

High-Pressure Crystallization of Poly(1-butene)

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Abstract: - This work study influence of high-pressure crystallization on two homopolymers of poly(1-butene) (PB-1). Samples were non-isothermally crystallized under pressure range from 20 to 200MPa using a pvT 100 device. Obtained specimens were analyzed by using wide-angle X-Ray scattering (WAXS), differential scanning calorimetry (DSC) and polarized light microscopy (PLM). Significant impact of the pressure of crystallization on the phase I' and phase I appearance was observed.

Key-Words: - Poly(1-butene), crystallization, pressure, morphology, polyolefin, phase transformation

1 Introduction

Poly(1-butene)(PB-1) is stereospecific polyolefin. It was produced in 1951 by using Ziegler-Natta catalyzators. Presently it is produced by LyondellBasell Industry and most of the PB-1 production is used for water pipes manufacturing. Main difference between common polyolefins and PB-1 is the crystallization into different phases and subsequent recrystallization of the metastable phases into stable phases. Compared to other polyolefins, PB-1 is superior in terms of abrasive resistance, which is comparable to abrasive resistance of ultra-high molecular weight in wet conditions and elastic recovery. [1]

Phase composition of the PB-1 is dependent on crystallization pressure and there is five possible phases, namely phase I, I', II, II' and III. During the crystallization under atmospheric pressure, PB-1 contains phase II, which recrystallizes into phase I under room temperature and after few days. Phase I' will appear when the crystallization is execute under pressure approx. 100MPa or higher. Annealing under 90-100°C causes phase I' to recrystallize into phase II. Crystallization from the solution creates phase III which can also recrystallized into phase II by annealing at 90-100°C. However phase I can crystallize directly from the melt using built-in specific stereodefects in PB-1, as was described by Rossa et al.[2]

Transformation mechanism was examined by Marigo et al. [3] using WAXS and small angle X-ray scattering. The transition itself involves rearrangement of lamellar stacks and the transition nucleation is localized on lamellar distortion points. However, this transformation do not affects the surface morphology and inner morphology of the sample. Also additional crystallization from

amorphous phase occurs, decreasing the percentage of amorphous phase.

2 Problem Formulation

Crystallization under high pressure of the PB-1 is complex problem, which does have an impact of the manufacturing of the PB-1 products. Also recrystallization during aging of the products is important because this recrystallization is causing shrinkage and thus delaying distribution of the products. Mechanism of the phase transformation is not yet exactly described and further understanding of the coherence between structure, processing conditions and properties is needed.

3 Problem Solution

Two different commercial-available grades of isotactic poly(1-butene) produced by LyondellBasell, were examined. PB0300M with MFR(190 °C/2.16 kg) 4g/10min and DP0401M with MFR(190 °C/2.16 kg) 15g/10 min. Both materials have density 0,915g/cm³.

pvT 100 device, produced by SWO Polymertechnik GmbH, Krefeld, Germany, was used for sample preparation. Cooling rate 5 °C/min and set of pressures of 20, 50, 75, 100, 125, 150 and 175MPa was used. One sample was prepared for each pressure. Final samples were in the form of cylinders with 7,8 mm diameter and 20 mm length. These samples were analyzed using WAXS, DSC and PLM

WAXS samples were obtained from pvT prepared samples in form of cylinders with 5mm

thickness and they were smoothed by water grinder with sand paper. Used device for WAXS measurement was Philips X'Pert Pro 1 X-Ray with settings of wavelength 1.54 Å and step size of 0.0263° in diffraction angular range 7-30° 2 θ in transmission mode.

Also DSC samples were obtained from pvT cylinders by using microtome. Approximately 10 mg of the sample was placed into the aluminum pan and sealed in the sealing press. Used apparatus was TA Instrument 2010. Measurement was done under nitrogen atmosphere with flow rate of 20 ml/s and within temperature range of 40-180 °C with heating rate 10 °C/min.

Leica rotation microtome was used to prepare PLM samples. Thickness of the slices was 40 μ m. Slices were put onto glass slide, drop of silicone oil was added and sample was covered with slip cover. A Zeiss NU polarized light microscope with 40x magnitude and attached digital camera was used to take photos.

3.1 WAXS

Diffraction curves of the measured materials are shown at Fig. 1 and Fig. 2. As we can see, both curves show similar pattern, which corresponds with the pattern of the phase I [4]. However, differences can be found. Some crystallization pressures are missing peaks at 9,9° 2 θ , which is characteristic peak for phase I or phase I'. This could be caused by sample cutting or final polishing. Other characteristic peaks for phase I are 17.3, 20.2 and 20.5 2 θ . Characteristic peak for phase II are 11.9, 16.9 and 18.4° 2 θ . The peaks at 11.9 and 18.4° 2 θ are missing in all diffraction curves and we can observe only peaks at 16.9° 2 θ in both materials. All curves for both materials show peak at 28° 2 θ , which is not described in any available. This leads to conclusion that this peak is belonging to the unknown phase in PB-1, which is connected to the high-pressure crystallization or this peak can be caused by interference during the sample preparation.

3.2 DSC

Melting curves can be seen at Fig. 3 and Fig. 4. For material DP0401M, shown on Fig. 3, peaks for phase I are visible for crystallization pressure of 20 and 50 MPa with peaks of 124 °C and 133 °C respectively. Phase I' appears at pressure of 75 MPa with peak of 96.5 °C and further recrystallizes to phase II with peak at 117 °C. In pressure range from 75 to 175 MPa there are no important changes except small peaks belonging to the phase I which

are formed from early formed phase II. Obtained curves for material PB0300M are shown on Fig. 4. Curves for pressures 20, 50 and 75 MPa have peaks at 126, 125.1 and 125.9 °C respectively. Phase I' can be observed for pressures above 100MPa, however curves are significantly different. Exothermal peak is present at curves for 100 and 125 MPa but with further increase of the pressure to 150 and 175 MPa these exothermal peaks are not observed.

Results of the DSC implicate that occurrence of phase I' is dependent on the molecular weight of the polymer as both materials contains same stabilizers. DP 0401 M have lower molecular weight and higher melt flow rate compared to PB0300M and we can observe phase I' in DP0401M from 75MPa when in PB0300M the phase I' is observed at 100MPa.

3.3 PLM

Morphology of DP0401M is showed at Fig. 5. Both pressures 20 and 50 MPa have spherulitic structure with typical Maltese crosses evenly distributed on the edge and core of the sample. Morphology for the sample prepared at 75 MPa is significantly different. The core of the sample still contains only Maltese crosses however the edge is composed from microcrystalline structure with low number of Maltese crosses. This is very similar to the structure of sample prepared at 100 MPa, which does not have any Maltese crosses on the edge and core is composed from microcrystalline structure and Maltese crosses. Structure of the sample prepared at 125 MPa is homogenous with developed spherulites. Also the sample prepared at 150 MPa does not show any difference in core and edge of the sample but the whole area is composed from microcrystalline and spherulitic structure. Finally, sample prepared at 175 MPa possesses differences between core and the edge when the core is combination of microcrystalline and spherulitic structure and the edge is composed only from microcrystalline structure.

Morphology of the PB0300M is different, as we can see at Fig. 6. Structure of the samples prepared at 25 and 50 MPa is similar to the DP0401M in terms of composition but the size of the Maltese crosses is significantly greater. This is similar to the samples prepared at 75 MPa, which are composed from large and small Maltese crosses. The only sample containing microcrystalline structure is sample prepared at 100 MPa. In addition, this sample contains low number of spherulites spread evenly thorough the area of sample. Samples prepared 125, 150 and 175 MPa

have combination of large and small spherulites and with increasing pressure, the number of large spherulites is decreasing. The most significant difference between measured materials is the different in the core/edge structure. Also we can observe that appearance of the phase I' is connected with change in the morphology of the sample.

4 Conclusion

From obtained data we can see the connection between molecular weight and appearance of phase I'. According to DSC scans, phase I' occurs at lower pressures in PB-1 with lower molecular weight. Morphology of the PB-1 is dependent on the phase I' appearance and both measure materials show changes in spherulite percentage and size of the spherulites above the pressure critical for phase I' appearance. WAXS results shows peaks, which are not described in available literature sources and they could be cause either by unknown phase or the interference caused by the sample preparation. Further research is needed to fully understand and explain these anomalies

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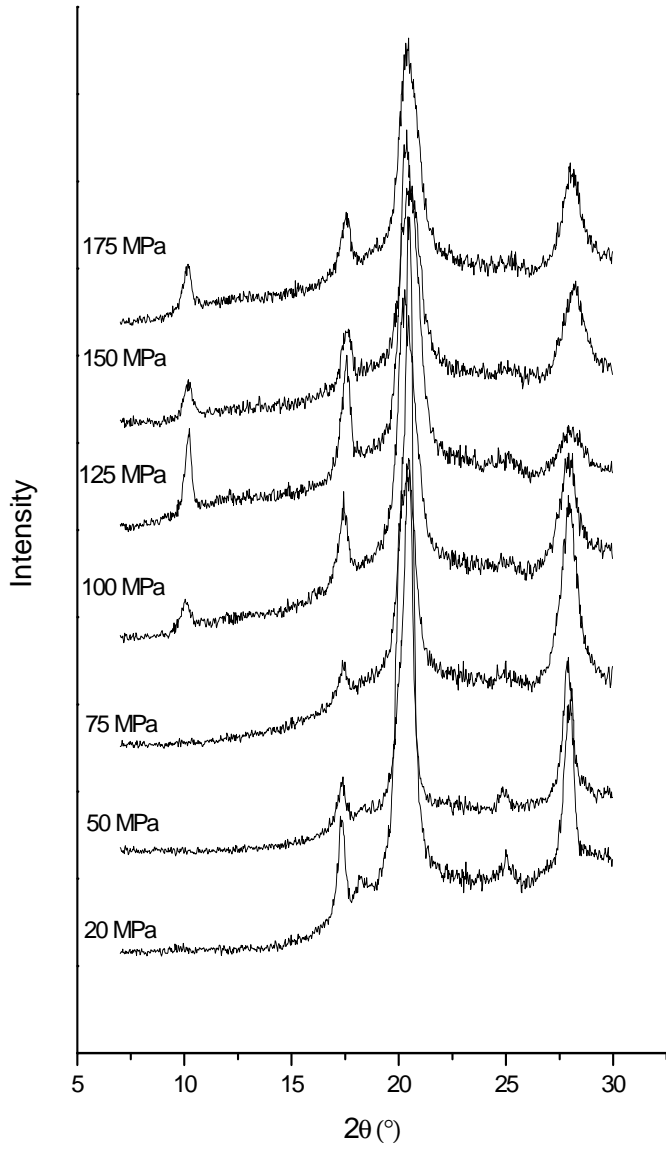


Fig. 1 DP0401 WAXS Diffractograms

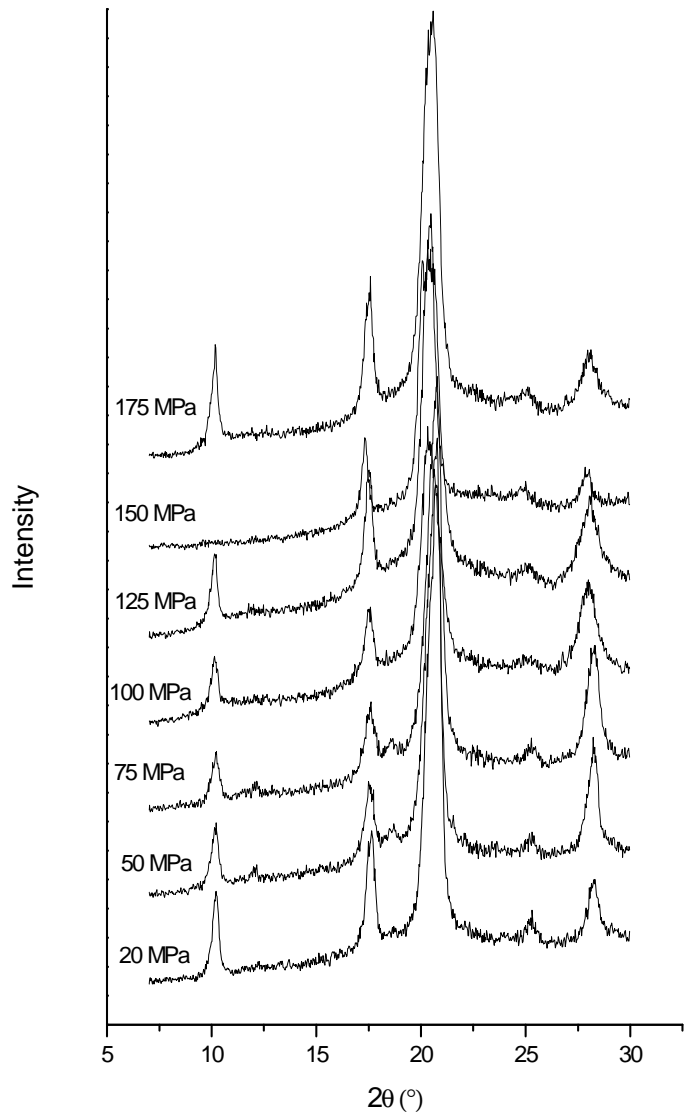


Fig. 2 PB0300M WAXS Diffractograms

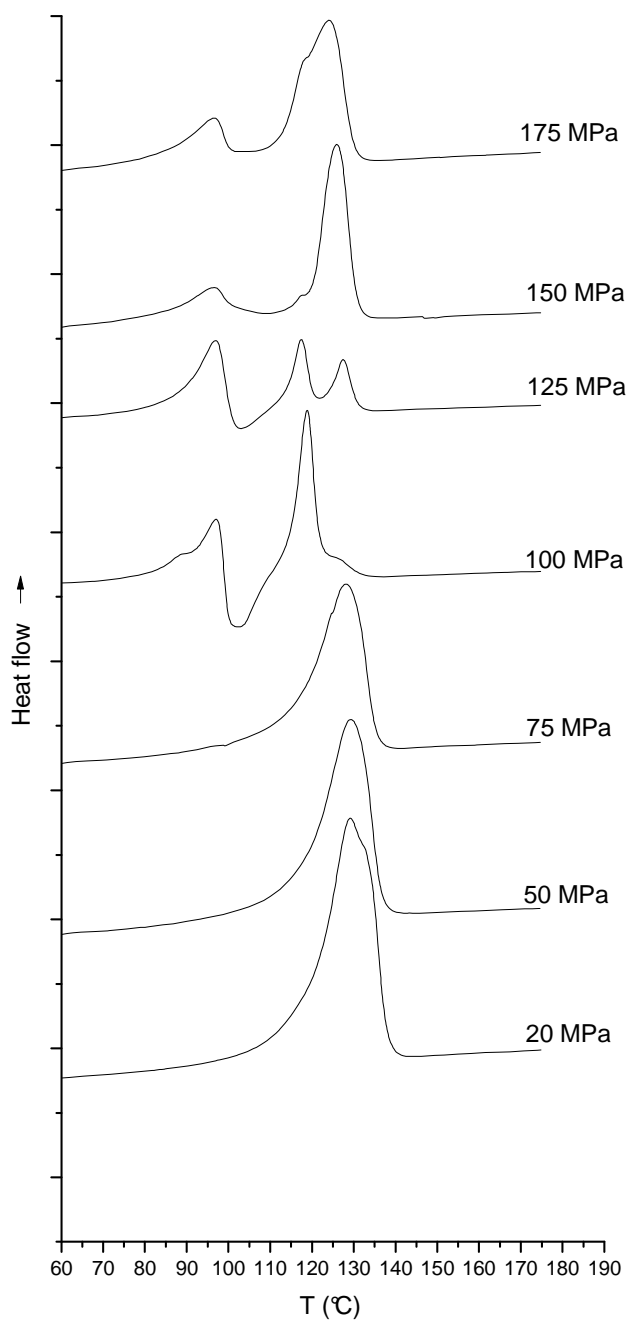


Fig. 3 DP0401 DSC Melting curves

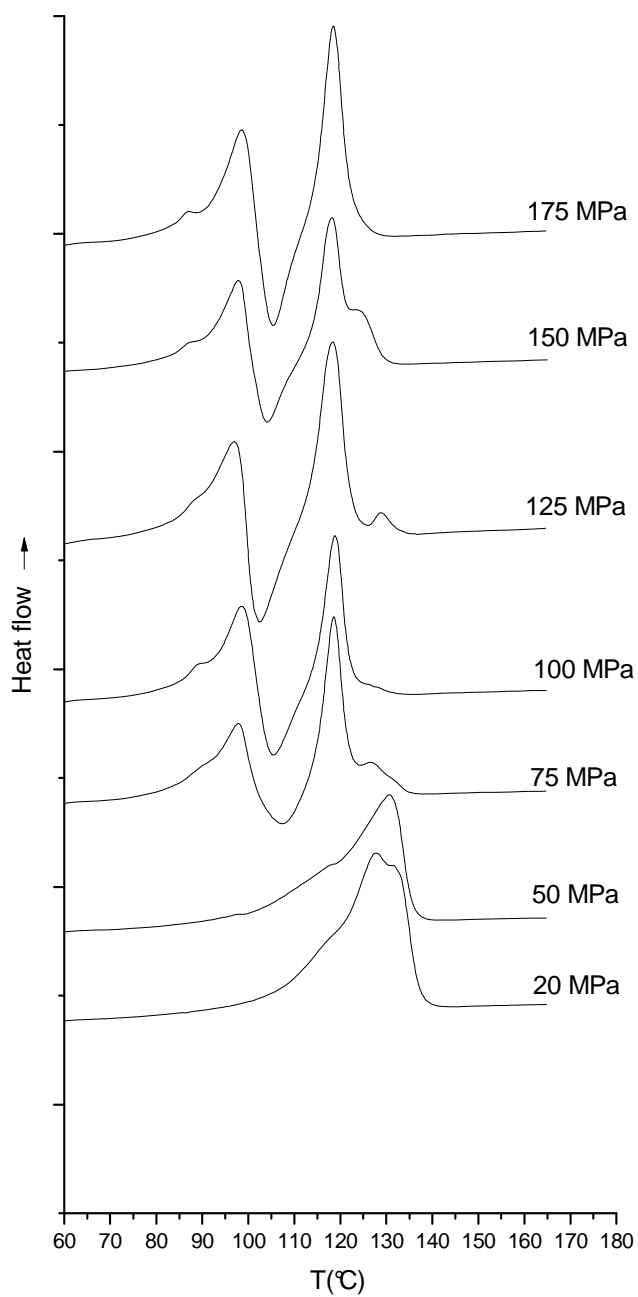


Fig. 4 PB0300M Melting curves

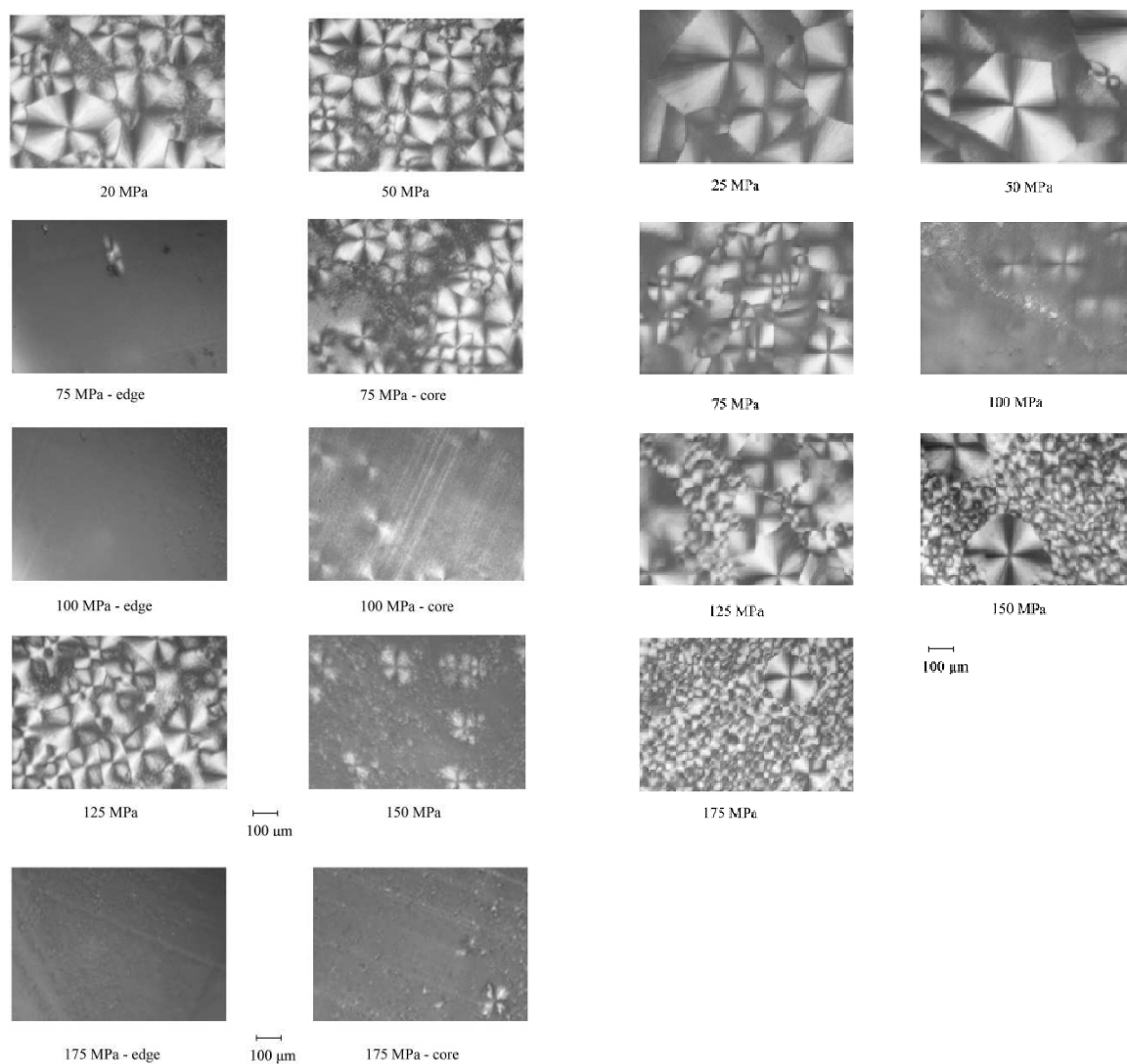


Fig. 5 DP 0401M Morphology

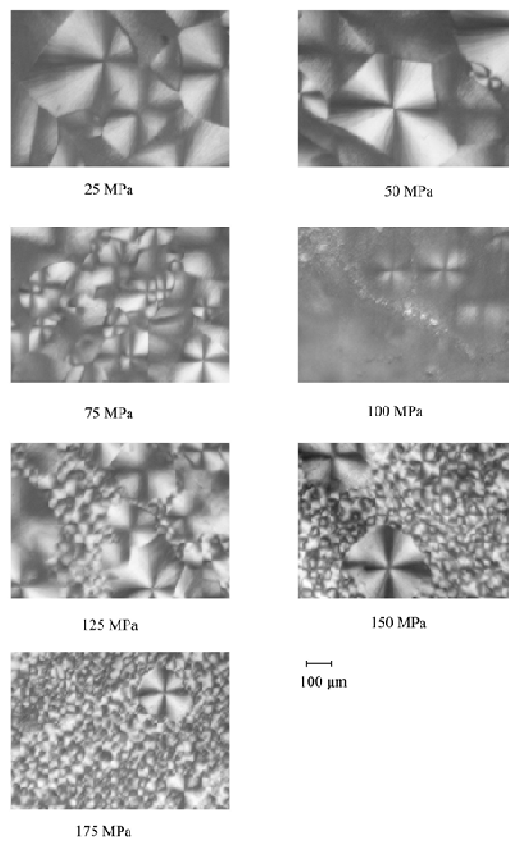


Fig. 6 PB0300Morphology