

SUPER POLYOLEFIN BLENDS ACHIEVED VIA DYNAMIC PACKING INJECTION MOLDING: MORPHOLOGY AND PROPERTIES*

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Abstract As a long-term project aimed at developing super polyolefin blends, in this paper we summarize our work on the mechanical reinforcement and phase morphology of polyolefin blends achieved by dynamic packing injection molding (DPIM). The main feature of this technology is that the specimen is forced to move repeatedly in the mold by two pistons that move reversibly with the same frequency during cooling, which results in preferential orientation of the dispersed phase as well as the matrix. The typical morphology of samples obtained via DPIM is a shear-induced morphology with a core in the center, an oriented zone surrounding the core and a skin layer in the cross-section areas. Shear-induced phase dissolution at a higher shear rate but phase separation at low shear rates is evident from AFM examination of LLDPE/PP (50/50) blends. The super polyolefin blends having high modulus (1.9–2.2 GPa), high tensile strength (100–120 MPa) and high impact strength (6 times as that of pure HDPE) have been prepared by controlling the phase separation, molecular orientation and crystal morphology.

Keywords Polyolefin blends, Shear, Morphology, Mechanical properties

INTRODUCTION

Polyolefins are the most important plastics. Among all polymers, polyethylene and polypropylene are produced on the largest scale. Blends of polyolefins are frequently used to get balanced mechanical and processing properties, for example, LLDPE/LDPE blends have properties which combine the high toughness of LLDPE with the good melt processability of LDPE^[1]. The properties of the individual polyolefins can be changed in a significant way by mixing with other components. For this reason, polyolefin blends have attained widespread commercial applications^[2–6]. Study of the properties and morphology of polyolefin blends has always attracted great interest, not only because of their wide application in industry, but more importantly because of their rich and fascinated morphology depending on molecular structure, thermal history and external stress field^[1,7–13]. The key issue is to establish the relationship between properties and morphology, in order to modulate the morphology of blends and improve the properties as much as possible.

Many reports about increasing the impact strength of polyolefins have been published^[14–18]. By blending them with rubber particles, the impact strength of polyolefins can be improved significantly. Moreover, various toughening mechanisms and models have been proposed. Several studies have documented the effect of various parameters such as rubber particle size, rubber concentration and inter-particle distance on the toughening efficiency of rubber particles^[19–21]. Unfortunately, with increasing impact strength, the tensile strength as well as the modulus always declines. In recent years, many researchers have paid more attention to the preparation of

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polyolefins with high impact strength, as well as high tensile strength and high modulus, which relies on structure manipulation during melt processing. Allowing for chain-folding, the high performance can be obtained by the *c*-axis orientation through the stacks of lamellae or chain-folded blocks with straight stem directions all parallel^[22]. In the light of this, recent efforts have been directed towards the achievement of high chain extensions in addition to chain orientation.

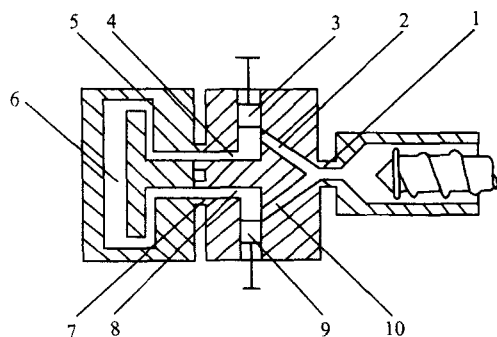


Fig. 1 Schematic representation of dynamic packing injection molding

(1) nozzle, (2) sprue A, (3) piston A, (4) runner A, (5) connector, (6) specimen, (7) connector, (8) runner B, (9) piston B, (10) sprue B

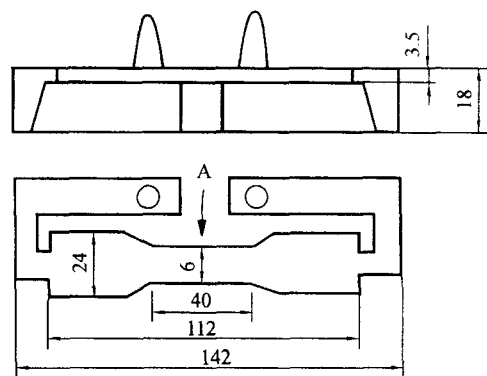


Fig. 2 Sketch of mechanical test specimen dimensions according to ASTM638 M standard

In recent years, dynamic packing injection molding (DPIM) has been found to be a very important way to control polymer morphology and mechanical properties^[23–25]. The main feature of this technology is that the specimen is forced to move repeatedly in the model by two pistons that move reversibly with the same frequency during cooling, which results in preferential orientation of the dispersed phase as well as the matrix. A schematic representation of this technology is shown in Fig. 1 and the specimen dimensions are shown in Fig. 2. We also carried out injection molding under static packing by using the same processing parameters but without shearing for comparison purpose. The specimen obtained by dynamic packing injection molding is called a dynamic sample, and the specimen obtained by static packing injection molding is called a static sample. The detailed experimental procedures were described in references^[26, 27]. We have performed extensive experimental work on the control of phase morphology of polyolefin blends, such as PP/LLDPE^[26], PP/HDPE^[27], PP/EPDM^[28, 29], HDPE/EVA^[30], PP/PS and PP/clay nanocomposites^[31] by using the DPIM technique. Super polyolefin blends with high modulus and tensile strength as well as high impact strength have been obtained^[26, 27, 30]. By controlling the elongation and orientation of EPDM particles in the PP matrix, a brittle-ductile-brittle transition of impact strength was found with increasing the EPDM content^[28, 29]. Our proposals are two-fold, one is to better understand the morphological development of polymer blends during external shear stress, and the other is to achieve super polyolefin blends by controlling the orientation, phase separation and crystal morphology of the studied blends. Following is a summary of the results on polyolefin blends obtained via dynamic packing injection molding.

THE MORPHOLOGY OF POLYMER BLENDS VERSUS PROCESSING

It is well known that the morphology of polymer blends depends mainly upon the rheological and interfacial properties, the blending conditions, and the volume ratio of the components. The size and the deformation of a purely viscous (Newtonian) droplet surrounded by another Newtonian fluid is determined mainly by two parameters^[32, 33]. The viscosity ratio λ is defined as

$$\lambda = \frac{\eta_d}{\eta_m}$$

(1)

In this equation, η_d is the viscosity of the dispersed phase and η_m is the viscosity of the matrix. The k -term has the form

$$k = \frac{\sigma}{\eta_m \dot{\gamma} R}$$

(2)

where σ is the interfacial tension, $\dot{\gamma}$ is the shear rate, and R is the droplet radius. The physical meaning of the k -term is a balance between the resistance to deformation of the droplet (σ/R) and the local acting shear stress ($\eta_m \dot{\gamma}$) which deforms the droplet. For polymers of viscoelastic rather than viscous nature, σ in the k -term has to be corrected by a factor that considers the effect of the normal forces arising from the elasticity of the phases^[34]. So by choosing the viscosity ratio, controlling the interfacial tension (for example, via using compatibilizer) and shear rate, the phase morphology of polymer blends can be well controlled.

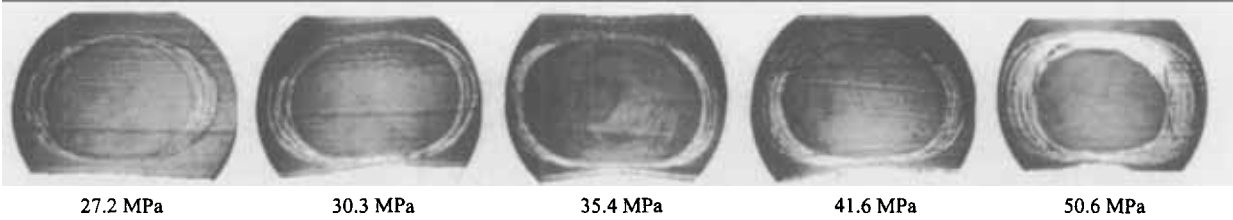


Fig. 3 Photographs of the cross section of HDPE/LDPE blends obtained via DPIM

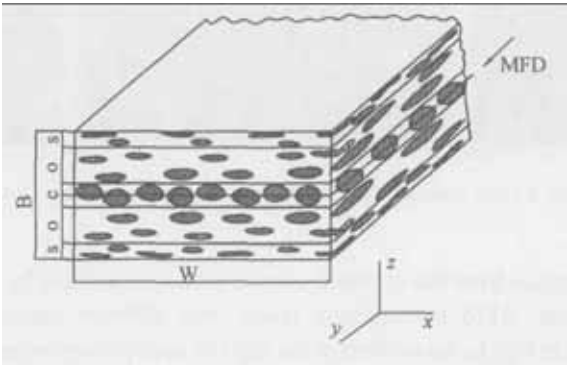


Fig. 4 Schematic representation of three-dimensional morphology of polyolefin blends obtained via DPIM

Macroscopically, the main feature of dynamic samples is the shear-induced morphology with a core in the center, an oriented zone surrounding the core and a skin layer in the cross-section areas of the samples. Photographs of the cross section of HDPE/LDPE are shown in Fig. 3 as an example. These photos are common microscope photographs obtained through a CCD transducer. The cross section is perpendicular to the shear stress direction. A schematic representation of the three-dimensional morphology of polyolefin blends obtained under shear stress is shown in Fig. 4. This morphology is formed due to the temperature difference between the mold and the melt, and due to the shear applied during cooling. The skin is frozen first, then the oriented zone and the last is the center. So the morphological development can be followed by checking the phase morphology of a sample from its skin to the center.

SHEAR INDUCED MORPHOLOGICAL CHANGE IN PP/LLDPE BLENDS

The morphology of a PP/LLDPE blend (50/50) obtained by phase dissolution at high shear rate combined with

dynamic packing injection molding at low shear rate was investigated by AFM. The phase dissolution under high shear rate is manifested by the co-continuous two-phase structure which, however, could be broken down to an island-sea like structure when a low shear rate is applied via dynamic packing injection molding. For the state sample, AFM photographs taken from the skin, the center and half position between skin and center respectively, are shown in Fig. 5. Since the modulus of PP is much larger than that of LLDPE, the bright region is assigned to PP-rich phase and the dark region is assigned to the LLDPE-rich region. A co-continuous two-phase pattern is clearly observed with a periodicity of about $0.1\ \mu\text{m}$ at the skin (Fig. 5a), $0.5\ \mu\text{m}$ at the center (Fig. 5c) and $0.3\ \mu\text{m}$ in between. Such a regularity could not be attained by a simple mixing of immiscible polymer blends. It can be attained only by spinodal decomposition from a homogeneous single-phase mixture produced under a high shear rate in the injection molder. The development of two-phase structure by spinodal decomposition is evident from the morphology at different positions from skin to center. The skin represents the early stage of spinodal decomposition and the center is due to the relatively later stage of decomposition. From skin to center, the co-continuous structure with nice regularity developed and grew self-similarly. This periodic structure could be fixed by the crystallization of both components during cooling, as suggested by Inoue after investigation of PP/HDPE blends^[35].

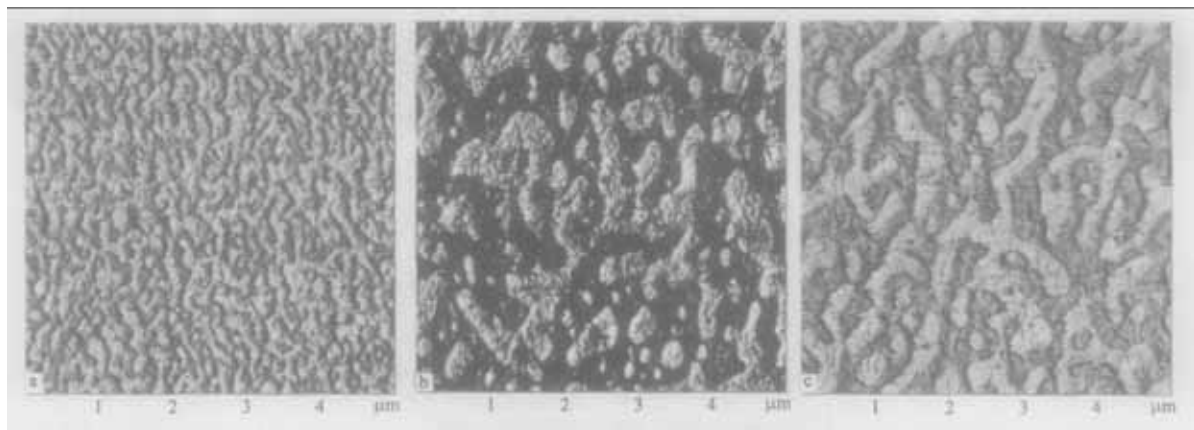


Fig. 5 AFM photographs of a state sample taken at different positions (a) skin layer, (b) oriented zone and (c) the center

Our interesting result comes from the dynamic sample, which is obtained by applying low shear stress on the above sample during cooling. AFM photographs, taken from different positions from skin to center of the dynamic sample, are shown in Fig. 6, the number at the top left each picture represents the distance to the edge of the sample (mm). One observes a very similar phase morphology in skin region ($0.4\text{--}1.5\ \text{mm}$) to that in the static sample. Due to the fast cooling of skin, applied shear has little effect on the morphology. A gradually change of co-continuous phase to island-sea structure under low shear rate is seen starting from $2.0\ \text{mm}$ to $2.5\ \text{mm}$. A clear-cut island-sea structure with $2\text{--}3\ \mu\text{m}$ domains is observed in the center ($3.1\ \text{mm}$). The results suggest that spinodal decomposition can be broken down when subjected to shear stress. Compared with the morphology of static samples, not only the phase pattern is different, but also the degree of phase segregation is quite large in dynamic samples. For example, at center, $0.5\ \mu\text{m}$ of domain size is seen for the state sample while $2\text{--}3\ \mu\text{m}$ for the dynamic sample. This can be explained by shear induced phase separation (low shear rate) and longer cooling time. Due to the heat released by friction during shearing, a longer time is needed for cooling down the dynamic sample, which gives the sample more time for phase separation.

TYPICAL STRESS-STRAIN CURVES AND SHEAR INDUCED MOLECULAR ORIENTATION

Among the materials used, namely, HDPE, LDPE, PP, LLDPE, PS, the highest enhancement of tensile strength is observed for HDPE, from $26.4\ \text{MPa}$ (static) to $107.3\ \text{MPa}$ (dynamic). The lowest enhancement of tensile strength

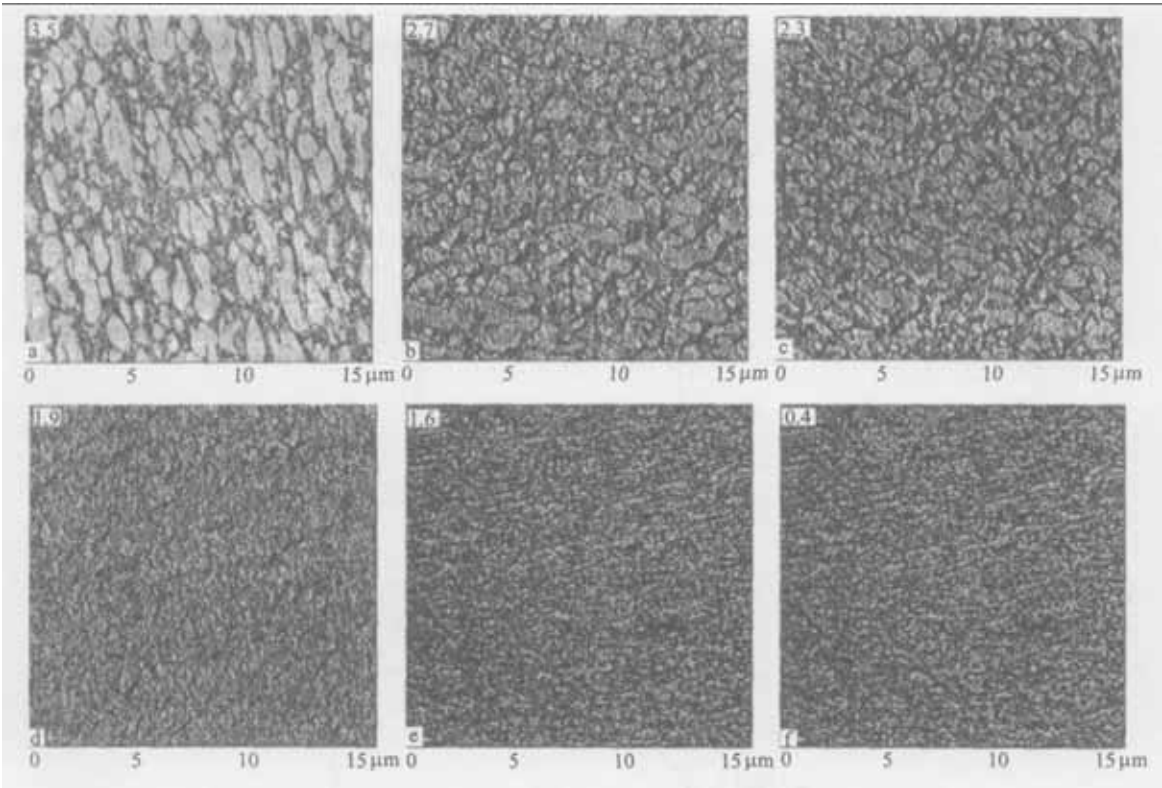


Fig. 6 AFM photographs of a dynamic sample taken at different positions, the number on each photo represents the distance to the edge

Table 1. Mechanical properties of pure polyolefin samples

	Tensile strength (MPa)		Elongation at break (%)	
	Static samples	Dynamic samples	Static samples	Dynamic samples
HDPE	26.4	107.3	180	40
LDPE	10.8	18.7	740	450
PP	35.2	63.6	200	100
LLDPE	17.1	37.4	240	50
PS	36.9	41.7		

is seen for LDPE, from 10.8 MPa (static) to 18.7 MPa, and for PS, from 36.9 MPa to 41.7 MPa. An intermediate enhancement of tensile strength is obtained for PP and LLDPE. The data of tensile strength and elongation are collected in Table 1. As examples, the typical stress-strain curves of pure HDPE and PP for both dynamic and static samples are shown in Fig. 7 and Fig. 8, respectively. The different enhancement of tensile strength can be understood as the result of the different molecular architectures among the polyolefins. HDPE has a linear structure, LDPE has a highly branched structure and PS has a benzene ring attached on the backbone. PP and LLDPE lie in between. The highest orientation for HDPE and lowest orientation for LDPE and PS are expected under the shear stress. This result suggests that the molecular chain orientation plays an important role in determining the tensile strength. A high level molecular orientation is obtained as a result of dynamic packing injection molding processing, and is the primary reason for the improved tensile strength of dynamic samples in comparison to the static samples. The enhancement of tensile strength, however, is accompanied by a substantial decrease of the elongation at break, which is closely related to the toughness of a material. For example, almost 4.5 and 4.8 times decrease of elongation at break is seen for HDPE and LLDPE after subjection to dynamic injection molding, from 180% and 240% to 40% and 50%, respectively (see Table 1). Nevertheless, by using the polyolefin blends, we have obtained the super polyolefin with high tensile strength and high elongation as well.

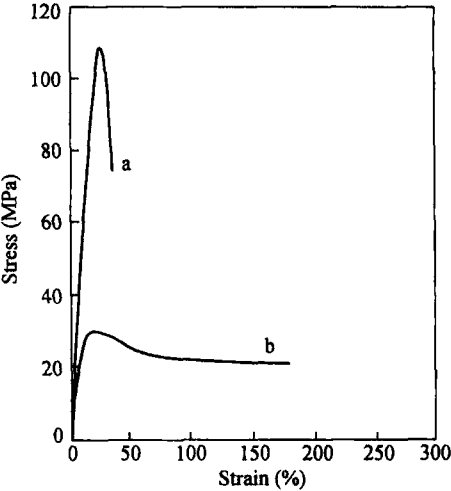


Fig. 7 Typical stress-strain curves for pure HDPE
a) Dynamic sample; b) Static sample

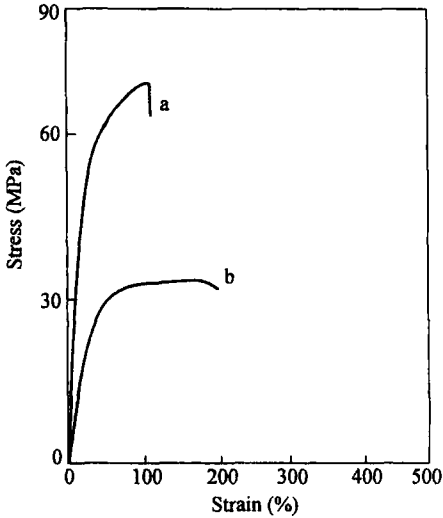


Fig. 8 Typical stress-strain curves for pure PP
a) Dynamic sample; b) Static sample

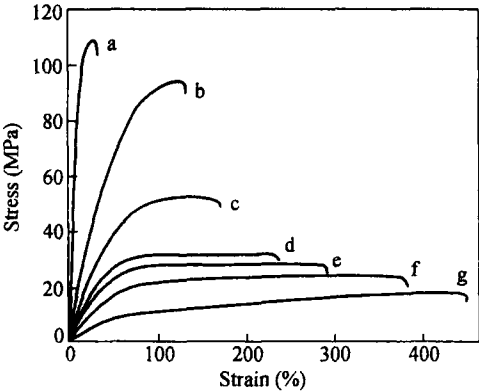


Fig. 9 Typical stress-strain curves of the dynamic samples for HDPE/LDPE blends
a) 100/0; b) 80/20; c) 60/40; d) 50/50; e) 40/60; f) 20/80; g) 0/100

As examples, the typical stress-strain curves of dynamic samples are depicted for HDPE/LDPE blends in Fig. 9. The tensile strength of HDPE/LDPE = 80/20 is 98.5 MPa, close to that of the dynamic sample of pure HDPE (107.4 MPa), but the elongation (140%) also approaches that of the static sample of pure HDPE (180%). To check the change of molecular orientation under shear stress, 2d-WAXD experiment was carried out. Figure 10 shows the 2d-WAXD results of HDPE/LDPE blends. One observes a decrease of orientation with increasing LDPE content, as expected. No orientation is seen for HDPE/LDPE = 20/80 and for pure LDPE. The molecular orientation changes not only with the molecular architectures, but with the sample position as well, as shown in Fig. 11, the highest orientation is seen in the oriented zone and little orientation in the center. The orientation in the skin zone lies in between.

TENSILE STRENGTH AND IMPACT STRENGTH OF HDPE/EVA BLENDS

An example, we discuss here the change of tensile strength and impact strength of HDPE/EVA with VA contents. The tensile strengths of HDPE/EVA blends obtained by both static and dynamic packing injection moldings are shown in Fig. 12 as a function of composition. For the static sample one finds an almost linear decrease of tensile

strength with increase of EVA content, as expected. The VA content in EVA does not have very much effect on the tensile strength of HDPE, which changes from 34 MPa to 12–17 MPa as the EVA content increases to 50 wt% for all three kinds of EVA. On the other hand, for the dynamic sample, the tensile strength of pure HDPE is greatly enhanced to 125 MPa. For the blends, the tensile strength declines to 70–90 MPa as the EVA content increases to 30 wt%. For HDPE/16EVA, a linear relationship is seen up to 50 wt% 16EVA. However, one observes a sharp drop of tensile strength at 30 wt% for HDPE/33 EVA and HDPE/41EVA blends. Young’s modulus of the dynamic samples is much higher than that of static samples as a result of shear induced-molecular orientation. This is listed in Table 2. For example, the modulus of HDPE is 0.71 GPa for static sample, but 2.47 GPa for the dynamic sample; for the blends of HDPE/EVA = 80/20, it was 0.48–0.52 GPa for the static samples, but 1.77–2.17 GPa for the dynamic samples. Moreover, the tendency of the modulus to vary with the composition (both dynamic and static) is similar to that of tensile strength.

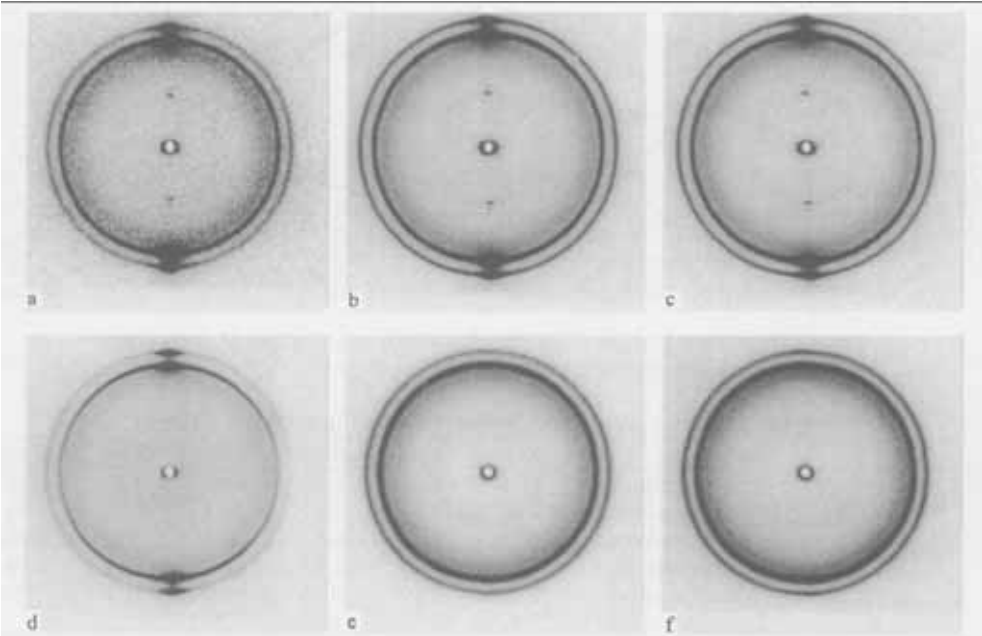


Fig. 10 2d-WAXD patterns of HDPE/LDPE as function of composition, HDPE/LDPE = (a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80 and (f) 0/100

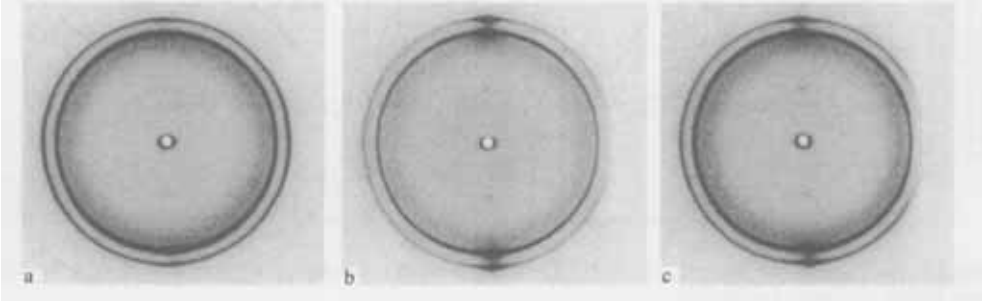


Fig. 11 2d-WAXD patterns of HDPE/LDPE = 60/40 at different position (a) in the core, (b) oriented zone and (c) skin

The enhancement of tensile strength and modulus mostly originates from the formation of an oriented layer that consists of microfibrils in the dynamic samples. Consequently, with the increase of EVA content, the amount

of molecules forming microfibers decreases, thus the tensile strength declines with the rising EVA content in HDPE/EVA (either 16EVA, 33EVA or 41 EVA). In addition, the amount of orientation structure that depends on rheological properties, melt temperature, die temperature as well as dynamic frequency and pressure plays a vital role for the tensile strength^[24]. Figure 13 shows the corresponding relative impact strength of HDPE/EVA blends produced by static and dynamic packing injection moldings. The impact strength of static specimens in general rises with increasing content of EVA, which is in agreement with the classic theory^[20]. For the dynamic specimens, one observes a maximum at 10 wt% EVA for HDPE/16EVA, and at 20 wt% EVA for HDPE/33EVA and HDPE/41EVA, respectively. At the maximum of HDPE/33EVA, a 6-fold increase of impact strength is achieved compared with the static sample of pure HDPE. Figure 14 shows the morphological change as a function of EVA content for HDPE/33EVA blends at the oriented zone where the effect of shear stress can be best demonstrated. Besides some spherical particles, the elongated and elliptical EVA particles are observed too.

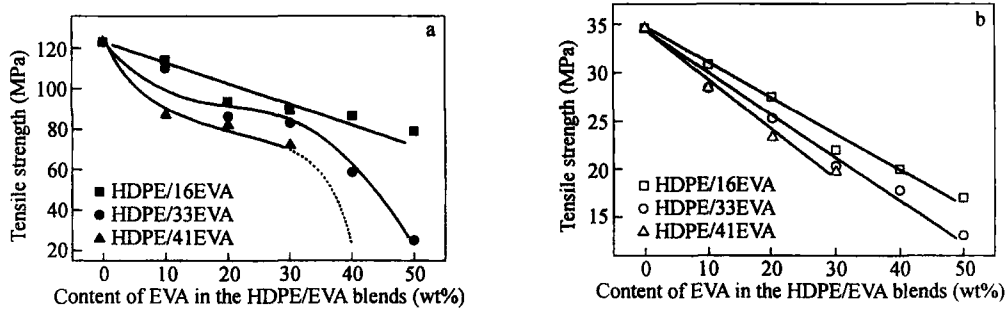


Fig. 12 The tensile strength of HDPE/EVA blends as a function of composition
a) Dynamic samples; b) Static samples

Table 2. The values of Young's modulus (GPa) of HDPE/EVA blends

		100/0	90/10	80/20	70/30	60/40	50/50
HDPE/16EVA	Static samples	0.71	0.65	0.49	0.46	0.42	0.36
	Dynamic samples	2.47	2.39	2.17	2.01	1.85	1.55
HDPE/33EVA	Static samples	0.71	0.59	0.52	0.41	0.36	0.26
	Dynamic samples	2.47	2.31	1.86	1.81	1.41	0.56
HPDE/41EVA	Static samples	0.71	0.59	0.48	0.39		
	Dynamic samples	2.47	1.84	1.77	1.51		

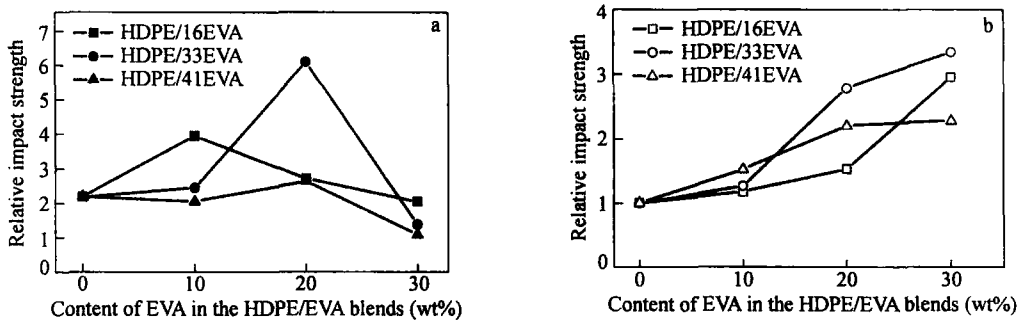


Fig. 13 The relative impact strength of HDPE/EVA blends as a function of composition, taking the value of pure HDPE of static sample as 1
a) Dynamic samples; b) Static samples

Therefore, it can be concluded that super HDPE/EVA blends having high modulus (1.9–2.2 GPa), high tensile strength (100–120 MPa) and high impact strength (6 times that of pure HDPE) can be obtained by controlling the phase separation, molecular orientation and crystal morphology of the blends via dynamic packing injection molding.

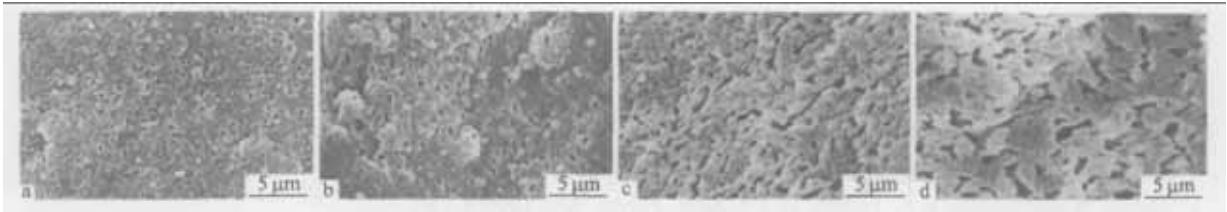


Fig. 14 Morphological change as a function of EVA content for HDPE/33EVA blends at the oriented zone, HDPE/33EVA = (a) 90/10, (b) 80/20, (c) 70/30, (d) 60/40

CONCLUSION AND REMARKS

In summary, dynamic packing injection molding is proven to be a powerful method to control the morphology, and hence the mechanical properties of polyolefin blends. Super polyolefin blends with high stiffness and high toughness can be obtained by this method. Molecular architecture, composition and interfacial interaction play important roles in determining the molecular orientation, phase separation and crystal morphology. Further studies are needed in the following several aspects. (1) Our preliminary result on LLDPE/PP blends has showed that phase dissolution may take place under high shear rate, it will be interesting to control the phase morphology of polymer blends via phase dissolution at high shear rate combined with dynamic packing injection molding at low shear rate. (2) Since the fracture direction and tensile direction also play roles in determining the impact strength and tensile strength, further fracture and tensile experiments are needed on samples with different orientation with respect to the fracture and tensile propagation direction. To do this, a proper specimen dimension is needed, as shown in Fig. 15, which allows us to get the impact and tensile strength both parallel and

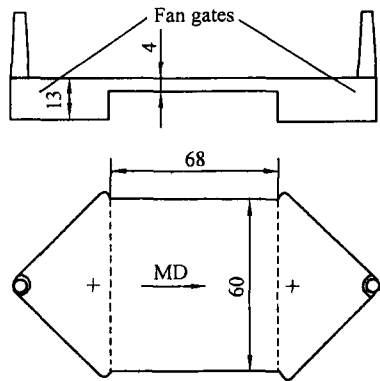


Fig. 15 The sketch of mechanical test specimen dimensions with large width

perpendicular to the shear flow directions. (3) The change of orientation of the matrix as well as the dispersed droplets will have a big effect on the mechanical properties of the obtained polyolefin blends. This holds particularly for polyolefin blends containing rubber particles. Since the glass transition temperature of a rubber is far below room temperature, it is logical to ask how long the elongated and oriented rubber particles still remain unchanged, and at which temperature they will change back to the spherical shape. Thus it is important to collect detailed information on the degree of orientation as function of molecular architecture, composition, shear stress, time and temperature.

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