA6 specimens were pretreated, in which the PA6 was extracted by formic acid and then left many cavities (as seen in these photographs), the white and black areas thus represent the PP and PA6 phases, respectively.

Figure 6(a) is from specimen 1. As previously stated, this specimen was sampled precisely at the inside radius and then consisted of only pure PP. As seen in this figure, therefore, a normal morphology of PP homopolymer is observed. Figure 6(b) and (c) show the photographs of specimens 2 and 3, respectively. These two specimens were selected from the sections near to the inside part of the columnar sample (see Fig. 3), where the materials can be considered to be a mixture of a large amount of polypropylene and a

small amount of polyamide-6. From these two figures, a common feature is recognized that the PA6 particles disperse in the PP matrix, resulting in a so-called sea-island morphology. By carefully comparing Figure 6(c) with 6(b), it is evident that both the size and quantity of the “islands” appearing in Figure 6(c) increase significantly. This can be explained by the higher content of PA6 in specimen 3 than that in specimen 2. Figure 6(d) gives the morphological image for specimen 4 in which the content of PA6 is 28.3%, with a relatively high magnification. By comparison with preceding photos, an evident effect of increased PA6 content may be observed. The appearance of PA6 phase looks to be obviously changed, where a morphological transition from particles to column occurs. After etching the PA6 phase, several columnar cavities with subtle structure can be identified. Specimen 5 was sampled at 0.88R and a weight ratio of PP/PA6 = 53/47 was determined from the results of elemental analysis (see Fig. 5). In the case of this specimen shown in Figure 6(e), with further increase of PA6, a cocontinuous interpenetrated morphology forms in which the continuous PP matrix is retrogressed to columns, ellipsoids, and/or spheres, which means that a phenomenon of phase inversion is beginning to occur. The last two photographs [Fig. 6(f) and (g)] represent the morphological feature of specimen 6, which was sampled at the outside radius of the gradient sample. These two photos were taken for the etched surfaces in either direction perpendicular or parallel to the radius, respectively. As shown in Figure 6 (f), a sandwichlike morphology is formed. The columnar cavities link closely with each other and form layers. Because the PA6 phase in the specimen has been extracted, only the interface of the two components can be observed. Figure 6(g) gives the detailed structure of the PP layer, in which PA6 particles disperse within the PP matrix. Because the weight percentage of PA6 in this region is dominant (~ 65%), it is also expected that there must be a large proportion of PP particles that disperse within the PA6 layer. This means a “dual mode” of dispersed morphology is formed in the sandwich zone,²⁸ even though such a photograph cannot be taken because the PA6 phase has been extracted.

The above observations indicate that the dispersed phase morphology forms when either polymer is at a lower level, and a cocontinuous morphological structure forms when the content of PA6 is increased to be close to that of PP. A phase-inversion phenomenon

Figure 6 SEM micrographs of various specimens sampled at different radii (R): (a) specimen 1, 0.47R, PA6 = 0; (b) specimen 2, 0.62R, PA6 = 1.7%; (c) specimen 3, 0.71R, PA6 = 14.4%; (d) specimen 4, 0.79R, PA6 = 28.3%; (e) specimen 5, 0.88R, PA6 = 47.3%; (f) specimen 6, R , PA6 = 64.6%, perpendicular to the radius; (g) specimen 6, R , PA6 = 64.6%, parallel to the radius.

appears when the content of PA6 is higher than that of PP. The morphological features of respective specimens are similar to those of the traditional blend in which the difference between any two domains could be neglected. The whole structure of the PGM prepared in this study, however, is very different from that of the traditional blend because the morphology of each sliced specimen varies gradually along the radius direction of the columnar sample. These results indicate clearly that the gradient structure has been formed in the material. It may bring some unusual properties and special applications into industrial fields. The performance of the PP/PA6 gradient material prepared by this technique will be examined in the future.

CONCLUSIONS

Polymeric gradient material (PGM) was prepared by gradually changing the weight ratio of two components during the extruding process. The morphological feature of the sliced specimen from this PGM was similar to that of the traditional blend in which the difference between any two domains could be neglected. The whole structure of the PGM prepared in this study, however, was very different from the traditional blend because the morphology of each sliced specimen varies gradually along the radius direction of the columnar sample. Experimental results showed that the PP/PA6 gradient material can be prepared successfully by use of this special extruding-winding technique. In comparison with the preparation techniques introduced by other researchers, this technique is relatively simple, efficient, and inexpensive, and may be extended to other polymer blends and composites.

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