

Super Polyolefin Blends Achieved Via Dynamic Packing Injection Molding: Tensile Strength

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ABSTRACT: The tensile strength of some polyolefin blends, HDPE/PP, HDPE/LDPE, HDPE/LLDPE, and PP/LLDPE, achieved by dynamic packing injection molding have been investigated as a function of composition and melt temperature. Molecular architecture and phase behavior play an important role in chain orientation, hence the tensile strength. For HDPE, which has a linear structure, the highest enhancement of tensile strength is obtained. LDPE, which has a highly branched structure, the smallest enhancement is seen. PP and LLDPE lie in between. Super polyolefin blends with high tensile strength and high elongation have been obtained by this method. The shear-induced morphologies with core in the center, oriented zone surrounding the core and skin layer were observed in the cross-section areas of the samples. The tensile strength was found to be directly proportional to the area of the oriented zone. When the area of oriented zone is less than 35%, the tensile strength is not only the orientation dependency but the blending components dependency as well. When the area of oriented zone is more than 35%, however, our new finding is that the orientation will be the dominating parameter to determine the tensile strength of the blends, independent of the components, the composition, molecular architecture, phase behavior, and crystal morphology. The maximum tensile strength for all the polyolefin blends is extrapolated as to 230MPa, as the area of oriented zone reaches to 100%. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 236–243, 2002

Key words: polyolefin blends; dynamic shear stress; orientation; tensile strength

INTRODUCTION

Polyolefin are the most important plastics. Polyethylene and polypropylene have the most products, and lies in the first position of plastics. Polyolefin blends are frequently used to get the balanced mechanical and processing property. For example, LLDPE/LDPE blends have properties which combine a high toughness of LLDPE with the good melt processability of LDPE.¹ The properties of the individual polyolefin can be changed

in a significant way by mixing with other components. For this reason, polyolefin blends have attained widespread commercial applications.^{2–6} Polymer researchers have long sought to understand the relationships between morphology and properties of polyolefin blends, and to control the micro-phase separation, morphology, and orientation of studied blends, in order to get excellent properties.

In recent years, dynamic packing injection molding has been found to be a very important way to control polymer morphology and mechanical properties. The pioneering work on dynamic packing injection molding began in 1986, when Professor Bevis reported such technology and

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Table I Product Characteristics of the Polymers Studied

Sample Code	Trademark	Melt Index (g/10 min)	Manufacturer
HDPE	7006A	6.8	Qi Lu petroleum chemical, China
LLDPE	7042	2.0	Ji Lin petroleum chemical, China
LDPE	1F7B	7.0	Yan Shan petroleum chemical, China
PP	1300	1.0	Yan Shan petroleum chemical, China

owned the patent.⁷ Since then, many investigations have been done on the self-reinforcement of injection-molded polyolefin by using high injection pressure,^{8,9} elongation flow,^{10,11} or successive macroscopic shears to a solidifying melt in the mold.^{12,13} Prox achieved a self-reinforcement of iPP with 2.5-fold increase of the modulus of elasticity and tensile strength compared with the sample normally processed (static packing injection molding).⁹ Guan and Shen used a similar technology to realize the self-reinforcement of HDPE and PP under low pressure.¹⁴ The Young's modulus and tensile properties have been greatly enhanced for HDPE and PP by this method. Biaxial self-reinforcement of iPP, prepared in uniaxial dynamic stress field by injection molding, has also been reported by Chen and Shen.^{15,16} The control of polymer properties by melt vibration technology was summarized in recent review by Ibar.¹⁷ Highly oriented polyolefin with high stiffness and high strength can also be produced via various routes,^{18–20} such as extrusion, die-drawing, and compression.

As part of long-term project aimed at super polyolefin blends, we are seeking to establish a fundamental understanding of structure–property–processing relationships through the control of phase separation, molecular orientation, and crystal morphology of polyolefin blends. The enhancement of tensile strength of some polyolefin blends achieved by dynamic packing injection molding is reported in this article, and the morphological details and phase relations will be reported elsewhere.²¹

EXPERIMENTAL

Materials

The high density polyethylene (HDPE), linear low density polyethylene (LLDPE), low density polyethylene (LDPE), and polypropylene (PP), used in the experiment are all commercialized products, and are summarized in Table I.

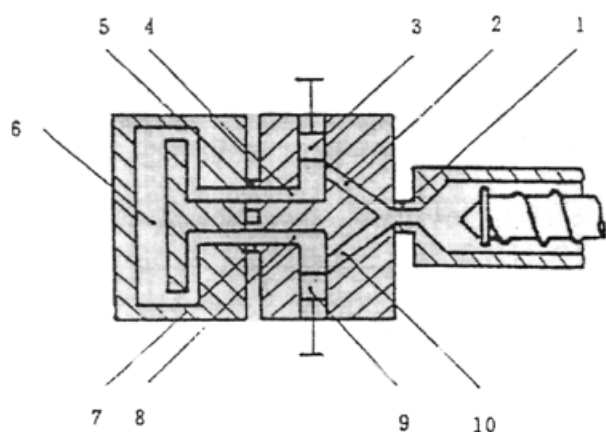


Figure 1 Presentation of dynamic packing injection molding. (1) nozzle, (2) sprue A, (3) piston A, (4) runner A, (5) connector, (6) specimen, (7) connector, (8) runner, (9) piston B, (10) sprue B.

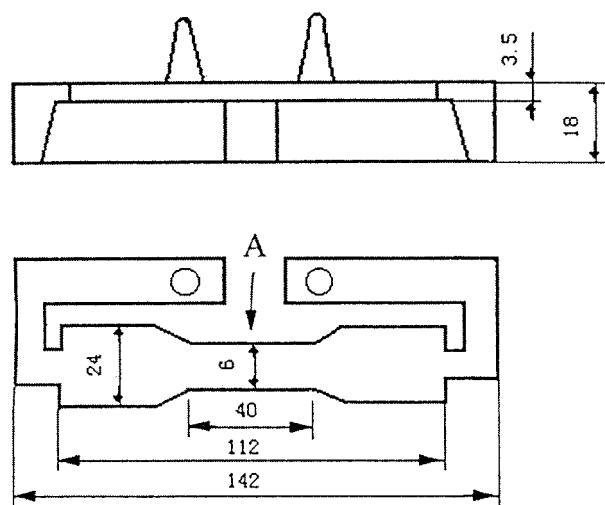


Figure 2 The sketch of mechanical test specimen dimensions according to the ASTM638 M standard.

Table II Processing Parameters in Dynamic Packing Injection Molding

Processing Parameters	Parameters Value
Injection pressure (MPa)	90
Packing pressure (MPa)	50
Melt temperature (°C)	180
Mold temperature (°C)	20
Dynamic packing pressure (MPa)	35
Dynamic packing frequency (Hz)	0.3

Sample Preparation

Four binary systems: (i) HDPE/LLDPE, (ii) HDPE/LDPE, (iii) PP/LLDPE, and (iv) HDPE/PP were chosen to make the blends. Melt blending of a pair of polymers was conducted using a twin-screw extruder (TSSJ-25 co-rotating twin-screw extruder). After making droplets, the blends were molded by dynamic packing injection molding technology. The schematic representation of this technology is shown in Figure 1 and the specimen dimension is shown in Figure 2. The detailed experiment procedures were described in references.¹⁴ The main feature is that the specimen is forced to move repeatedly in chamber 5 by two pistons that move reversibly with the same frequency during cooling. The processing parameters are listed in Table II. Injection molding under static packing was also carried out using the same processing parameters for comparison purposes. The specimen obtained by dynamic packing molding is called the dynamic sample, and the specimen obtained by static packing injection molding is called the static sample.

Tensile Strength Measurement

A Shimadzu AG-10TA Universal Testing Machine was used to obtain the stress–strain curves

and the tensile strengths; the moving speed was 50mm/min, and the measure temperature was 20°C.

RESULTS AND DISCUSSION

Typical Stress–Strain Curves

Let's start from the pure polyolefin. The highest enhancement of tensile strength is observed for HDPE, from 26.4 Mpa (static) to 107.3 Mpa (dynamic). The lowest enhancement of tensile strength is seen for LDPE, from 10.6 Mpa (static) to 18.7 MPa only. The intermediate enhancement of tensile strength is obtained for PP and LLDPE. The data of tensile strength and elongation are collected in Table III. As examples, the typical stress–strain curves of pure HDPE and PP for both dynamic and static samples are shown in Figure 3 and Figure 4, respectively. The different enhancement of tensile strength is due to the different molecular architectures among the polyolefin. HDPE has a linear structure, and LDPE has a highly branched structure. PP and LLDPE lie in between. The highest orientation for HDPE and lowest orientation for LDPE are expected under the shear stress. This result suggests that the molecular chain orientation plays an important role in 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 the dynamic samples in comparison to the static samples. The enhancement of tensile strength, however, is accompanied with a substantial decrease in the elongation at break, which is closely related to the toughness of the material. For example, almost 4.5 and 4.8 times decrease in elongation at break is seen for HDPE and LLDPE after subjecting to the dynamic injection

Table III Mechanical Properties of Pure Polyolefin Samples

	Tensile Strength (MPa)			Elongation at Break (%)		
	Static Sample	Dynamic Sample	Increase (%)	Static Sample	Dynamic Sample	Decrease (%)
HDPE	26.4	107.4	4.07	180	40	4.5
LLDPE	17.1	37.4	2.19	240	50	4.8
LDPE	10.8	18.7	1.73	740	450	1.64
PP	35.2	63.6	1.81	200	100	2.0

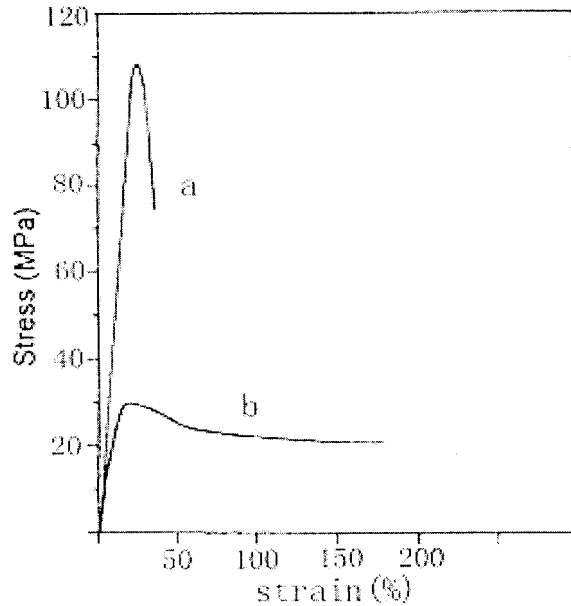


Figure 3 Typical stress-strain curves for pure HDPE: (a) dynamic sample, and (b) static sample.

tion molding, from 180% and 240%, to 40% and 50%, respectively (Table III). Nevertheless, by using the polyolefin blends, we have obtained the

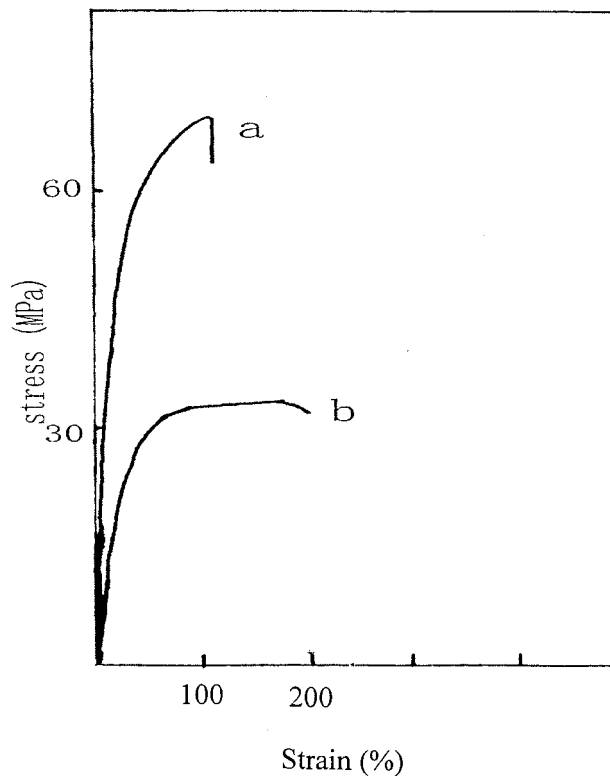


Figure 4 Typical stress-strain curves for pure PP: (a) dynamic sample, and (b) static sample.

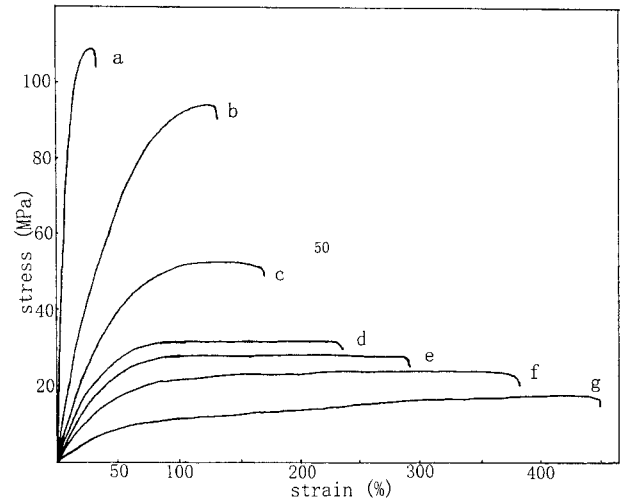


Figure 5 Typical stress-strain curves of the dynamic samples for HDPE/LDPE blends: (a) 100/0, (b) 80/20, (c) 60/40, (d) 50/50, (e) 40/60, (f) 20/80, and (g) 0/100.

super polyolefin with high tensile strength and high elongation as well. For example, the typical stress-strain curves of dynamic samples for HDPE/LDPE blends are depicted in Figure 5. 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 reaches to that of the static sample of pure HDPE (180%). Therefore, making blends is a good way to achieve high performance materials with high stiffness and high toughness as well.

Tensile Strength Versus Composition

The tensile strengths of the four polyolefin blends, as a function of composition, are shown in Figure 6–9, respectively. For static samples, a rough linear relationship of the tensile strength with composition can be obtained for all the blending systems. So the additive law can be used, that is:

$$P = \beta_1 \times P_1 + \beta_2 \times P_2,$$

where P , P_1 and P_2 are the tensile strength of the blends and pure polyolefin, respectively; and β_1 and β_2 are corresponding weight percentages. The four systems have different phase morphology both in the solid state and the liquid state. HDPE/LDPE blends can form a single phase in the melt for almost all the concentrations,^{22,23} and HDPE/PP blends are subject to liquid-liquid phase separation in most of the composition range.^{24,25} The result suggests that the additive

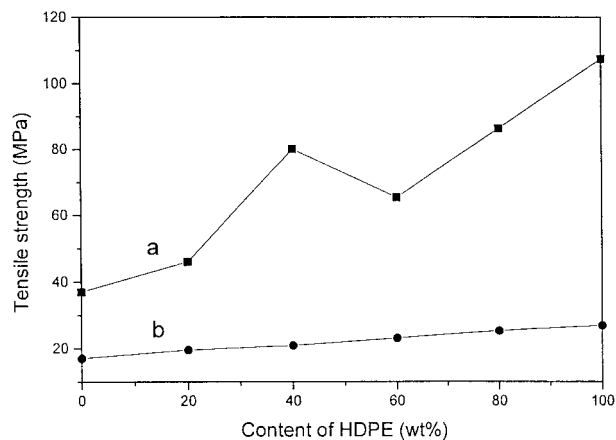


Figure 6 Tensile strength of HDPE/LDPE blends as a function of composition: (a) dynamic samples, and (b) static samples.

law always fits, whether the blends are phase-miscible or phase-separated. Thus, the additive law is not sensitive to phase behavior for static samples. The tensile strength is 26.4 MPa for HDPE, 16.54 MPa for LLDPE, 12.8 MPa for LDPE, and 35.8 MPa for PP, so the tensile strength for any two polyolefin blends can be obtained easily by the above additive law. For examples, the tensile strength for HDPE/LLDPE (80/20) can be calculated as: $26.4 \times 0.8 + 16.54 \times 0.2 = 24.4$ MPa, while the measured value is 22.1 MPa; the tensile strength for HDPE/LDPE (50/50) is calculated at $26.4 \times 0.5 + 12.8 \times 0.5 = 18.5$ MPa, measured is 17.7 MPa, the tensile strength for PP/LLDPE (40/60) equals $35.8 \times 0.4 + 11.5 \times 0.6 = 21.2$ MPa, measured is 20.4 MPa. So the calculated values and measured values fit well within experimental error.

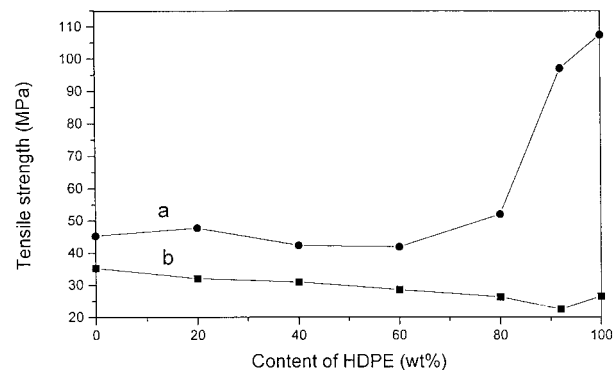


Figure 7 Tensile strength of HDPE/PP blends as a function of composition: (a) dynamic samples, and (b) static samples.

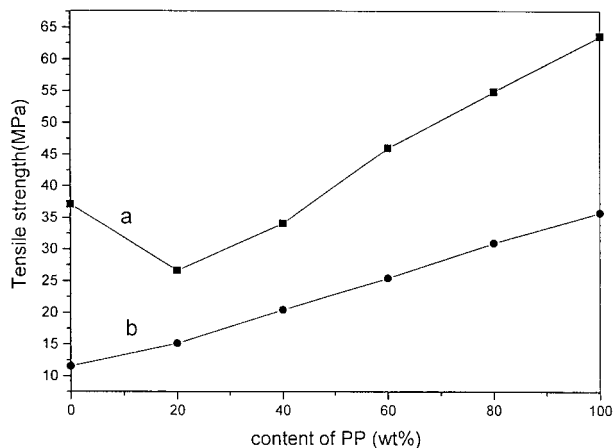


Figure 8 Tensile strength of PP/LLDPE blends as a function of composition: (a) dynamic samples, and (b) static samples.

The tensile strength for dynamic samples changes from one system to another. For HDPE/LLDPE blends, the additive law holds true, except when HDPE/LLDPE equals 40/60, where the positive deviation is found. For HDPE/LDPE, PP/LLDPE, and HDPE/PP blends, there exists a negative deviation from additive law in almost the whole range of compositions. For PP/LLDPE, the minimum tensile strength at PP/LLDPE equals 20/80; some special interaction and crystal morphology have been reported.^{26,27} For HDPE/PP and HDPE/LDPE systems, only when HDPE composition is more than 90 wt % or 80 wt % can remarkable enhancement of tensile strength be achieved. More work has to be done to understand

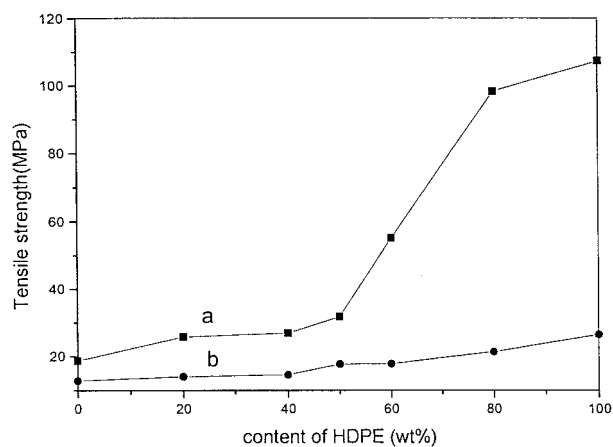


Figure 9 Tensile strength of HDPE/LLDPE blends as a function of composition: (a) dynamic samples, and (b) static samples.

Table IV Tensile Strength (MPa) of Dynamic Samples for HDPE/LDPE Blends at Different Temperatures

HDPE/LDPE (wt %)	Temperature (°C)		
	180	200	220
40/60	26.9	25.8	27.7
55/45	27.6	27.1	28.4
50/50	31.7	28.0	28.6
55/45	33.8	28.0	29.6
60/40	55.1	29.0	31.5

the change of tensile strengths for each of the systems. Several factors should be considered, such as phase behavior in the melt, viscosity ratio, molecular entanglement, crystal morphology, and chain orientation, and this will be reported in our next article.²¹

The Effect of Melt Temperature

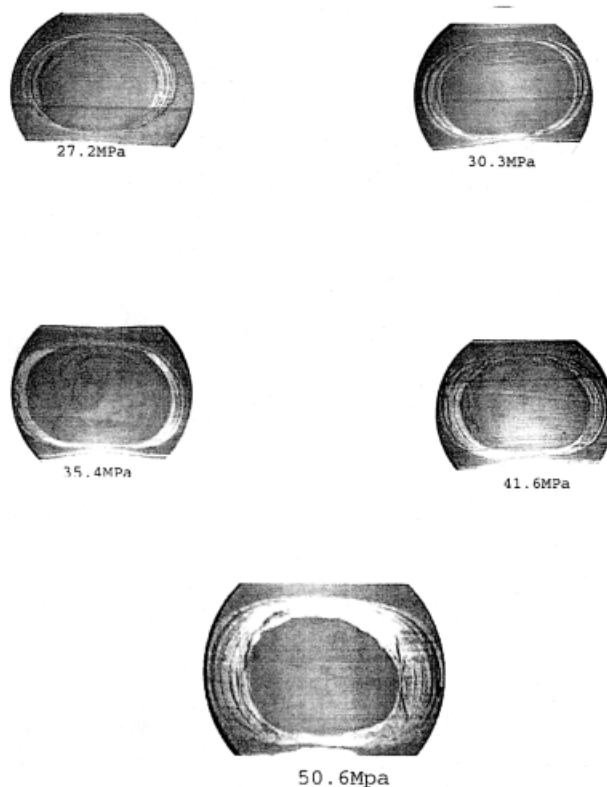
Not only the composition but the melt temperature also greatly affects the tensile strength. The change of tensile strength with melt temperature for HDPE/LDPE system is listed in Table IV, for one example. When the melt temperature is more than 200°, the tensile strength is not much enhanced for all the selected compositions. The similar result can also be found for the other systems. As another example, the tensile strengths of PP/LLDPE for two compositions (20/80 and 80/20) at three melt temperatures are listed in Table V. The tensile strength decreases with the increasing of the melt temperature. This is probably due to the fact that the orientation induced by shear stress can't be easily fixed when the melt temperature is getting higher.

Tensile Strength Versus Oriented Zone

Macroscopically, the main features for dynamic samples are the shear-induced morphologies with

Table V Tensile Strength (MPa) of Dynamic Samples for PP/LLDPE Blends (20/80, 80/20) at Different Temperatures

PP/LLDPE (wt %)	Temperature (°C)		
	180	200	220
20/80	26.6	23.6	19.4
80/20	54.8	41.1	36.5

**Figure 10** The photographs of the cross-section of the dynamic samples for HDPE/LDPE blends.

a core in the center, an oriented zone surrounding the core, and the skin layer in the cross-sectional areas of the samples. The photographs of the cross-section of HDPE/LDPE are shown in Figure 10. The corresponding tensile strengths are also given in the Figure. The general trend is that the larger the oriented zone, the higher the tensile strength. The percentage of the oriented zone, S , can be calculated by: S equals the area of oriented zone/the whole area of the cross-section. In reality, we measure the weight of the whole cross-section of the photographs, W_c , then cut out the core and skin layer from the photographs and measure the weight of the remaining paper, W_o . So $S = W_o/W_c$, which also can be considered the degree of orientation in the samples. We plot the tensile strength dependency of the percentage of the oriented zone, S , in one common figure, for all the systems except PP/LLDPE (Fig. 11). The data for PP/LLDPE are not presented because the oriented zone is not easily distinguished from the other parts. The tensile strength was found to increase linearly with increasing S for all the three systems, up to $S = 35\%$. But the slope is different from system to system, which indicates

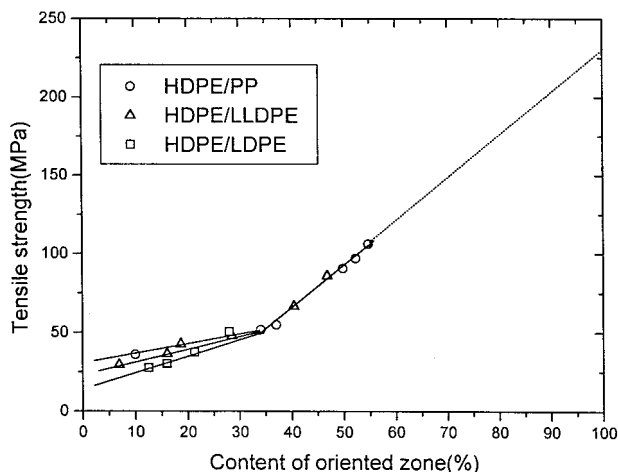


Figure 11 Tensile strength versus the percentage of the oriented zone.

that tensile strength is not only dependent on molecular orientation but on blending components as well when the degree of orientation is less than 35%. In this case, the phase behavior and crystal morphology of the blends may also play an important role to determine the tensile strength. All the data in three systems, however, fit one common line when S is larger than 35%. This result suggests that the molecular orientation will be the dominating parameter to determine the tensile strength of the polyolefin blends when S is larger than 35%. All the polyolefin blends will have the same tensile strength provided that their orientations are more than 35%, disregarding their composition, molecular architecture, phase behavior and crystal morphology. If we extrapolate that $S = 100\%$, the maximum tensile strength that can be obtained is 230 MPa, which is close to the value of ultrahigh-molecular weight polyethylene (UHMWPE) obtained by high pressure injection molding.²⁸ However, the tensile strength of UHMWPE produced by the gel spinning can be as high as 5 GPa.²⁹ A big potential to improve the tensile strength of polyolefin blends exists by processing methods.

CONCLUSIONS

In summary, the dynamic packing injection molding is proven to be a powerful method to enhance the molecular orientation, hence, the tensile strength of polyolefin blends. Super polyolefin blends with high stiffness and high toughness can

be obtained by this method. Molecular architecture has a big effect on chain orientation. The highest enhancement for HDPE and a small enhancement for LDPE are seen. Additive law can be used to roughly describe the tensile strength for the static samples. However, the tensile strength does not fit additive law for the dynamic samples, and a negative deviation is found in most of the cases. When the degree of orientation in a sample is less than 35%, the tensile strength is dependent both on blending components and on orientation. However, when the degree of orientation is more than 35%, the orientation will be the dominating parameter in determining the tensile strength, independent of blending components, the composition, molecular architecture, phase behavior and crystal morphology. More work is needed to investigate crystal and phase morphology, as well as the orientation details of the obtained samples, in order to fully understand the mechanism of property enhancement.

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