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The effect of different structure parameters on the crosslinking behaviour and network performance of LDPE

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Abstract

In the present study, we investigate the crosslinking behaviour of 6 ordinary low density polyethylenes, and the effect of relatively modest changes in the polyethylene structure on the properties of the resulting network. The observed variations in gel formation are mainly explained by differences in molecular weight, where both $\bar{M}_n$ and $\bar{M}_w$ affect the results. The presence of long chain branches (LCB) present on the polymer main chain is shown to have a significant effect on the network quality. The occurrence of LCB affects the ability in making effective entanglements, a behaviour which is largely dependent on the length of the branches. At high LCB frequencies, the long chain branches are relatively short and therefore more prone to disentangle. The frequency and the amount of LCB, together with the molecular weight, have a large impact on the coil size. The coil size is believed to be an important parameter for the crosslinking behaviour, as a large coil size facilitates interconnections between adjacent polymer coils. In addition, LCB increases the probability of creating intramolecular crosslinks. However, this study shows that a very high amount of LCB is needed in order to obtain any significant effect on the network quality originating from intramolecular crosslinks.

Keywords: Polyethylene; Long chain branching; Crosslinking

1. Introduction

Polyethylene (PE) is the most widely used thermoplastic polymer in the world, with a big versatility of application possibilities. Several desirable application properties can be obtained by choosing one of a large variety of polyethylene grades. To achieve a better dimension stability during heat exposure, crosslinks are introduced between the polyethylene chains in order to create a three dimensional network. The network not only improves the heat resistance, but also makes the material more resistant towards chemicals and stress-cracking which makes it a very durable material [1]. Crosslinked polyethylene, XLPE, has further extended the application fields for PE. The material is commonly used as insulation for electrical wires and cables, as hot water pipes, and in other applications where high demands are put on the durability of the polymer [2,3]. In addition, crosslinked materials also exhibit a memory effect which makes them very useful for the production of heat shrinking products [4].

There are several possible ways of introducing crosslinks into polyethylene [5], but the most commonly used method in industrial settings today is peroxide crosslinking. A number of peroxides are suitable crosslinking agents, but dicumylperoxide (DCP) is most frequently used for the crosslinking of low density polyethylene (LDPE). The decomposition temperature for DCP is high enough to keep the pre-curing during processing at a low level, and sufficiently low to allow an efficient and rapid crosslinking at a relatively moderate temperature where unnecessary degradation is avoided. The peroxide decomposes into radicals, which abstracts hydrogen from the polymer. The crosslinking reaction is then described as a combination of macroradicals. For a more detailed description, see references [5,6].

Various factors affect the crosslinking process. Besides external aspects, such as crosslinking temperature and time, a number of structural characteristics of the polymer strongly influence both the crosslinking ability and the resulting network. For example, the presence of vinyl groups on the LDPE chain has a large impact on the crosslinking efficiency [7–10]. The introduction of vinyl groups into LDPE gives higher amounts of gel at shorter crosslinking times at a specific peroxide concentration. Furthermore, a high $\bar{M}_n$-value is important, since short polymer chains are more difficult to incorporate into a crosslinked matrix, and therefore decrease

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the potential for obtaining a high gel-content. Also, the possibility of trapping the entanglements, physical crosslinks, greatly affects the resulting network density of a crosslinked polymer. High $\bar{M}_n$-values have been proven to increase the network density as long chains (and thereby fewer chain ends) increase the importance of trapped entanglements on the network formation [11,12]. Two recent studies by Smedberg et al. [13,14], discuss the influence of long chain branches (LCB) on the crosslinking efficiency for LDPE. Their findings are based upon that a polymer coil with long chain branches occupies a smaller volume than a linear polymer of the same molecular weight. They suggest that this difference in size leads to a difference in 'network efficiency' of the crosslinked polymer; the long chain branched polymer with its smaller coil size would be more inclined to make intramolecular crosslinks, i.e. within its own coil, than a more expanded coil which could more easily form crosslinks with adjacent polymer coils. The intramolecular crosslinks do not contribute to the effective network as they do not tie together two polymer molecules, which thereby impair the network strength of the crosslinked polymer. A recent quantitative analysis supports these findings [15].

In this work, we have chosen to work with 6 'ordinary' LDPEs in order to investigate potential differences in crosslinking behaviour and/or network properties. The previous studies mentioned above [13–15] included samples of a somewhat more extreme character, especially regarding the MFR_2 (melt flow rate) values and in amount of long chain branches. As numerous factors affect the crosslinking, we have chosen to investigate a more 'normal' selection of LDPEs, which can all be used in the production of XLPE. The main goal of this study is to further analyse the importance of LCB for the crosslinking and network formation of LDPE. Size Exclusion Chromatography in combination with Multi Angle Laser Light Scattering (SEC-MALLS) was used as an important tool in the determination of LCB. The original polyethylenes, the subsequent crosslinking, and the network formation and resulting quality of the network were evaluated using SEC, FTIR, gel content determinations, swelling measurements, dynamic mechanical analyses, and uniaxial strain experiments.

2. Experimental

2.1. Materials

This work is based on a study of 6 LDPEs, provided by BOREALIS AB, Stenungsund. The polymers were chosen to constitute a selection of normal LDPEs, covering a range of different MFR values and densities. The range was kept quite narrow as we wanted to avoid extreme values in molecular weight and branching content. All samples were taken during the production of commercially available LDPE qualities. However, to avoid unwanted interactions from potential additives such as stabilizers, all LDPEs, except PE F, were taken manually from the production line prior to the addition of additives. Since PE F was purchased at a later time, ordinary commercial grade was used. All samples were delivered as pellets. It should be mentioned that despite the precautions made when selecting the materials, sample PE B showed signs of being inhomogeneous. We decided to keep the material in the investigation, bearing in mind that the results might be affected.

2.2. MFR measurements

Melt Flow Rate (MFR) measurements, according to ISO1133:1997, give an estimation of the melt viscosity of the material. A certain weight is used to force polyethylene at 190 °C through a standard die and the amount of polyethylene that flows through the die during 10 min is measured. In this study, the MFR_2 value was measured, meaning that a weight of 2.16 kg was used.

2.3. FTIR

To investigate the presence of double bonds, FTIR was performed on all non-crosslinked samples. Thin films were made as described below and the FTIR-spectra were recorded on a Perkin-Elmer FTIR Spectrum 1000 using 20 scans and a resolution of 4 cm^{-1}. Different unsaturated groups such as vinyl, vinylidene, and *trans*-vinylene can be detected by FTIR. Only vinyl bonds were investigated here, as they most strongly affect the crosslinking. The vinyl group absorbs at both 909 and 990 cm^{-1}, but only the peak at 909 cm^{-1} is used here, due to its stronger absorption. The number of double bonds/1000 C was calculated using the peak at 2020 cm^{-1} as an internal standard, and the extinction coefficients reported by Haslam et al. [16].

2.4. Crosslinking

The polyethylenes were crosslinked in the melt using dicumylperoxide (DCP) as a crosslinking agent. Three different concentrations were used: 0.5, 1, and 2% (w/w). To ensure a more homogenous impregnation of DCP, and to facilitate the penetration of the crosslinking agent into the material, the pellets were cooled in liquid nitrogen and thereafter ground to a powder. A suitable amount of DCP was dissolved in methanol and added to the powder at a ratio of 1 ml DCP-solution/1 g of LDPE. The impregnation lasted for 1 h at ambient temperature and pressure, with agitation every 15 min. The powder was then dried under vacuum for 5 h at 20 °C to reach a complete evaporation of the solvent. This mode of procedure ensures a complete uptake of the peroxide into the polymer.

Crosslinking was performed at 180 °C. A pressure of approximately 25 bar was applied for 10 min when the curing was considered as completed [17,10]. The samples were then removed from the press and left to cool, still with a certain weight applied to avoid bubble formation during cooling. Prior to crosslinking, the polymers were allowed to melt for 2 min at 125 °C with no pressure applied, allowing a homogeneous distribution of the peroxide. In all experiments, except for the hot set test, thin films of approx. 0.5 mm were made from 1 g of