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Crosslinked polyolefins using a modified filler

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Abstract. The aim of this study was to investigate the crosslinking of different polyolefins with the support of a modified mineral filler. The modified filler, talcum, acts as a crosslinking agent and improves the crosslinking network. Therefore, a thermal initiator is linked to the talcum surface. During the extrusion process, the initiator decomposes and radicals are formed. These radicals support the crosslinking process between the polymer chains. To produce the crosslinking agent, two steps were necessary. The first step was the grafting of alkoxy silanes onto the talcum surface. The next step was the linking between the initiator and the silanes grafted onto the talcum surface. To optimize the crosslinking network, two different polyolefin blends were used. The aim was to investigate the influence of the different chain branching behavior of the polymer network on the crosslinking process. Therefore, compression molded plates out of the polymer blends and the modified talcum were produced and analyzed with a plate/plate rheometer.

Keywords: crosslinking, talcum, thermal initiator, polyolefins

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INTRODUCTION

Depending on process and catalysts, several types of polyethylene exist with different numbers and types of chain branching [1, 2]. For example, low-density polyethylene (LDPE) with a high number of long chain branches, high-density polyethylene (HDPE) with a very low amount of short branching and linear low-density polyethylene (LLDPE) with a higher amount of short chain branches [1, 2]. The development of metallocene catalyst made it possible to produce ethylene-octene copolymers (EOC) with a molecular structure with narrow molecular weight distribution and homogeneous distribution of comonomer [3]. However, their field of application is limited by temperature. To shift the field of application to higher temperatures, several methods to crosslink polymer chains exist [4]. One is electron beam irradiation, a method where radicals are produced without any additives [5]. A common method to form free radicals at the polymer chains is the use of peroxide [6]. Another technique is to use peroxide in combination with silane. The formed radicals of the peroxide eliminate the hydrogen atoms of the chains, and then the silane groups are grafted to the polymer chains and link to a crosslinked network [4, 6, 7].

There is also some literature about crosslinking of LLDPE and EOC available [8, 9, 10, 11, 12, 13]. In some of these studies, the crosslinking of LDPE, LLDPE and HDPE was investigated [8, 11]. Because of its higher content of tertiary carbon atoms, the LLDPE can establish a better crosslinking network than the other polyethylene types [8, 11]. Yussuf et al. compared the crosslinking of LDPE and the metallocene catalyzed LLDPE [10]. They found out that the metallocene catalyzed polyethylene showed a higher degree of crosslinking than LDPE due to the different molecular structure [10].

The purpose of this study was to improve the crosslinking of LDPE. Because of the influence of chain branching on crosslinking [8, 9, 10, 11], we used different polyolefins (LLDPE and EOC) to investigate their influence on the crosslinking network. Another idea was to link the thermal initiator 4,4'-azobis(4-cyanovaleric acid) to the surface of a filler, which is already in the compound for other purposes (e.g. nucleation). This initiator is also used in some other studies for grafting of polymers onto solid surfaces [14, 15, 16, 17]. The modified filler, talcum, acts as additional crosslinking agent to improve the crosslinked network.

For the linkage of the initiator to the talcum surface three steps, which were performed according to the study of Gert Boven et al. [17], were necessary.

MATERIALS

In this study, a low density polyethylene (LDPE) with a melt mass flow rate (MFR) of 0.65 g/10 min (at 190 °C/2.16 kg), an ethylene octane copolymer (EOC) with an MFR of 0.5 g/10 min (at 190 °C/2.16 kg) and a linear low density polyethylene (LLDPE) with an MFR of 2 g /10 min (at 190 °C/2.16 kg) were used. As filler, a standard talcum grade by Mondo Minerals B.V. was utilized. For the silanization alkoxy silane (3-aminopropyl)trimethoxysilane and as solvent toluene were used. Dichloromethane, hexane, phosphorus pentachloride, the thermal initiator 4,4'-azobis(4-cyanovaleric acid) (ABCA), triethylamine and ethanol were utilized in the second and third step of the modification. All chemicals were purchased from Sigma Aldrich and used without any purification. For the crosslinking experiments, 3-methacryloxypropyltrimethoxysilane from Wacker Chemie AG and dicumyl peroxide from Sigma Aldrich were used.

EXPERIMENTAL

Modification of talcum

The filler was modified in three steps: The first step was the grafting of alkoxy silanes onto the talcum surface (silanization) (figure 1). The second step was the chlorination of the thermal initiator 4,4'-azobis(4-cyanovaleric acid). This step was necessary to achieve an easier linkage between the functional groups of the aminosilanes and the chlorine. The last step was the linkage of the thermal initiator to the functional groups of the silane grafted onto the talcum surface (figure 2). All steps were performed corresponding to the study of Gert Boven et al. [17].

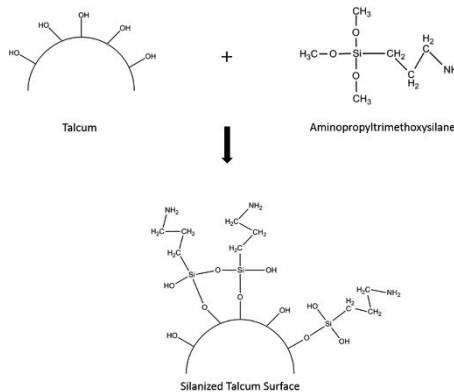


FIGURE 1. Grafting of the aminosilane onto the talcum surface

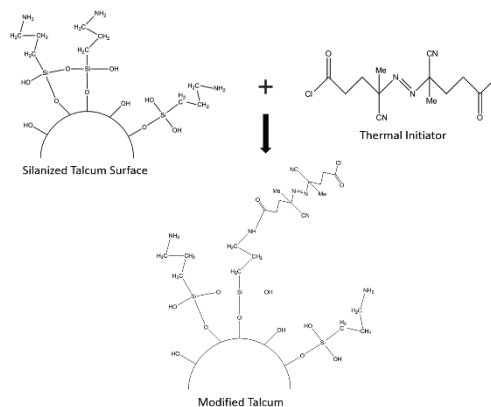


FIGURE 2. Modification of the silanized talcum surface

Crosslinking experiments

For the crosslinking experiments, polymer blends with a ratio of 80 wt.-% LDPE and 20 wt.-% LLDPE or 20 wt.-% of EOC with 4 phr silane, 0.5 phr dicumyl peroxide and with and without modified talcum were produced in a kneader (Haake Rheocord 3000/600, Thermo Fisher Scientific GmbH, Karlsruhe, Germany). The used material formulations are shown in table 1. The compression molded plates (produced on a vacuum press Type P200PV, Dr. Collin GmbH, Ebersberg, Germany) were stored at 60 °C for a defined time and rheologically analyzed using a plate/plate rheometer (Physica MCR501, Anton Paar GmbH, Graz, Austria).

TABLE (I). Used material formulations.

LDPE (ratio)	LLDPE (ratio)	EOC (ratio)	Silane (phr)	Dicumyl peroxide (phr)	Modified talcum (wt.-%)
100	-	-	-	-	-
80	20		4	0.5	-
80	20		4	0.5	1.6
80		20	4	0.5	-
80		20	4	0.5	1.6

Results and Discussion

For the polymer blends the complex viscosity (η^*), loss modulus (G'') and storage modulus (G') were determined. Figure 3 shows the complex viscosity of the crosslinked polymer blends after different storage times. The crosslinking of the chains has increased the complex viscosity of the polymer blends in a lower frequency range and, compared to the non-crosslinked LDPE, no longer shows a Newtonian plateau [18]. All samples with the modified talcum show a higher complex viscosity, at lower angular frequencies, than samples without the modified filler. These results reveal that the thermal initiator linked to the talcum surface acts as an additional crosslinking agent and leads to a better crosslinking network. Figure 3 also shows that the polymer blend with EOC achieved a higher complex viscosity after four days, at lower angular frequencies, than the blend with LLDPE after six days. The LDPE/EOC compound without modified talcum reached also a higher viscosity than the LDPE/LLDPE compound with modified talcum. This indicates that the numerous short-chain branches of the EOC lead to a better crosslinking network compared to LLDPE.

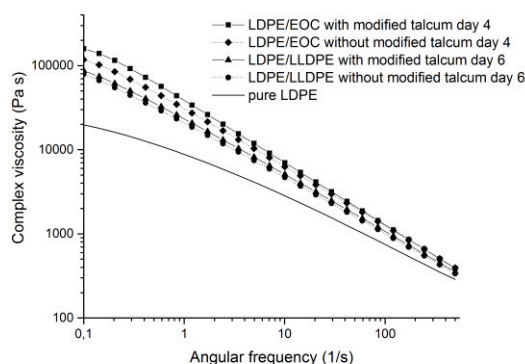


FIGURE 3. Complex viscosity of non-crosslinked and crosslinked polymer blends depending on storage time

The crosslinking network can also be determined by measuring the loss and storage moduli (figure 4). Compared to the non-crosslinked polymer the crosslinked samples show no cross over point of the loss and storage moduli. This material behavior indicates a crosslinking network [19]. Figure 4 also shows a higher storage modulus for the crosslinked blend with EOC at low frequencies (ω) compared to the blend with LLDPE. This effect can be explained by the restricted movement of the chains in the crosslinked network [20]. This suggests that the polymer EOC leads to better crosslinked chains than the LLDPE.

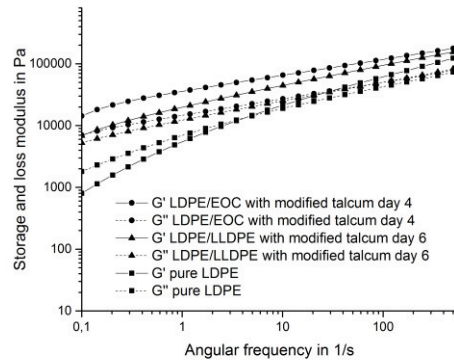


FIGURE 4. Storage and loss moduli of crosslinked polymer blends after different storage times and non-crosslinked polymer

Figure 5 shows the influence of the modified talcum by comparing the storage and loss moduli of the samples using EOC as a blend partner of LDPE. At low angular frequencies the sample with the modified talcum shows a higher storage modulus than without the filler. This indicates that the additionally formed radicals of the initiator linked to the talcum surface leads to a better crosslinked network. Details of the results are shown in table 2.

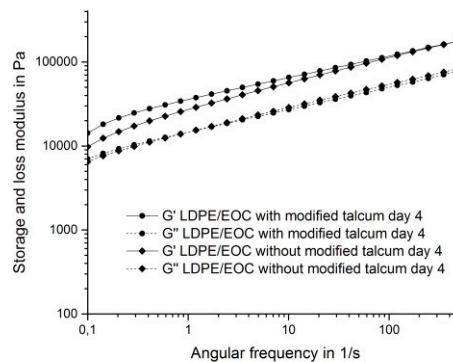


FIGURE 5. Storage and loss moduli of LDPE/EOC with and without modified talcum

TABLE (2). Measured values of the zero viscosity and storage modulus at an angular frequency of 0.1 s^{-1} .

Sample	η_0 (kPa s)	G' (kPa)
LDPE	19.8	0.8
LDPE/EOC without modified talcum	117.7	6.5
LDPE/EOC with modified talcum	159.1	14.3
LDPE/LLDPE without modified talcum	79.1	6.2
LDPE/LLDPE with modified talcum	86.6	6.9

Conclusions

In this study, we investigated two influences on crosslinking LDPE. The use of polyolefins with different amounts of chain branches, and the influence of a modified filler as additional crosslinking agent were investigated. Before crosslinking, a thermal initiator was linked to the surface of the talcum particles to produce the crosslinking agent. For the crosslinking experiments, polymer blends with silane, dicumyl peroxide and with/without the modified talcum were produced and stored at $60 \text{ }^\circ\text{C}$ for a defined time. Afterwards the samples were examined using a plate/plate rheometer. The results of the complex viscosity showed an increase at a lower frequency region for the polymer blends with the modified talcum compared to the compounds without the modified filler. The higher storage modulus of these

blends also indicates that the formed radicals of the thermal initiator linked to the talcum surface supports the crosslinking process and lead to a better crosslinking network. Therefore, the use of a modified talcum with a thermal initiator is a possibility to support and improve the crosslinking process for polyolefins.

We also investigated the influence of two different polyolefins with different amount of chain branches. The experiments showed that blends with EOC achieved a higher complex viscosity and a higher storage modulus, at lower angular frequencies, than blends with LLDPE. For the complex viscosity, LDPE/EOC blends with and without the modified talcum reached a higher level than the LDPE/LLDPE blends. This indicates that the polymer EOC leads to a better crosslinking network due to the highly branched chains.

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