

## Influences of the Crystallization Behavior of n-HA Reinforced PA66 Biocomposite on Its Mechanical Properties

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**Abstract.** The crystallization behavior of n-HA/PA66 biocomposites at different processing pressure and annealing temperature were investigated by XRD and DSC. The results showed that increasing annealing temperature would weaken the crystalline intensities of pure PA66 and its composites. For n-HA/PA66 composites, the peaks of  $\alpha 1$  crystals of PA66 disappeared, only  $\alpha 2$  crystals existed, and with the increase of injection pressure and annealing temperature, the crystalline intensity of PA66 decreased. The degree of crystallinity ( $X_c$ ) of PA66 in composites increased with the increase of injection pressure, however, annealing temperature had no obvious effects on crystalline degree. The mechanical properties had close relationship with the crystallization behavior of the materials.

### 1. Introduction

Fillers are commonly added to commercial thermoplastic resins to improve the properties such as stiffness, tensile strength, heat distortion, and mould ability. Based on the similar rationale, bioceramics/polymer composites with mechanical properties analogous to bone as well as bioactivity and biocompatibility have been developed. Hydroxyapatite reinforced high density polyethylene (HA/HDPE) composite [1] is the first bioactive ceramic-polymer composite that is designed to mimic the structure and match the properties of bone [2], which has given rise to the research and development of other bioactive composites using the same rationale. After then, hydroxyapatite reinforced polysulfone [3], Bioglass<sup>®</sup> reinforced polyethylene [4-6], A-W glass-ceramic reinforced high density polyethylene [7], hydroxyapatite reinforced polyetheretherketone [8] composites have been produced.

Polyamides are widely used engineering thermoplastics. Considering that polyamides have the similar amide structures with proteins, Yubao Li et al [9-11] developed a novel biocomposites with nano-hydroxyapatite (n-HA) reinforced polyamide 66 (PA66) for load bearing bone repair. In the composites HA particles can keep their nano-grade dispersion in the matrix and the content of n-HA can reach 65wt%. The mechanical properties of n-HA/PA66 composites are similar to those of natural bone. Animals and clinical experiments proved that these composites have good compatibility to bone and can bond to bone directly.

The target of this paper is to examine the influences of processing conditions on the crystallization behavior and the mechanical properties of n-HA/PA66 composites by injection molding.

### 2. Experimental

#### 2.1. Materials

Polyamide 66 (PA66) with a viscosity-average molecular weight ( $M_v$ ) of 18 kDa was from BASF, Germany. The preparation of n-HA/PA66 composites was given in Ref.[10]. The samples for XRD, DSC and mechanical test were prepared by injection molded. And the molding conditions

are listed in Table 1.

## 2.2. Wide angle X-ray diffraction (WAXD)

WAXD was conducted using Philips XRD analyzer in the reflection mode. X-ray analysis was performed at room temperature on sheets excised from injection molding samples.

## 2.3. Differential scanning calorimetry (DSC)

The thermal and crystallization behavior of pure PA66 and n-HA/PA66 composites was determined using a Perkin–Elmer DSC7. The specimens were excised from injection molding samples that were processed and annealed at different conditions. All the samples were dried under vacuum for approximately 24h at 80°C prior to the thermal analysis. Samples were heated from room temperature to 300°C at a rate of 10°C/min, held for 5 min to ensure totally melting, then cooled to room temperature at a rate of 10°C/min.

Tab.1 Processing and annealing conditions for PA66 and n-HA/PA66 composites by injection molded

Samples	Injection Pressure/	Processing Temperature	Moulding Temperature	Annealing Temperature
PA66	90	260-280	80	20
				100*
				150
40wt%n-HA/PA66	90	260-280	80	20
				100
				150
				20
				100
	110	260-280	80	20
				100
				150

## 2.4. Mechanical properties testing

Compressive strength testing samples at different processing conditions were conducted on Shimadzu AUFOGRAPH testing system with a crosshead speed of 2mm/min.

## 3. Results and discussion

### 3.1 Crystal structures of pure PA66 and n-HA/PA66

Fig.1 shows that the influences of the annealing temperature on the crystalline property of the pure PA66 at 90MPa injection pressure by XRD. It can be seen that for all the samples two strong reflection peaks, (100) and (010,110) of  $\alpha$  phase crystals of PA66 [12] are observed at  $2\theta=20.4^\circ$  and  $24.2^\circ$ , respectively. With the increasing the annealing temperature, the positions of the reflection peaks remain almost unchanged while the relative intensity of (010,110)/ (100) gradually increases. This probably indicates that a preferential packing of the crystals along the (010,110) plane, which may be induced by rearrangement of PA66 molecules at higher annealing temperature.

The XRD patterns of n-HA/PA66 composites with 40wt% n-HA at different injection pressures and after-treated temperatures are shown in Fig.2 and Fig.3. It is interested that the peaks of  $\alpha_1$  phase of PA66 disappear with the introduction of n-HA, and the peaks of  $\alpha_2$  become wide and the intensities of the  $\alpha_2$  peaks decrease, which proved that the addition of n-HA changes the structure of the crystalline phase. The  $\alpha_1$  peak in XRD pattern of PA66 arises from the distance between hydrogen-bonded chains, which is the diffraction of hydrogen bonded sheets, and the  $\alpha_2$  peak arises from the separation of the hydrogen bond sheets [13]. The disappearance of the  $\alpha_1$  peak in n-HA/PA66 indicates that the addition of n-HA disturbs the perfect arrangement of hydrogen bonded sheets of the  $\alpha_1$  phase. The similar phenomenon has been observed in polyamide 66 /clay nanocomposites other researchers [14]. Compared Fig.2 and Fig.3, it can be found that processing pressures also affect the crystalline behaviour of PA66 in composites, the crystalline intensity

decreased with the increase of the processing pressure.

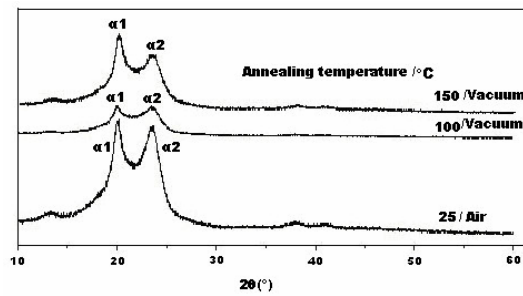


Fig.1 XRD patterns of pure PA66 at 90MPa injection pressure and different annealing conditions

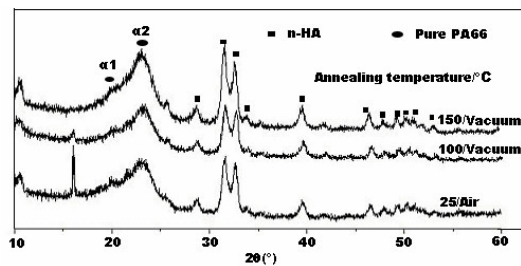


Fig.2 XRD patterns of the specimens of n-HA/PA66 composites at 90MPa and different annealing conditions

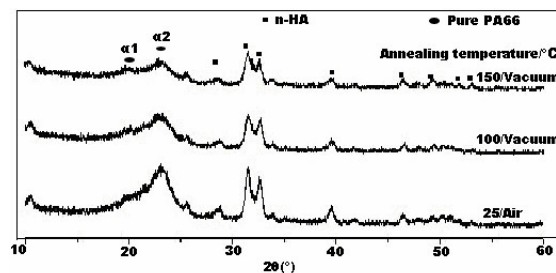


Fig.3 XRD patterns of the specimens of n-HA/PA66 composites at 110MPa and different annealing conditions

### 3.2 Thermal properties

Table 2 The thermal dynamic properties of pure PA66 and n-HA/PA66 composites\*

Samples	Injection Pressure/MPa	Annealing Temperature/°C	$T_p/°C$	$T_0/°C$	$T_0-T_p/°C$	$X_c$
Pure PA66	90	20	238.2	230.9	7.3	33.2
		100	239.1	232.4	6.7	34.5
		150	238.2	231.2	7.0	33.2
40wt.%n-HA/PA66	90	20	237.3	233.6	3.7	31.5
		100	235.9	231.5	4.4	29.7
		150	235.8	232.0	3.8	30.7
40wt.%n-HA/PA66	110	20	236.6	232.8	3.8	32.6
		100	235.3	231.3	4.3	32.5
		150	235.8	232.5	3.3	33.2

\*  $T_p$ -- peak temperature of crystallizing;  $T_0$  -- onset temperature of crystallizing;  $X_c$  -- degree of crystallinity

The data listed in table 2 are thermal dynamic parameters from DSC curves of pure PA66 and

n-HA/PA66 samples. The data in table 2 revealed that the introduction of n-HA weakened the degree of crystallinity ( $X_C$ ) of PA66, and with the enhancement of the processing pressure, the  $X_C$  increased. Gupta [15] suggested that  $(T_o-T_p)$  could characterize total crystallizing rate of the polymer. Table 2 shows that  $(T_o-T_p)$  of composites are much lower than those of pure PA66, indicating that the crystallizing rates of PA66 in composites are much higher than those of pure PA66, because of the addition of n-HA in PA66 playing a role of nucleating agent and enhanced the crystallization rate.

### 3.3 Mechanical properties

To study of the effects of the crystallizing behaviour of n-HA/PA66 composites on their mechanical properties, the compressive strength of pure PA66 and n-HA/PA66 composites by injection molded under different processing pressure and annealing temperature are given in Fig. 4. For all the composites, the compressive properties are much higher in contrast with those of pure PA66, and compressive strength increased with the increase of injection pressure, however, decreased with the increase of annealing temperature resulted from the decrease of degree of crystallinity of PA66.

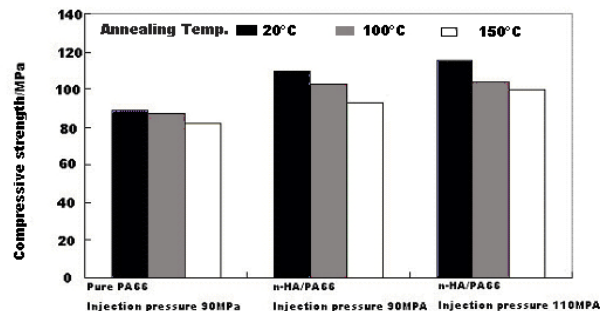


Fig. 4 Compressive strength of pure PA66 and n-HA/PA66 composites samples at different processing conditions

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