



B.5.1. Mécanismes de réticulation dans le polyéthylène basse densité

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Résumé

Le polyéthylène basse densité, PEBD, est le polymère traditionnellement choisi pour de nombreuses applications, comme la câblerie, lorsqu'il doit être réticulé pour améliorer sa stabilité thermique. Nous avons entrepris d'étudier les mécanismes de la réaction de réticulation par voie chimique pour différents types de PEBD. L'importance des groupements fonctionnels présents dans le PEBD a été étudié sur des résines ayant différents niveaux d'insaturation sur la chaîne polymérique.

Dans cette étude, les échantillons de PEBD ont été réticulés à l'aide de peroxyde de dicumyle selon diverses conditions. Les réactions ont été suivies par une analyse en IR-TF, et des mesures du degré de réticulation et de taux de gonflement en solution. Les résultats laissent apparaître que les groupes vinyliques sont rapidement consommés et il est même possible d'obtenir une très forte teneur en insolubles avec un faible niveau de peroxyde. Les groupes vinyliques disparaissent par un mécanisme de polymérisation.

L'explication du réseau compact formé durant la formation des gels de PEBD est la formation de liaisons carbone-carbone, conduisant à un enchevêtrement permanent des chaînes, qui confère au polymère réticulé ses bonnes propriétés thermiques.

Introduction

Thermoplastic polyethylene is the major bulk polymer with an annual production of 37 mil tons/y [1]. Roughly 1/3 of this is low density polyethylene, LDPE.

Due to its non polar structure and cleanliness PE, mainly LDPE, has become the favourite in W&C applications, which consume 4% of the total LDPE produced.

For some applications the properties of PE are enhanced by crosslinking [2]. There are several ways to induce crosslinks, namely peroxide, silane, and radiation [3].

In this work we have focused on base resin properties correlated to peroxide crosslinking behaviour.

Several workers have proposed crosslinking mechanisms involving vinyl groups mostly in linear PE's [4, 5, 6], but much less has been done on LDPE despite its commercial importance. Because of this we have undertaken a study of LDPE's with different amounts of double bonds and also synthesized a novel copolymer [7].

Polymers

The results reported here were obtained from four different polymers, Tab. 1.

B.5.1. Crosslinking mechanisms in low density polyethylene

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Abstract

Low density polyethylene, LDPE, is the preferred polymer in many applications, like wire & cable, where crosslinking is performed to achieve an improved thermal stability. We have undertaken a study in order to investigate the reaction mechanisms in the chemical crosslinking of different LDPE polymers. The importance of the chemical functionalities present in LDPE has been studied with resins having different amounts of unsaturation in the polymer chains.

In this study the LDPE samples were crosslinked with dicumyl peroxide under varying conditions. The reactions were followed by FT-IR, gel content, and swelling measurements. The results reveal that vinyl groups are rapidly consumed and it is possible to form a high content of gel, even with a low amount of peroxide. The vinyl groups disappear via a polymerization mechanism.

The explanation to the close network formed during LDPE gel formation is carbon-carbon bond formation, resulting in permanent polymer chain entanglements which yield the good thermal properties of the crosslinked polymer.

- A) LDPE with 0.13 vinyl groups/1000C, reference.
- B) LDPE with 0.45 vinyl groups/1000C; propylene was used as a chain transfer agent, CTA, in the polymerization.
- C) The polymer C was synthesized, under free radical conditions with 1,9-decadiene as a comonomer [7], so as to achieve a similar amount of terminal vinyl groups in the polymer as in B. The number of vinyl groups were determined to be 0.42/1000C.
- D) The polymer D was synthesized as for C, with an increased number of vinyl groups equal to 0.68/1000C.

Sample	Polymer	Vinyl/1000C -CH=CH ₂	Mn* (g/mole) (RI)	Mw* (g/mole) (LS)	LCB*/1000C
A	Ref.	0.13	17.000	187.000	1.5
B	Prop.	0.45	16.000	265.000	1.7
C	Diene	0.42	14.900	224.000	1.8
D	Diene	0.68	16.100	221.000	1.8

*) Determined by size exclusion chromatography

Tab. 1. Data for the Investigated LDPE Polymers.