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# Study on the in-situ synthesis and the crystallization, mechanical, dielectric properties of Polypropylene/Polybutene-1

Lingfei Li<sup>1</sup>, Qiu Sun<sup>1,\*</sup>, Hegang Ren<sup>2</sup>, Yongjun Xu<sup>1</sup>, Zhaohua Jiang<sup>1,\*</sup>

<sup>1</sup>School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, China

<sup>2</sup>Daqing Petrochemical Research Center, Petrochemical Research Institute of China National Petroleum Corporation (CNPC), Daqing, China

\*Corresponding author e-mail: jiangzhaohua@hit.edu.cn, sunqiu@hit.edu.cn

**Abstract.** Polymeric materials are widely used as capacitor diaphragm materials because of their good pressure resistance, low dielectric loss, good processing performance and good compatibility with devices. In this experiment, the Polypropylene/Polybutene-1 (PP/PB-1) resin was prepared by the reaction of butene-1 polymerization using the modified intermittent bulk polypropylene polymerization reactor. The structure and morphology of the prepared PP/PB-1 were characterized by DSC, POM and FT-IR so on. The effects of different prepolymerization time on their crystalline morphology and mechanical properties were investigated. As the polypropylene prepolymerization time becomes longer, the content of Polypropylene in the synthesized polybutene-1 sample increased gradually, and the spherulitic size and nucleation time of polybutene-1 were changed. In addition, the tensile properties of the product were also improved. The PP/PB-1 film was prepared by the film drawing machine using synchronous biaxial stretching method. It was found that when the tensile temperature was 130 °C and the tensile rate was 40mm / min, the prepared PP/PB-1 films had the best dielectric properties. At this time, the dielectric constant was 2.9, and the dielectric loss tangent was low (<0.005).

## 1. Introduction

High density capacitors[1,2] (HEDC) refer to capacitors which can store more energy in a unit volume. Dielectric materials with high dielectric constant and low dielectric constant are usually used as charge storage thin films. Polymer materials are widely used as the diaphragm material because of its good pressure resistance, low dielectric loss, good processing performance and good compatibility with the device. Polybutene-1 is called "plastic gold", which has good mechanical properties, heat resistance and insulation properties. At present, the application of PB-1 at home and abroad is mainly in the aspect of pipe materials, accounting for about 80%. There are few studies on thin films. The properties of PB-1 are mainly focused on the crystallization properties, mechanical properties and flame retardant properties. The relationship between viscoelastic behavior and morphology of polypropylene/polybutene-1 blends was investigated by F. Ardakani[3,4]. They studied the morphology and rheological behavior of PP/PB-1 blends with different compositions. Guozheng Ping[5] studied the dielectric properties of graphene/polybutylene-1 composites, and found that adding graphene will make the dielectric constant of the composite membrane increased, and dielectric loss is



low. At the same time, tensile properties and thermal stability of films were also improved.

Solution or gas phase polymerization is usually used for PB-1 production in foreign, but the solution method usually needs a large number of solvent recoveries, which is complicated in postprocessing technology. The gas phase method has a high demand for the technology and equipment, and the investment is large, currently in development and trial production stage. In this study, we use of bulk polymerization, namely the use of batch bulk propylene polymerization kettle to transform the butene-1 polymerization. The preparation of PP/PB-1 resin material can be finished. The prepared PP/PB-1 samples were hot-pressed into the sheets by hot pressing. Using the self-made polyolefin stretching equipment, the prepared sheets were made into films under the set process conditions. The dielectric measurements of films were carried out using a broadband dielectric spectrometer[6]. The effects of different prepolymerization time on the crystalline morphology, mechanical properties and dielectric properties of PP/PB-1 were investigated in this paper.

## 2. Experimental

### 2.1 Materials

N-Hexane (Analytical Pure), Rionlon Bohua (Tianjin) Pharmaceutical Chemical Co., Ltd.; triethylaluminum, Albemarle; cyclohexylmethyldimethoxysilane CHMMS (> 99%), Alfa Aesar; spherical catalyst, Daqing Petrochemical company; propylene, butene-1, hydrogen, Daqing Petrochemical Company; argon, 99.9%, Tianjin Burke gas plant.

### 2.2 Preparation of polypropylene / polybutene-1 resin

A 2L stainless steel stirred tank was thoroughly replaced with high-purity argon, followed by the addition of 1.0 mol/L triethylaluminum hexane solution, external electron donor silane compound, spherical catalyst, propylene into the tank, and a pre-polymerization reaction took place at the temperature of 50 °C. The time of pre-polymerization reaction was set to 0min, 10min, 20min, 40min respectively. When the pre-polymerization finished, the unreacted propylene monomer and the n-hexane solvent were evacuated under reduced pressure. After the addition of butene-1 and hydrogen, the system was heated to the needed temperature, and kept the polymerization reaction for 3 hours. Then the excess butene-1 was released and cooled to room temperature. Finally a series of PP/PB-1 resin materials were obtained, and the samples were labeled PB0, PB10, PB20 and PB40.

### 2.3 Preparation of polypropylene/polybutene-1 film

The sample obtained in the last step was put into a mold for hot pressing at the temperature of 190 °C for 10min, without extra pressure initially, and then the material was melted and filled with mold cavity. In the Next step, an extra pressure of 15 MPa was put on the mold. 8min later the pressure was relieved and the gas inner was released, immediately after this process the pressure was recovered to 15 MPa and maintained for 10 min.

Then the mold was put into the cold press with the maintained pressure of 15 Mpa until the sample was naturally cooled to room temperature when the sheets of the samples were obtained. By simultaneous stretching at the set temperature 130 °C and rate 40mm/min through biaxial stretching machine in the laboratory, the sheets of the samples were transformed to the PP/PB-1 films, which were labeled PBM0, PBM10, PBM20 and PBM40 afterward.

### 2.4 Characterization of Polypropylene / Polybutene-1 Materials and Films

#### 2.4.1 DSC examination

The DSC examination was performed under the protection of N<sub>2</sub>, using indium as a reference substance for calibration of temperature and melt enthalpy. The sample was examined after being loaded into a vessel, subsequently the sample was heated to 200 °C and held for 5 min to eliminate the thermal history. The temperature then was cooled to 30 °C and maintained for 2min, with the heating and cooling rate set at 10 °C/min. The melting temperature was subjected to the second temperature rise curve.

$$X_c = (\Delta H / \Delta H_f) \times 100\% \quad (1)$$

In the equation,  $\Delta H$  is the heat when the sample melts, whereas  $\Delta H_f$  is the heat when the sample completely crystallizes. According to literature [7], the standard value of  $\Delta H_f$  of polybutene-1 is 118.5 J/g, for polypropylene the value is 209 J/g.

### 2.4.2 Polarizing Microscope

Polarized photographs were gained using DMLP polarized light microscopes from LEICA, Germany. The samples were heat treated at 200 °C for 3 min, covered with coverslips, and then left at room temperature for 7 days to observe the crystalline form of the polymer.

### 2.4.3 FT-IR examination

The polymer was melted and laminated, and the crystal transition process and crystal state of the polymer were determined by Fourier transform infrared spectroscopy (FT-IR) from Nicolet Corporation.

### 2.4.4 Mechanical performance test

Shore hardness of the sample was tested according to GB/T531-92. The melt index was measured using the GT-4000-MI melt flow rate meter according to GB/T 3682-2000. The test was conducted under the temperature of 230 °C and the load of 2.16 kg. The cutting interval was set to 10 s and the number of cuts was 3. Tensile strength, yield strength and elongation at break were tested using AI-7000S tensile testing machine, according to GB/T1042-92 for testing and analysis.

### 2.4.5 Scanning Electron Microscope Observations

The morphology of the films was investigated with an S-4800 model scanning electron microscopy (SEM). Since the materials were non-conductive, the surfaces of films were sprayed with gold using the Gatan Precision Etching Coating System (PECS, Model 682) before the observations.

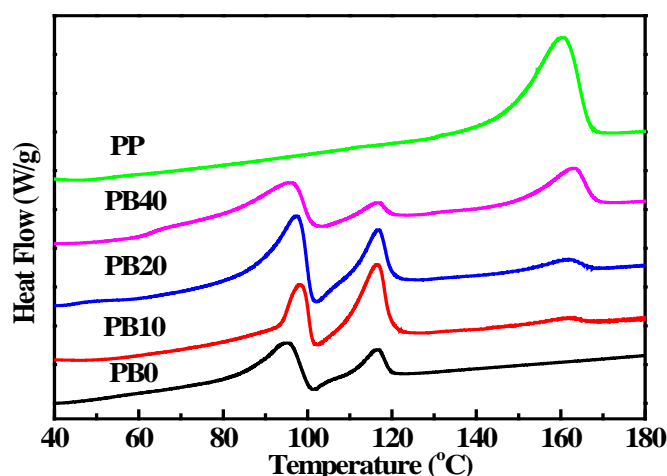
### 2.4.6 Dielectric properties test

Dielectric property was tested using a broadband dielectric impedance spectrometer (Novocontrol GmbH Concept 40 broadband dielectric spectrometer). The electrode was a rubber electrode under a frequency range of 0.1-10<sup>7</sup> Hz and 25 °C and 80 °C temperature.

## 3. Results and discussion

### 3.1 DSC examination

The isotactic polybutene-1 is a polycrystalline polymer with five types of I, II, III, I', II'. The melting points of the crystals are different, and the III and I' crystal structures are unstable. When the temperature is heated to near the melting temperature, the III and I' type crystals are converted into type II crystal form, and the metastable state II crystal form is converted to stable type I crystal form after being left at room temperature for more than 7 days. Therefore, the melting crystallization of the polymer was characterized by DSC. In order to study the problem of crystal transformation of polybutene-1, the polymer products were subjected to four DSC tests. The polymerization product was first heated and melted. After the thermal history was eliminated, cool to crystallize and then heat up to melt. Then the sample was placed at room temperature for 7 days, and then two further heating molten test were performed. The test results are shown in Figures 1 and 2 and Tables 1-3.

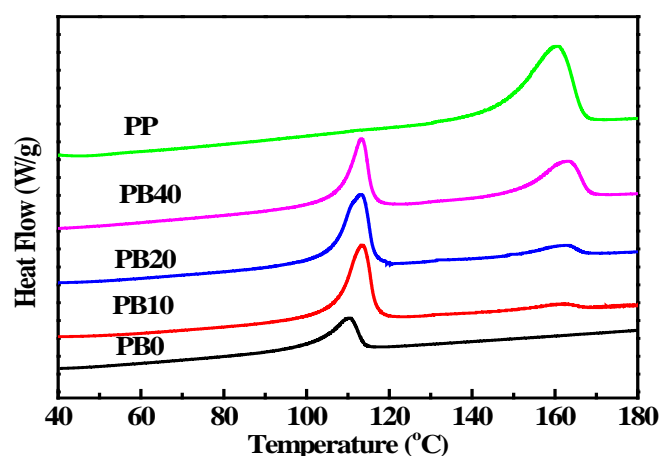


**Figure 1** DSC curves for the first temperature rise of different polymers

**Table 1** The results of the first heating of different polymers

Samples	PB-1 phase				PP phase		
	$T_{m1}$ (°C)	$\Delta H$ (J/g)	$T_{m2}$ (°C)	$\Delta H$ (J/g)	$T_m$ (°C)	$\Delta H$ (J/g)	$T_c$ (°C)
PB0	94.82	32.03	116.44	9.37	-	-	-
PB10	98.28	23.52	116.46	23.06	162.66	6.90	101.26
PB20	97.06	44.81	116.08	11.01	162.15	7.94	106.52
PB40	95.63	32.19	116.30	4.75	163.22	17.25	107.25
PP	-	-	-	-	160.21	79.15	117.13

Figure 1 and Table 1 show the results of the first temperature rise melting of the polymer. It can be seen from the table that pure polybutene-1 has two melting points, while pure polypropylene has only one melting point at 160.21 °C. However, there are three melting points of polymers prepared by in-situ polymerization, indicating that there are polybutene-1 and polypropylene. With the extension of the polymerization time of propylene, the melting peak of polypropylene is getting bigger and bigger, which is further confirmed that the content of polypropylene in the polymer is more and more. It can also be seen from Table 1 that the presence of a small amount of polypropylene in the polymer changes the spherulite size and nucleation time of polybutene-1, so that the melting point of the polymer changes. In addition, compared with the melting point and crystallinity of pure polypropylene, the melting point of the polypropylene in the product prepared by in-situ polymerization increased. At the same time, the crystallinity became smaller and the crystallization temperature decreased, indicating that there was a small amount of polypropylene chain dispersed in the polybutene-1 molecular chain.

**Figure 2** DSC curves of different polymers for the second heating time**Table 2** The results of the second melt of different polymers

Samples	PB-1 phase			PP phase		
	$T_m$ (°C)	$\Delta H$ (J/g)	$T_c$ (°C)	$T_m$ (°C)	$\Delta H$ (J/g)	$T_c$ (°C)
PB0	110.20	32.03	67.17	-	-	-
PB10	113.35	41.86	72.57	162.66	6.90	101.76
PB20	113.68	41.60	77.87	162.19	9.64	106.52
PB40	113.23	36.65	82.82	163.23	19.20	107.25
PP	-	-	-	159.24	79.15	112.82

Table 2 and Figure 2 show the results of the second temperature melting of the polymer. As can be seen from Table 2, the melting point and crystallinity of polybutene-1 are improved by in-situ polymerization, compared to pure polybutene-1. This may be due to the fact that the crystallization temperature of polypropylene is higher than that of polybutene-1. And in the process of cooling, the polypropylene crystallized first. Crystallized polypropylene, as a nucleating agent for polybutene-1, promotes the crystallization of polybutene-1. The crystallization temperature of polybutene-1 by in-situ polymerization increases and its peak width become narrow as shown in Figure 2. Compared with pure polypropylene, the melting point of polypropylene in polybutene-1 was increased slightly, but the crystallinity and crystallization temperature decreased. With the increase of the content of polybutene-1, the lower the crystallinity and crystallization temperature of the polypropylene phase. This may be due to the fact that the polybutene phase is in the molten state during the crystallization of the polypropylene, diluting the polypropylene molecular chain, and hindering the crystallization of the polypropylene.

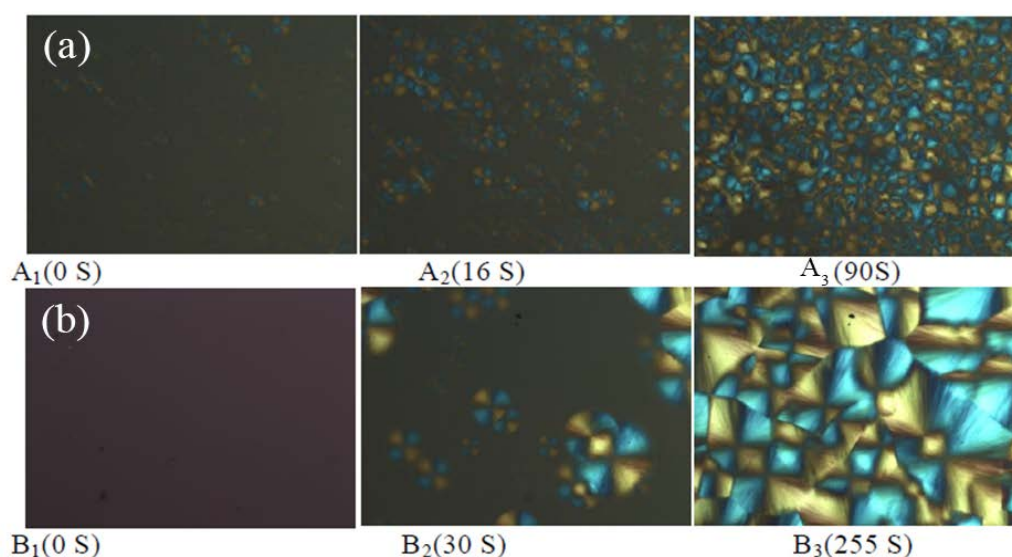
The samples were subjected to DSC test and left at room temperature for 7 days. The metastable II crystal was transformed into a stable I crystal form. The DSC test was carried out again. The melting temperature and melting enthalpy were also shown in Table 3. It can be seen from the table that polybutene-1 produced by in-situ polymerization exists crystalline transition, but its melting point and crystallinity are obviously improved. However, with the polymerization time of propylene, the melting point and crystallinity of polybutene increase first and then decrease later. It may be due to that polybutene-1 produced by in-situ polymerization contains a small amount of polypropylene to play the role of nucleating agent, promoting the crystallization of polybutene-1. So the polymer's melting point and crystallization increased. However, when the polypropylene phase exceeds a certain value, it will hinder the crystallization of polybutene-1, and reduce the melting point and crystallinity. The crystallization of the polypropylene phase in the polymer is affected by the amount of the molten polybutene-1 phase. The molten polybutene-1 acts as a dispersant, thereby lowering the crystallinity of the polypropylene.

**Table 3** The melting results of different polymer placed for seven days

Samples	PB-1 phase		PP phase	
	$T_m (^{\circ}\text{C})$	$\Delta H (\text{J/g})$	$T_m (^{\circ}\text{C})$	$\Delta H (\text{J/g})$
PB0	124.32	59.63	-	-
PB10	126.98	63.56	162.16	2.35
PB20	124.71	53.83	162.02	9.28
PB40	122.97	46.34	163.48	21.00
PP	-	-	159.24	79.15

### 3.2 Polarizing Microscope (POM)

Polymer crystals, like other crystals, are anisotropic in light, which can cause birefringence. Direct observation of crystal changes using polarized light microscopy (POM) is one of the important means of studying crystalline polymers. The polybutene-1 prepared by prepolymerization and the polybutene-1 product prepared without prepolymerization were analyzed by POM. The results are shown in Figure 3.

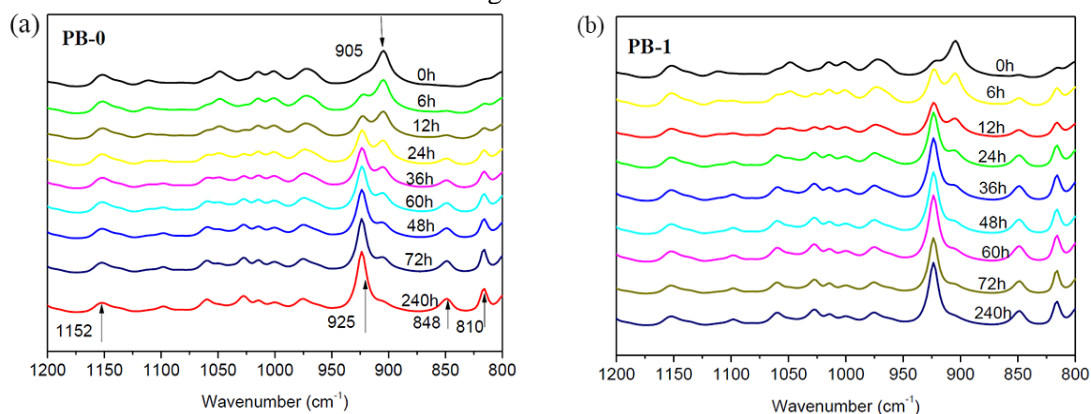


**Figure 3** The POM test results of (a) polybutene-1 prepared by prepolymerization, and (b) polybutene-1 prepared without prepolymerization

The polymer was isothermally crystallized at 80 °C and the polymer crystal growth process was observed by a heat microscope (POM), as shown in Figure 3. The "black cross race" phenomenon can be seen in photographs of the polybutene-1 and homopolymer PB prepared by in-situ polymerization, indicating that they are three-dimensional spherulites. After 30s of isothermal crystallization at 80 °C, a large number of grown spherulites were visible in the polarized photographs of the in-situ polymerization product (Figure 3a). However, the number of spherulites observed in the homogeneous PB (Figure 3b) is small and the spherulite volume is too large. After the isothermal crystallization of the in-situ polymerization product for 90 s, the spherulites are almost full of the field of view. While homopolymer products are basically completed crystallization after 255s, and the spherulite size is relatively large, not enough refinement. It indicated that the crystallization rate of propylene produced by in-situ polymerization was significantly faster than that of butene-1 homopolymer, while the crystal form was smaller and homogeneous.

### 3.3 FT-IR

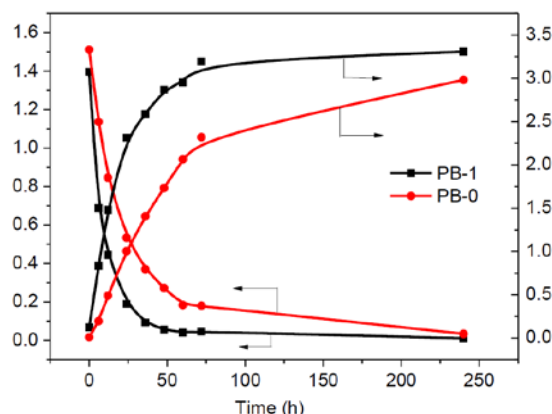
The polybutylene-1 is a multi-crystalline polymer. Metastable crystalline II formed by melting gradually transformed into stable crystal form I, which is irreversible, and it usually takes 7 days. In order to investigate whether the in-situ polymerization had an effect on the crystal transition time, the prepolymerized PB-1 and unpackaged PB-0 samples were subjected to Fourier Transform Infrared Spectrometer. The test results are shown in Figure 4.



**Figure 4** Infrared spectra of (a) polybutene-1 without prepolymerization, and (b) polybutene-1 via prepolymerization



Figure 4 shows the effect of the prepolymerization technique on the crystal transition rate of the polybutene-1 product. It can be seen from the figure that the  $905\text{ cm}^{-1}$  absorption peak gradually decreases with the prolongation of the placing time, while the absorption peaks of  $925\text{ cm}^{-1}$ ,  $848\text{ cm}^{-1}$  and  $816\text{ cm}^{-1}$  are increasing. According to the literature, the characteristic absorption peak of  $905\text{ cm}^{-1}$  is form II, and  $925\text{ cm}^{-1}$ ,  $848\text{ cm}^{-1}$ ,  $816\text{ cm}^{-1}$  are the characteristic absorption peaks of Form I. The prepolymerized PB-1 had a significant absorption peak at  $925\text{ cm}^{-1}$  at 0 h, indicating that the polybutene-1 prepared by prepolymerization was more likely to form a crystalline form I after melt-cooling. When the absorption peak of  $1152\text{ cm}^{-1}$  does not change with time, the absorption peak area (A) of  $1152\text{ cm}^{-1}$  is chosen as the internal standard. The ratios of  $A_{905} / A_{1152}$  and  $A_{925}/A_{1152}$  are used to characterize the transition rate of the crystal form II and form I, as shown in Figure 5.



**Figure 5** Transition rate of polybutene-1 crystal

It can be seen from Figure 5 that the polybutene-1 product without prepolymerization was subjected to the transition from Form II to Form I for 10 days, and the polybutene-1 product produced by prepolymerization was subjected to the transition from Form II to Form I for 72h. It can be seen that the propylene prepolymerization technique not only improves the form of the polybutene-1 product but also shortens the crystal transition cycle of the polybutene-1 product.

### 3.4 mechanical properties test

In order to test the mechanical properties of polybutene-1 produced by in-situ polymerization, we selected the in-situ polymerization products whose propylene polymerization time is 10, 20 and 40min, respectively. The results are shown in Table 4.

**Table 4** Mechanical properties of PP / PB-1 alloy

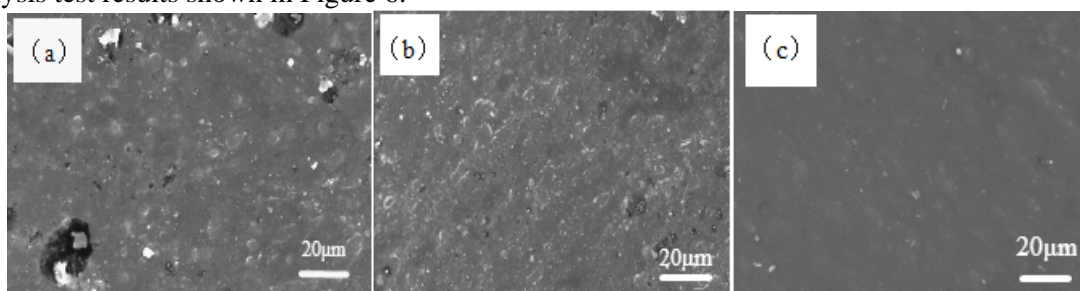
PP/PB-1	unit	PB10	PB20	PB40
Melt flow rate	g/10min	4.9	3.0	2.5
Density	$\text{g/cm}^3$	0.9023	0.8999	0.8966
Tensile strength	MPa	17.55	19.68	20.67
Flexural strength	MPa	524	585	645
Tear strength	MPa	15.0	15.9	18.1
Elastic Modulus	MPa	17.1	15.2	15.91
Impact strength	$\text{kJ/m}^2$	461	553	604
Hardness D		15.58	25.95	16.79
		64	63	65



From the analysis of the results in Table 4, it can be seen that the content of polypropylene in the PP / PB-1 sample increases slightly with the increase of the prepolymerization time, and the tensile strength of the alloy sample is gradually increased due to the increase of the polypropylene content in the sample. Because PP has a high tensile strength. Since PP is a material with high flexural strength and modulus, the flexural strength and flexural modulus of the alloy are increased with the increase of PP content. Therefore, due to the existence of a small amount of polypropylene, the PP/PB-1 alloy has improved the shortcomings of low strength and low modulus of PB. In addition, the hardness of PP is much higher than that of PB, so the hardness of the alloy is slightly improved.

### 3.5 Scanning Electron Microscope Observations

The polymer film samples PBM10, PBM20, and PBM40 were fabricated under conditions of a stretching temperature of 130 °C. and a stretching rate of 40 mm/min. To observe the surface morphology of the film samples, the prepared films were subjected to scanning electron microscopy. Analysis test results shown in Figure 6.

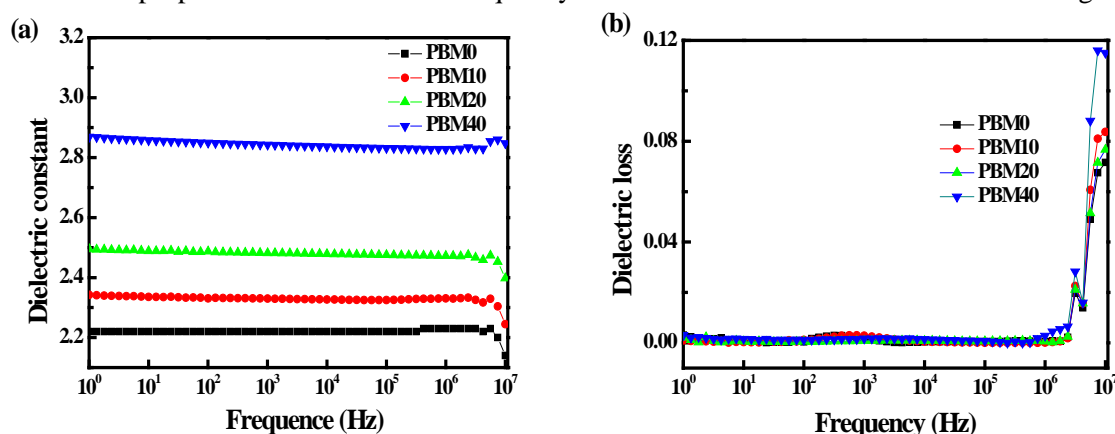


**Figure 6** SEM photograph of polymer film samples of (a) PBM10 ,(b) PBM20, and (c) PBM40

As shown in Figure 6 (a), the particle size on the surface of the PBM10 film is relatively uniform, but there are holes in the local area, indicating that the microstructure has been damaged during the stretching process. Figure 6 (b) In the figure, the PBM20 film has a uniform particle size from the surface roughness, and no pinholes have appeared. Figure 6 (c) The film formed by PBM40 in the figure has good compactness, and no holes are found. After analysis, it was found that due to the increase in pre-polymerization time of the alloy sample, higher isotactic polypropylene was produced. As the polypropylene content increased, the tensile properties of the sample increased, and the compactness of the wave film formed from the sample PBM40 changed it is good.

### 3.6 Dielectric properties

The dielectric measurements of films were carried out at 25 °C and 80 °C temperature using a broadband dielectric spectrometer over the frequency range of 1 to 10<sup>7</sup> Hz. The relationship between the dielectric properties of the films and frequency was discussed. The results are shown in Figure 7.



**Figure 7** Frequency dependence of PP/PB-1 film samples at room temperature: (a) dielectric constant ,(b) dielectric loss tangent

As can be seen from Figure 7 (a), the dielectric constants of the film samples prepared under the same stretching conditions are different. With the prolongation of the prepolymerization time, the dielectric constant of the obtained thin film sample also increased. Among them, the dielectric constant

of PBM40 was the highest, which was mainly due to the more uniform and dense film formed by the PBM40 sample. At the same time, it is found that the dielectric constant of the film hardly changes with the frequency, and when the frequency is close to  $10^7$  Hz, the dielectric constant of the film tends to decrease. From the polarization point of view, when the frequency of the electric field is low, multiple polarization modes act on the dielectric and the dielectric polarization is sufficient. At high frequencies, some polarization modes of the dipole lag behind changes in the electric field, resulting in dielectric internal poles. Insufficientization, so the dielectric constant has a slight downward trend.

From Figure 7(b), it can be seen that the dielectric loss tangent of film samples prepared under the same stretching conditions is similar and stable in a certain frequency range, and the material prepared with different prepolymerization time has no effect on the dielectric loss of the film. Big. Due to the relaxation phenomenon. The dielectric loss of the film sample is basically a horizontal line in the low-frequency region, but when the frequency is  $2.24 \times 10^6$  Hz, the dielectric loss increases suddenly. Since all samples show the same pattern, it shows that the material itself nature.

**Table 5** The relationship between dielectric properties of thin film and temperature at 1Hz frequency

Dielectric properties	Temperature/ °C	PBM10	PBM20	PBM40
Dielectric constant	25	2.34	2.50	2.87
	80	2.53	2.70	3.04
Dielectric loss	25	0.0032	0.0032	0.0046
	80	0.022	0.010	0.016

From Table 5, it can be seen that, at the same test frequency, changing the test temperature produces a change in both the dielectric constant and the dielectric loss of the film. Which has a greater impact on dielectric loss. After increasing the test temperature, the dielectric constant of the sample slightly increased, and the dielectric loss increased significantly.

#### 4. Conclusion

(1) The synthesis of polybutene-1 resin was carried out by batch polypropylene polymerization. The morphology and structure of PP/PB-1 alloy materials were analyzed by DSC, POM and FT-IR testing methods respectively. The composition of each polymer can be adjusted by changing the prepolymerization time. The crystallization rate of propylene by in-situ polymerization was significantly faster than that of butene-1 homopolymer, and the crystal size was smaller. The results of FR-IR show that PB-1 prepared by in-situ polymerization has significantly shortened the crystal conversion time, compared with homopolymerized PB-1. The in-situ synthesis process is simple, and single-pass conversion is high. Without solvent, the product is a granular powder, and it can be applied directly.

(2) The PP/PB-1 alloy material was prepared into a thin film using a laboratory bidirectional stretching apparatus. The dielectric properties of the film were found to be related to the compactness of the film. Its dielectric constant value increases with the increase of propylene content in the alloy sample, and the dielectric loss value does not change much. When the stretching temperature is  $130^\circ\text{C}$  and the stretching rate is 40mm/min, the dielectric constant value of PBM40 can reach 2.9 and the dielectric loss value is low ( $<0.005$ ).

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