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Miscibility assessment and thermal oxidative stability of blends of branched polyethylene and poly(1,2-butadiene)

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SUMMARY

Poly(1,2-butadiene) promotes crosslinking of branched polyethylene, which indeed indicates partial miscibility of the two polymers. Dynamic mechanical spectroscopy and transmission electron microscopy of blends of branched polyethylene and poly(1,2-butadiene) indicated that the polymers are partially immiscible even in the blend with only 3% of poly(1,2-butadiene). The thermal oxidative stability at temperatures above the melting point of samples stabilized with antioxidants was essentially unaffected by the percentage concentration of poly(1,2-butadiene), whereas the stability towards external partial discharges was lower in crosslinked polyethylene blends containing poly(1,2-butadiene) than in pure crosslinked polyethylene.

INTRODUCTION

In a previous paper (1) it was shown that the addition of different percentages of poly(1,2-butadiene) to branched polyethylene containing 2% (w/w) of dicumyl peroxide had a significant effect on the crosslinking process, indicating semi-compatibility of the two polymers. The strong increase in gel content and the strong decrease in molar mass of the soluble fraction of the crosslinked polymer confirmed that poly(1,2-butadiene) enhanced crosslinking of polyethylene. It was shown that the crosslinking efficiency increased from 0.86 in pure polyethylene to 1.3 at 5% (w/w) of poly(1,2-butadiene).

It was suggested that the crosslinking efficiency increases because, in addition to the hydrogen abstraction followed by combination of two alkyl radicals producing a crosslink, other reactions leading to crosslinks must occur in the poly(1,2-butadiene)-containing systems. Free-radical chain reactions involving the vinyl groups in poly(1,2-butadiene) and in polyethylene may account for the observed increase in crosslink density. The levelling-off tendency in the gel content increase observed at 3-4 % poly(1,2-butadiene) content indicated a saturation of polyethylene - poly(1,2-butadiene) solution at this composition.

For blends with a higher concentration of poly(1,2-butadiene), it was suggested that a separate poly(1,2-butadiene) phase was formed which led to retardation of the enhancement of the crosslinking of polyethylene. It was proposed that the observed decrease in crosslinking efficiency with increasing poly(1,2-butadiene) content observed in this poly(1,2-butadiene) range may be

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due to a lowering of the dicumyl peroxide concentration in the polyethylene-rich phase.

This paper presents data obtained by dynamic mechanical spectroscopy and electron microscopy for the assessment of miscibility of the polymer components in the branched polyethylene-poly(1,2-butadiene) blends. Secondly, it presents data relating to the thermo-oxidative stability and the stability towards external partial discharges measured in crosslinked blends of polyethylene and poly(1,2-butadiene) and in pure crosslinked polyethylene.

EXPERIMENTAL

Binary blends of branched polyethylene (DFDS-47, Neste Polyeten AB, Sweden; $\overline{M}_n$ = 14 000 g mol^{-1}, $\overline{M}_w$ = 77 900 g mol^{-1} from size exclusion chromatography (SEC); 0.3 mol% ethyl branches, 0.7 mol% butyl branches, 0.1 mol% pentyl branches, 0.3 mol% long chain branches and 0.016 mol% vinyl groups from C-13 NMR; containing antioxidants) and poly(1,2-butadiene) (Grade B-1000, Nisso Soda Co, Ltd, Japan; $\overline{M}_n$ = 1170 g mol^{-1}; 89.3% of 1,2-vinyl content and 10.7% of trans-1,4 content) were prepared by mechanical mixing at 130°C for 12 minutes. Different blends with 0 to 8% (w/w) of poly(1,2-butadiene) were prepared. Prior to the melt-blending, the polyethylene pellets were impregnated with dicumyl peroxide (Merck-Schuchardt, Germany) at 70°C for 24 hours. All blends contained 2±0.2% dicumyl peroxide.

The oxidative induction time (OIT) was determined by differential scanning calorimetry (DSC) in a temperature-calibrated Perkin-Elmer DSC-2. The crosslinked polymer samples weighing 5.2±0.2 mg were exposed to an oxygen atmosphere at different temperatures between 175.7 and 185.7°C in the DSC. The purge gas flow (oxygen) was 60 ml min^{-1}. The induction time was obtained from the intersection of the isothermal baseline with the tangent at 0.5 mW exothermal deviation from the scanning baseline.

Crosslinked samples were aged in an oven at three different temperatures: 140±1°C, 150±1°C, and 160±1°C. The dumb-bell-shaped specimens (thickness: 1 mm, width: 4 mm) were suspended vertically in the middle of the oven, the space between them being at least 20 mm. The ageing period was 6 h to 2534 h and each ageing treatment included five test samples. The tensile tests were carried out in an Instron 1122 Tensile Testing Machine at 23±2°C. The crosshead speed was 5 mm min^{-1} and the distance between two applied ink spots (L_0) on the specimen was 5 mm. The strain at fracture was determined.

The crosslinked thin films (215±15 µm) for the electrical degradation testing were prepared by compression moulding according to the following procedure: 130°C for 5 minutes (melting), 180°C for 15 minutes (crosslinking) and finally cooling to room temperature under pressure. Before the electrical testing, all samples were coated on the rear with evaporated aluminium. The polymer films were exposed to external partial discharges (PD) (corona) by applying an 1 kHz AC-voltage of 3.0 kV in air at 27±2°C. The tests were carried out in a specially designed vacuum oven (STW 65, Visimar Ass). The AC-voltage was controlled by a 4 MHz function generator (Motel 182A, Wavetek) and a M900 Mos-Fet power amplifier from HH Electronics. The time to breakdown was recorded by an attached clock. The air gap between the needle electrode (Ogura X253-20 treeing needles) and the film was 1 mm and the radius of the needle was 15±2.5 µm.

The breakdown time data consisting of 22 data points for each sample was fitted by the maximum likelihood method to the two-parameter Weibull distribution function [$1-F(t) = \exp(-(t/t_{0.63})^b)$], where $F(t)$ is the cumulative frequency, $t_{0.63}$ is the scale parameter, and b is the shape parameter.

Oblong-shaped specimens (15 mm long, 2.1±0.05 mm wide and 0.55±0.05 mm thick) for dynamic mechanical measurements were prepared by compression moulding at 120±1°C for only 1.5 minutes (to avoid crosslinking) and cooled at 100°C $\min^{-1}$ to room temperature. The dynamic mechanical spectra of the blends were recorded using a Polymer Laboratories Mk II instrument. A temperature scan from -70°C to 50°C at a rate of 1°C $\min^{-1}$ in the tensile mode was carried out for each sample. The frequency was 1 Hz and the applied sinusoidal dynamic strain was 0.07% (11 μm peak to peak) prestressed by a static tensile load of 3.0 N (reducing mode). The samples were clamped at room temperature with a torque wrench set to 10 Ncm.

Samples for transmission electron microscopy were cut from the uncrosslinked polymer samples. The samples were stained using osmium tetroxide at room temperature and normal pressure according to ref. (2), embedded in epoxy and sectioned at 100 K. The stained sections were examined in a JEOL JEM 100 B electron microscope.

RESULTS AND DISCUSSION

Miscibility

Figure 1 shows that the loss factor (tan δ) vs. temperature curve exhibits a weak shoulder appearing at temperature of about -50°C in the blends containing 3% poly(1,2-butadiene). This shoulder was absent in the pure branched polyethylene sample and in the sample with 1.5% poly(1,2-butadiene). The shoulder appeared with stronger intensity in the blends with 5 and 8% of poly(1,2-butadiene). DSC, showing that the glass transition temperature of pure uncrosslinked poly(1,2-butadiene) is -43°C, confirmed that the shoulder in the loss curve is due to the glass transition of immiscible poly(1,2-butadiene).

The electron micrograph shows typical features of immiscibility in the sample with 8% poly(1,2-butadiene) (Fig. 2). The small spherical particles which appear dark are thus enriched in poly(1,2-butadiene). Similar electron micrographs were also obtained for blends with only 3% of poly(1,2-butadiene).

It may thus be concluded that data from dynamic mechanical spectroscopy and electron microscopy show that poly(1,2-butadiene) is present as a separate globular phase even in blends with only 3% of poly(1,2-butadiene). The blend with 1.5% poly(1,2-butadiene) showed, according to dynamic mechanical spectroscopy, no signs of phase separation. The pronounced effect on the crosslinking process of an addition of poly(1,2-butadiene) to branched polyethylene (1) constitutes evidence in support of the hypothesis that low molar mass poly(1,2-butadiene) is partially miscible with polyethylene.

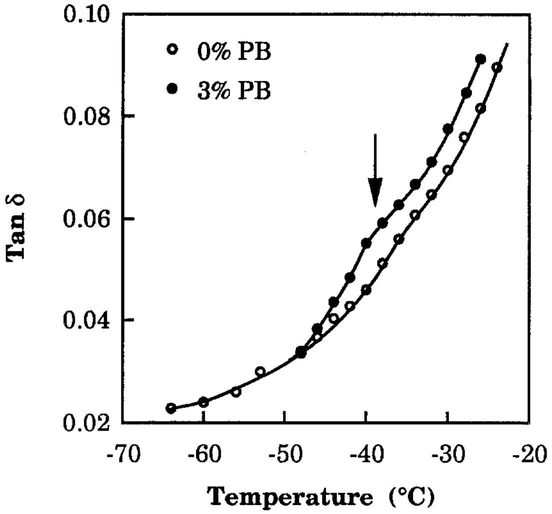

Figure 1. Mechanical loss factor (1 Hz) as a function of temperature for pure polyethylene and for the blend with 3% poly(1,2-butadiene).

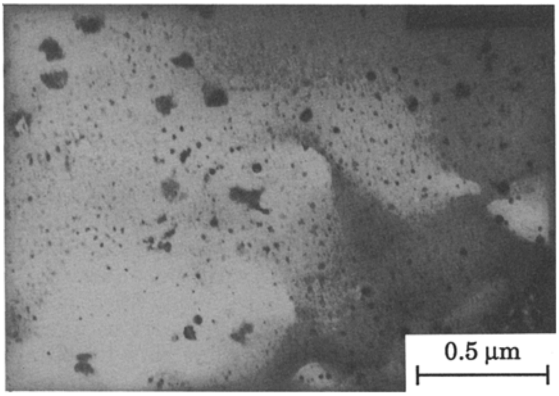

Figure 2. Transmission electron micrograph of osmium-tetroxide-stained blend with 8% of poly(1,2-butadiene).

Thermo-oxidative and electrical stability

Figure 3 presents the Arrhenius temperature dependence of the DSC-OIT-data for polyethylene and for a blend containing 3% (w/w) poly(1,2-butadiene). It should be noted that all blends contained the same amount of antioxidants. The activation energy (ΔE) is almost the same for both samples, about 180-

185 kJ mol^{-1} in the temperature range from 175.7°C to 185.7°C. Included in the same diagram are the induction times determined in the oven ageing tests. The strain at fracture remains practically constant with ageing time until there is suddenly a very large drop in fracture strain. The samples fracturing at low strain levels showed discoloration which is indicative of thermal oxidation. The (oxidative) induction time is defined as the ageing time at which the fracture strain is 50% of the original value.

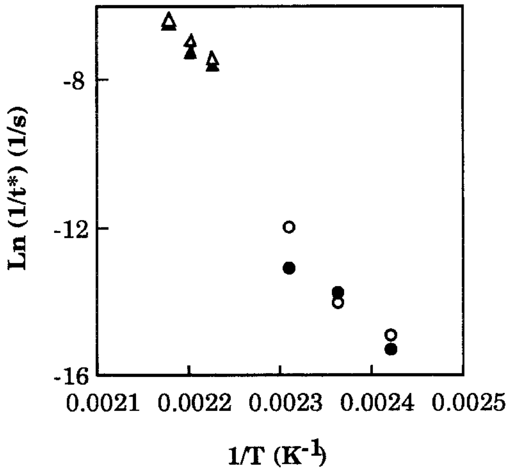

Figure 3. Natural logarithm of the reciprocal of the induction time for oxidation as a function of reciprocal temperature: ▲ XLPE (3% poly(1,2-butadiene)); DSC-OIT; △ XLPE; DSC-OIT; ● XLPE (3% poly(1,2-butadiene)); oven ageing; ○ XLPE; oven ageing.

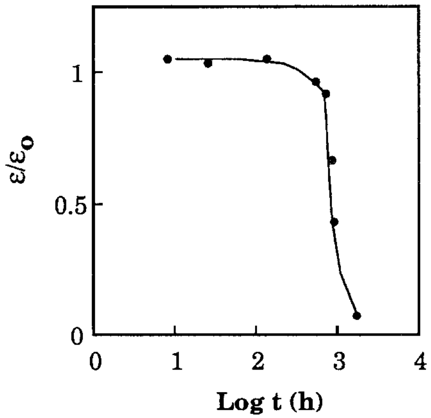

Figure 4. Fracture strain of crosslinked polyethylene aged at 140°C for different periods of time. Each data point is an average value based on five independent samples.

The oven ageing induction time data (Fig. 3) showed Arrhenius temperature dependence with an activation energy of about 165-220 kJ mol^{-1}. The differences in activation energy and thermo-oxidative stability between the pure crosslinked polyethylene and the crosslinked binary blend are insignificant.

The pure crosslinked polyethylene showed a greater stability towards partial discharges than the crosslinked blend with 3% poly(1,2-butadiene): pure polyethylene:$t_{0.63}$=22.9 h; b=5.4; blend with 3% poly(1,2-butadiene): $t_{0.63}$=20.9 h; b=4.3. The relatively high concentration of unsaturation present in the blended sample, 7% of the initial content remained after crosslinking, is most probably the reason for the lower stability of the poly(1,2-butadiene)-containing polymer.

CONCLUSION

Dynamic mechanical spectroscopy and transmission electron microscopy of blends of branched polyethylene and poly(1,2-butadiene) show that the polymers are partially immiscibility even in the blend with only 3% of poly(1,2-butadiene). The blend with 1.5% poly(1,2-butadiene) showed according to dynamic mechanical spectroscopy no signs of phase separation. The thermal oxidative stability at temperatures above the melting point of samples stabilized with antioxidants was essentially unaffected by the percentage concentration of poly(1,2-butadiene) whereas the stability towards external partial discharges was lower in crosslinked polyethylene blends with poly(1,2-butadiene) than in pure crosslinked polyethylene.

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