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Material Behaviour

Effect of short chain branches distribution on fracture behavior of polyethylene pipe resins[☆]Xuelian He^a, Xiaojuan Zha^a, Xiao Zhu^a, Xin Qi^a, Boping Liu^{b,*}^a Shanghai Key Laboratory of Multiphase Material Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China^b College of Materials and Energy, South China Agricultural University, Guangzhou 510642, China

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ABSTRACT

In this paper, a series of unimodal and bimodal high density polyethylene (HDPE) pipe resins with the similar molecular weight distribution and low short chain branches (SCB) contents were investigated to discover the relationship between short chain branches distribution (SCBD) and fracture behaviors. Three characterization methods, namely temperature rising elution fractionation (TREF), high temperature gel permeation chromatography (HT-GPC) and self-annealing fraction (SSA), have been effectively combined to qualitatively analyze investigate the SCBD of HDPE pipe resins. The results showed the preference of incorporation of SCB into long chains caused the enhancement of yielding stress and strain hardening (SH) modulus, and thus the extension of rupture time. On one hand, this kind of SCB distribution is conducive to induce the nucleation of long chains and form more void volume in the neighborhood of long chains indicating faster migration speed of polymer chains. On the other hand, short chains with less SCBs are easy to rapidly occupy nearby sites on the crystal growth front of long chains to co-crystallize. Whereas, these HDPE resins with the more SCBs incorporated into short chains spent much longer time occupying the growth front, so that parts of these types of short chains form very thinner lamella differentiated from the main crystallizing region. During the initiation and propagation of craze, these parts were firstly broken and their resistance to slow crack growth was based on the incorporating degree of SCBs into short chains. Therefore, besides molecular weight distribution, SCBD is another main cause for long-term properties of HDPE pipe resins.

1. Introduction

Since it was initially employed as plastic pipe resins in the 60s decade, high-density polyethylene (HDPE) were gradually produced and updated for the transportation and distribution of natural gas and water, which is mainly attributed to its outstanding long-term properties, chemical tolerance and low cost. HDPE pipe resins have evolved from grade PE63, PE80, PE100, PE125 to grade PE100-RC during the past 50 years, based on incremented innovation of catalysis and polymerizing process and deeper understanding of molecular architecture [1]. Synchronously, a series of standards toward higher performance pipe materials have been continually established and modified [2].

In the current industries, PE-80 and PE-100 grade resins are still most commonly used for gas pipe applications, which means that pipes made from such materials must withstand a minimum hoop stress of 8 and 10 MPa for no less than 50 years at 20 °C, respectively [3]. In this way, the pipes can fail in a time-dependent brittle fracture under the

load below its yield stress, named as slow crack growth (SCG) [4,5]. SCG is a dominant failure mode affecting HDPE pipes, normally occurs under low stress levels in long service time. The SCG failure mechanism is proposed as follows [6–8]: When the applied stress is less than yield stress, the bulk inhomogeneity such as residual catalyst and inorganic filler, and the surface defects notched or scratched during trenchless installation will act as stress concentrator. It is easy to yield and cause the lamellae fragmentation and partial chain unfolding. In this case, a craze structure as numerous uniaxial oriented fibrils bridged micro voids is generated. The fibrillated structures further will grow and fail due to disentanglement or break-up of inter lamellar connections and result in the propagation of cracks in the bulk of pipes till the final material failure.

Therefore, largely agreed that the resistance to SCG is mainly governed by the mechanical resistance of the craze fibrils [9]. E.J. Kramer and co-workers [10,11] have discovered the relationship between the micro-fibrils stretching process and molecular connections between the crystallites such as tie molecules, chain entanglements and trapped

[☆] Effect of SCB distribution on fracture behavior.

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chain entanglements. During craze fibrils propagation under low stress, the intercrystalline links bear most of the stress in the amorphous layers and then favor the transmission of the load between crystals lamellar. Thus, only if these important intercrystalline links and lamellar crystal become intertwined into a macromolecular network [12,13], the whole network can commonly bear outside force. During a long-time service, the network is subsequently relaxed and micromechanical properties will be decreased.

As a matter of fact, the number and density of intercrystalline links are sensitive to changes in the molecular structural parameters including molecular weight (MW), short chain branch (SCB) and long chain branch (LCB), and the chemical composition distribution. Huang and Brown [7,8] proposed a molecular model of the formation of tie molecules and found that interlamellar connections were raised with the increasing molecular weight and short chain branch contents. Hubert and Séguéla [14,15] revealed that the major role of the co-units during crystallization were disturbing chain folding and chain reeling. Wagener and co-workers [16–18] has made it possible to synthesize PEs with precisely spaced branches length, contents and distribution, and they found that methyl branches included in crystal unit and longer one excluded, but branches with length above 10 CH₂ included in crystal unit due to crystallization with main chains. They further revealed that the higher the SCB concentration, the greater the tie chain and chain entanglement density of the semi-crystallizing polymers. Laragon and co-workers [19] studied that under the same macroscopic strain the molecular stress in all-trans C-C sequences within lamellar are less in a bimodal copolymer as compared with equivalent unimodal copolymers. This can be taken as a piece of evidence that tie molecules and chain entanglements are more numerous in a bimodal material. Moreover, the incorporation of branches in high molar weight chains is especially beneficial for the occurrence of intercrystalline links, but this has not been given clear evidence. Thus, the understanding of the relationship between the SCBD, lamellar and intercrystalline links, and long term properties of HDPE pipe resins which had great value and significance for its preparation and application.

As to evaluate the SCG resistance, from the economy and applicability perspective, the Pennsylvania Edge Notched Tensile (PENT) test, the Full Notch Creep Test (FNCT) and et al. [20,21] are the most common methods which are usually conducted at room temperature. With the improvement of evaluation indexes for gas pipelines, some researchers currently proposed that evaluation of long-term properties for PE 100 resins are not reasonably carried out at room temperature (RT), thus the latest PE 100 + standards was put it forward by PE100 Association and pointed out that the test temperature should be raised to 80 °C. In this case, parts of PE 100 resins cannot meet the new criteria of PE 100 +, even if they have terribly similar molecular structure and crystallizing behavior. It can be inferred that the SCG properties are still derived from some extremely tiny polymer chain structure undiscovered in previous papers.

In this work, we investigated two categories of HDPE resins, Philips Chromium based unimodal HDPE resins (UMPEs) and Ziegler-Natta based bimodal ones (BMPEs) with similar crystallization degree and rheology behavior, but remarkably differential resistance of SCG. It was shown that they have similar molecular weight distribution and low SCB contents. A new TREF-HT-GPC-SSA method was employed to discriminate the extremely subtle differences of molecular chains and lamellar structures of these HDPEs. The tensile tests were carried out at elevated temperatures to investigate the variation in SCG resistance. Based on these results, a model was proposed to disclose how the SCBD affects the SCG resistance of HDPE resins.

2. Experimental

2.1. Materials

There were seven kinds of unimodal HDPE resins with a broad

Table 1
The materials parameters of HDPE pipe resins.

Sample	MW/10 ⁴	MWD	Density (g/cm ³)	MFI (g/10min, 21.6 kg)	Rupture time (h, 30 °C)	Grades
BMPE-1	30.3	26.8	0.948	10.1	1000	YGH041T
BMPE-2	33.3	18.4	0.946	9.9	> 500	HIDEN P600
BMPE-3	34.7	22.0	0.959	9.9	> 500	YEM4902T
UMPE-1	35.3	28.7	0.942	9.6	500	DGDB 2480H
UMPE-2	34.3	26.2	0.943	10.3	500	DGDB 2480H
UMPE-3	31.9	24.4	0.942	10.0	300	DGDB 2480H
UMPE-4	31.0	22.7	0.941	9.7	100	DGDB 2480H
UMPE-5	32.2	26.4	0.941	9.8	10	DGDB 2480H
UMPE-6	32.9	26.8	0.941	9.8	10	DGDB 2480H
UMPE-7	31.4	21.5	0.942	10.4	10	DGDB 2480H

unimodal molecular weight distribution and three kinds of bimodal HDPE resins with a bimodal molecular weight distribution in this work. The unimodal HDPE were polymerized with Philips Chromium catalyst (UCC S-2) in one reactor, and the bimodal ones were prepared with Ziegler-Natta catalyst in two reactors. The BMPE-1 and BMPE-3 were commercial grade samples and provided by SINOPEC Company. The BMPE-2 was also donated from Korea Petrochemical Ind. Co., LTD. For unimodal ones, the UMPE-1 used in this study was commercial grades sample and other products were rolled off the production line after changed the polymerization technology. Their property parameters were listed in Table 1. All of these materials had similar density and melt flow rate (MFR) but significantly different rupture time.

2.2. The isothermal and nonisothermal crystallization experiments

The isothermal and nonisothermal crystallization experiments were performed in a differential scanning calorimetry (DSC, Q200, TA Company, USA) calibrated with high purity indium. 5 mg of samples was used for every experiment in a nitrogen atmosphere.

Isothermal crystallization program: the specimens were heated and equilibrated at 160 °C for 5 min, and then cooled to designated temperature (121.5 °C) at 40 °C/min to crystallize for 30 min, then heated to 160 °C at 25 °C/min to record melting curves.

Nonisothermal crystallization program: the specimens were heated and equilibrated at 160 °C for 5 min, and then cooled to 40 °C at the speed 5, 10, 15, 20, or 25 °C/min. Subsequently, the melting curves were evaluated by heating from 40 to 160 °C at 25 °C/min.

2.3. Temperature rising elution fractionation

In order to further discover the tiny molecular differences between these materials, Temperature rising elution fractionation (TREF) has been performed to collect fractions at different temperatures for targeted analysis. In this work, a home-made TREF system was used to fractionate the samples, which were mainly composed of a silicone oil bath with a Huber thermostat (POLYSTAT CC3 ± 0.02 °C), a 850 mL column type fractionation column filled with quartz sand (AR), a pump (KNF Lab, STEPDOS 08 S) and a rotary evaporator (EYELA). 1.5 g of the specimens were dissolved in 250 mL xylene at 135 °C with the aid of a magnetic stirrer under nitrogen atmosphere with stirring for at least 2 h. Then the dissolved samples are quickly moved into an elution flask, which were equilibrated at 135 °C for 5 h. The solution was then cooled from 135 °C to room temperature at a rate of 5 °C/min. The solution was coated on the surface of quartz sand in turn. After that the specimens gradually heated up from room temperature to 125 °C and the polyethylene dissolved in different temperatures was pressed into the eggplant shaped bottle through the diaphragm pump with nitrogen. After vacuum distillation of the polymer fraction, the whole was cleaned with isopropanol. The polymer fraction is dried in a vacuum oven 60 °C for 1 night and the mass was recorded.

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