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Identification of polymer deposits in the high-pressure recycling system of low-density polyethylene production

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Abstract

This paper outlines the results of analysis of Low-Density Polyethylene (LDPE) depositions on filter elements of upstream II cascade compressor by means of X-ray and Fourier transform infrared spectroscopies, gel permeation chromatography and viscometry, differential scanning calorimetry and ¹³C NMR spectroscopy. Based on comparison with experimental data of process designers the supposition has been given to the cause of the formation.

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1. Introduction

As previously reported the revamp of the unit of low-density polyethylene (LDPE) synthesis in tubular reactors based on Polimir process and implementation of improved initiating system enabled to make 1.6 increase in output^{1,2}. When making further attempts to intensify reactor block operation there was observed return ethylene temperature rise and pressure drop increase in the high pressure recycle (HPR) system with decreasing II cascade compressor capacity. Routine heat-exchange equipment purging procedures failed to eliminate this constraint. PFD and temperature parameters are shown in Figure 1 as an illustration to the discussion.

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Following uncovering the detailed basic equipment inspection gave the evidence of the following: rubber-like deposition occurrence in high pressure product separators (HPPS) and pipelines, powdery polymer carry-over in a gas flow through heat-exchangers and separators with build-up on filter screens upstream compressor suction. Qualitative HPPS deposition analysis performed in paper³ demonstrated that the polymers were hyper-branched polyethylene (PE) corresponding by density to ULDPE. In spite of the low melting temperatures ($< 50\text{ }^{\circ}\text{C}$), they are not characterized by the fluidity within the recycle temperature range due to partial structurization (about 20 % of xylene – non-soluble fractions); that leads to non-removable depositions. The further investigations were aimed at the finding out the mechanism of this polymer formation in reactors and elimination of contributing conditions.

The aim of this paper is an identification of powdery polymers on filter elements in order to understand purification system inefficiency reasons for ethylene returning to HPR, that leads to pressure drop rise and in case of late screen replacement to the “breakthrough” and polymer penetration the compressor cylinders (Fig. 1).

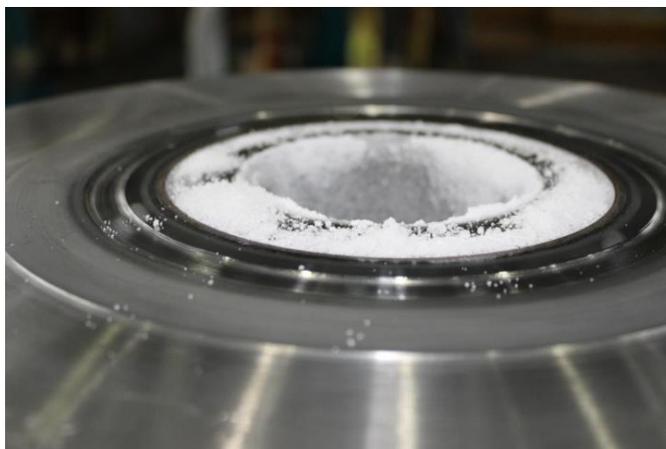


Fig. 1. Polymeric deposition in a flow part of the compressor cylinder

2. Experimental

Measurement of the phase transition temperature and thermal effects has been performed with DSC 204 F1 (NETZSCH) instrument in accordance with the methods ASTM D3418-82 and ASTM D3417-83 in Argon (flow rate is 30 ml/min) in aluminum 25 μl NETZSCH[®] crucibles. Instrument calibration has been carried out in accordance with ASTM D3418-82; D3417-83 against standard – indium (99.999 %, ALDRICH) and zinc (99.8 + %, ALDRICH). During the test the sample mass variation has not been observed. The sample surveying involved a melting – crystallization – melting cycle with $10\text{ }^{\circ}\text{C}/\text{min}$ velocity in the following temperature interval: the first melting is from $-10\text{ }^{\circ}\text{C}$ up to $180\text{ }^{\circ}\text{C}$, the second melting is from $-10\text{ }^{\circ}\text{C}$ up to $210\text{ }^{\circ}\text{C}$.

Crystallinity has been measured with XRD-700 Shimadzu X-ray diffractometer.

Analysis of the polymer molecular-weight characteristics has been performed with Agilent 1200 solution chromatograph in tetrahydrofuran at room temperature according to ISO 16014-3-2003.

^{13}C NMR spectra of the deposition extracts have been registered with the BRUKER AVANCE 500 spectrometer on 125.76 MHz frequency at $125\text{ }^{\circ}\text{C}$ in the standard cylindrical ampoules of 10 mm diameter. Registering parameters are the following: scanning – 6700 Hz, cumulation frequency - 0.125 Hz, cumulation number 8000. Chemical shifts have been shown with regard to tetramethyl silane (TMS). Signal assignment has been carried out according to⁴.

3. Results and Discussion

Polymer viscosity-average molecular weight is about 10 thousand c.u., being significantly higher the values for low-molecular-weight polyethylene (PE) liquids – up to 3 thousand⁵ and mixed fractions from separators of high pressure (HP) and low-pressure (LP) waxy recycling systems – up to 5 thousand, as well as commercial waxes produced at a similar plant⁶.

As it has been shown by the experiment before at the phase equilibrium facility in ethylene – PE system⁷, a polymer with such molecular weight (MW) is non-soluble in ethylene at temperature < 240 °C and pressure of 28 MPa and below being maintained in HPPS and the recycling system. The polymer therefore could be dissolved only when a two-phase system is formed in the 2nd product cooler at higher P and T parameters, or it could be carried away by gas flow from HPPS if it was in the form of aerosol particles of micro sizes being not in line with sedimentation by Stoke's law.

Comparative analyses of deposition polymer MWD and LMWPE mixed fraction shown in a figure demonstrate the following: the bimodal LMWPE MWD curve is shifted toward higher MW in comparison with statistical data for the process with oxygen initiation; high MW side unsymmetrical low-molecular mode broadening gives evidence of appearance of significant amount of polymers with different MWD which mode applying causes peak form distortion. Deposition MWD curve also having a complicated view with low and high molecular “tails” according to MW range of the main polymer amount corresponds to the emerged overlapping mode. It allows to make an assumption that the most of polymers with such characteristics are separated in a recycling system, but a portion is blown off by a gas flow due to the fact that when the system was developing the polymers of this structure and properties were unknown.

As it has been shown before by GPC method on LDPE commercial samples synthesized in various processes, PE with such MW values makes the low-molecular “tail” of MWD curves⁸.

Comparative results of the molecular structure analyses of deposition samples and basic PE by ¹³C NMR spectroscopy method are given in Table 1 and in Figure 3. The received growth of combined and end methyl group content corresponds to experimental regularities when decreasing PE MW⁷. Multiple excess of ethyl branching content in comparison with butyl ones at the given total content of the methyl groups are in contradiction with literature data and may indicate the synthesis of macromolecules of such structure under conditions differed from process macroparameters.

The M assessment result of the end methyl group content based on NMR data corresponds to the results of determination by GPC method (Table 1, Figs. 2,3).

Table 1. MWD sample data

Sample	Mn (NMR)	Branching (type and branching number)			
		ΣCH ₃ /1000C	CH ₃ ¹⁾ /1000C	C ₂ H ₅ /1000C	C ₄ H ₉ /1000C
Deposition	1000	48	28	16.2	3.8
LDPE	3500	32	9.0	7.5	11.5

¹⁾ Terminal methyl groups.

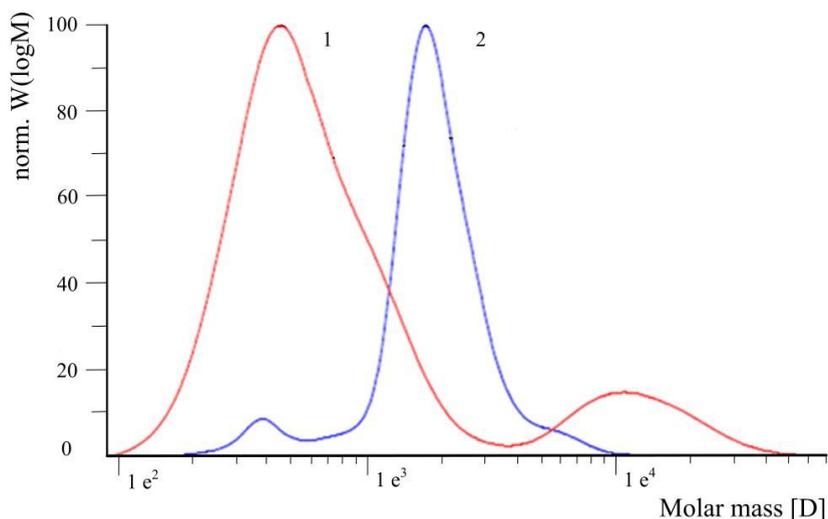


Fig. 2. Combined differential curves of LDPE (1) and deposition (2)

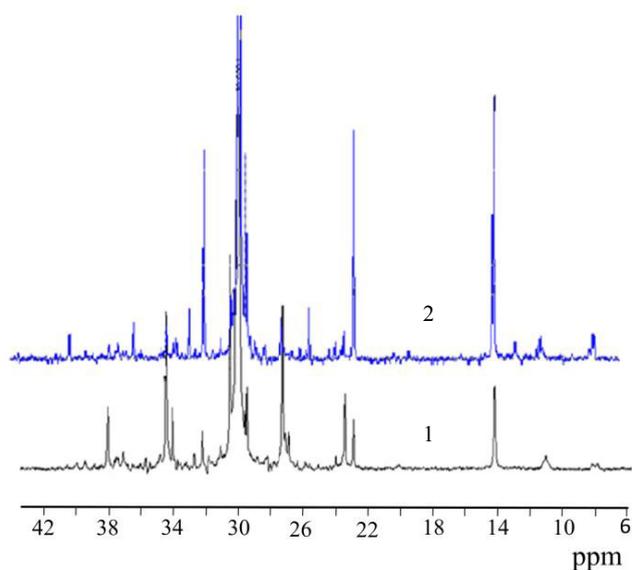


Fig. 3. NMR ^{13}C spectra of LDPE (1) and deposition (2)

X-ray spectrum of polyethylene is given in Fig. 4. Spectrum type and 65 % crystallinity are more appropriate to HDPE than to LDPE produced – 30-35 % according to statistical data of the authors⁹. Crystallite sizes are about 130 Å as compared with 110 Å for LDPE. Besides there is no practically any diffuse scattering superposition in the range of 2θ about 19° , being lapped over with the reflex 110 of orthorhombic phase in LDPE attributed to impurity amounts of PE¹⁰ monoclinic phase, according to other suppositions to hexagonal one¹¹. Absence of significant quantities of polymorphous crystal structure is obviously explained by keeping polymer without subsequent thermomechanical effects¹². It appears to be interesting for the follow-up studies of various factor influences upon crystal structure transformation.

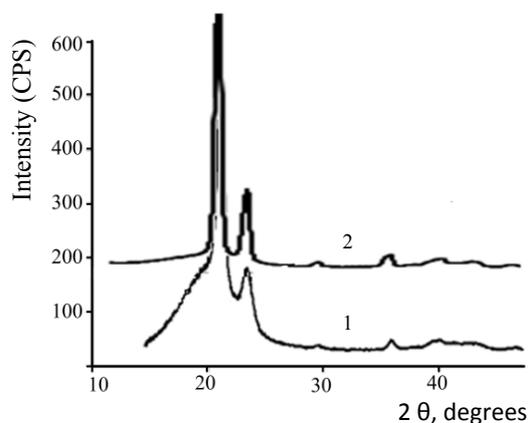


Fig. 4. X-ray diffractograms of LDPE (1) and depositions (2)

In IR-spectra there are depositions along with intensive signals of the CH₃-groups with maximum at 1378 cm⁻¹ obviously due to a great number of terminal methyl groups at low number-average MW intensive vinylidene and vinyl bond signals are observed. This bonding resulting from macroradical depolymerization according to the schemes given in paper¹³ appears to be the most logical: at higher polymerization process temperatures when chain transfer input with polymer participation is reasonably growing up. Obviously the content of vinyl groups may increase as a result of radical disproportionation reaction contributing to LMW polymer formation.

Characteristics of calorimetric depositions and PE produced are given in Figure 5 and in Table 2. More narrow and more symmetric melting and crystallization thermograms in case of deposition indicate crystal structure to crystal structure homogeneity supporting XFA data. High melting and crystallization enthalpy values received and rated crystallinity 74 % as well as 65 % according to XFA are not observed for LDPE but typical for HDPE¹⁴. Relatively low transition maximum temperatures look conflicting; however, previously similar data have been obtained for high molecular weight linear alkanes⁵. Besides, flat character of low temperature melting and crystallization thermogram branching of market PE leads to the penetration of deposition transition regions into these temperature intervals. Taking into account a negligible quantity of the synthesized PE with such characteristics it is permissible to assume the presence of similar polymers in basic grades.

Table 2. Calorimetric characteristics of the samples in melting-crystallization-melting cycle.

Sample	T _m , °C		ΔH _m , J/g		T _{cr} , °C	ΔH _{cr} , J/g
	1	2	1	2		
LDPE	110	108	-114	-108	88	110
Deposition	96.3	93.9	-222	-214	84.2	212

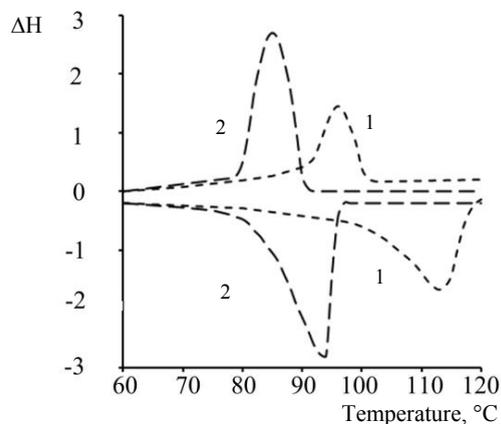


Fig. 5. Experimental curves of the first melting point (top) and crystallization (bottom) of LDPE (1) and deposition (2).

4. Conclusions

1. Based on the results of physical and chemical analysis the deposition polymer is relatively low molecular weight branched polyethylene with large amount of double bonds that permits to assume major depolymerization mechanism contribution into this macromolecule generation.
2. Quantitative ratio of ethyl and butyl branching content with identified methyl group content contradicts to experimental data array.
3. XRD and DSC data reveal a significant difference between crystal deposition polymer structure and basic PE grades, being attractive for the further investigations such as high crystallinity degree and transition enthalpy.
4. Inefficiency of polymer recovery in separation equipment of the HPR (high pressure recycling) system is probably explained by the equilibrium conditions changed in ethylene – polyethylene system when two-phase system is formed as a result of polymer synthesis and different molecular-mass structure in a significantly intensified process.
5. Being under study further reactor block production output increase possibilities require process synthesis condition correction as well as development of adequate design solutions for the polymer separation system in HPR system.

Acknowledgement

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