Dynamic Vulcanisation of EPDM-Based Thermoplastic Vulcanisates during Extrusion: Effect of Processing Conditions

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Abstract

Dynamic vulcanisation of EPDM/PE blends using the resol/ $SnCl_2$ system was studied in a co-rotating twin screw extruder using a series of sampling devices. In order to study the effect of the processing conditions on chemical development along the extruder and on the mechanical properties of the extrudate material, the same recipe (having the same polyolefin/EPDM ratio) was compounded under different processing conditions. The results showed that both chemical evolution and mechanical properties depend on the processing conditions.

Introduction

Thermoplastic elastomers (TPEs) are currently the fastest growing rubber market. They are comprised of a wide range of material types, each being characterised by its typical chemical composition, production technology and structure-properties relationship. TPEs combine the elastic and mechanical properties of thermoset crosslinked rubbers with the melt processability of thermoplastics. They can be processed by a variety of techniques, such as extrusion, blow moulding, injection moulding, vacuum forming and calandering. Moreover, production scrap and waste can be recycled after use. TPE-Vs, or TPVs, are

thermoplastic vulcanisates, i.e., TPEs with a crosslinked rubber phase [1-3]. Typically, they are produced via dynamic vulcanisation of immiscible blend of a polyolefin resin and a EPDM rubber, which is selectively crosslinked with a phenolic compound while melt mixing with the polyolefin. As a result, the products obtained consist of crosslinked rubber particles dispersed in a thermoplastic matrix. The thermoplastic matrix explains the melt processability of TPVs while the crosslinked elastomer particles, "glued" together by thermoplastic inter-layers, explain the elasticity. Crosslinking during blending is essential for producing TPVs products with optimum properties. In contrast to simple non-crosslinked blends, TPVs have enhanced elasticity and oil resistance. In addition, dynamic vulcanisation is a way to disperse rather large amounts of elastomer phase in the thermoplastic matrix, resulting in products with a low hardness.
Most commercial TPVs are based on blends of polypropylene (PP) and ethene/propene/diene terpolymers (EPDM). PP is used because of its high melting point and high crystallinity, resulting in superior TPV properties even at elevated temperatures. EPDM is used because of its stability against high temperatures, oxygen and ozone, thus giving the corresponding TPVs good heat oxidation and ozone resistance. As a result of the compatibility of PP and EPDM, TPVs based on PP/EPDM blends are characterised by a finely dispersed EPDM phase (1-3 μm) without the need of a special compatibiliser. However, in this work the dispersion and the crosslinking of HDPE/EPDM blends are studied along the axis of an extruder during dynamic vulcanisation with resol. HDPE was chosen, because it can be replaced by a wide variety of other PE types (LDPE and VLLDPE) and/or ethene-containing polyolefins (like plastomers), allowing an extension of this work in future studies.

A very broad range of TPVs can be produced by varying the composition and the crosslink density. With respect to TPV composition, should be realized that not only the type and the amount of elastomer, thermoplastic and oil can be optimised, but that additional fillers, stabilisers, flame retardants, colourants etc. can also be added for tuning the TPV for a particular application. On an industrial scale, TPVs are typically produced on twin-screw extruders, allowing a large degree of process flexibility. Therefore, in order to optimize the final properties, it is important to understand the effect of the processing conditions on chemical and morphological evolution, as well as on rheological and mechanical properties of the final product.
The present work investigates the chemical evolution along the extruder and the mechanical properties of the extrudate TPV compound prepared in a co-rotating twin screw extruder under different processing conditions.

Experimental

Materials. Oil-extended EPDM (Keltan ® DE2322: 60 wt. % ethene), PE (Stamylex ® 2H280 HDPE), resol and $\mathrm{SnCl_2.2H_2O}$ were kindly supplied by DSM

Compounding.A Leistritz LSM 30.34 intermeshing co-rotating twin-screw extruder with 29 L/D was used (Figure 1). The same recipe of oil-extended EPDM (70wt%), PE (30wt%), resol and $\mathrm{SnCl_2.2H_2O}$ were fed into the extruder via the hopper. The screw configuration was kept constant, while different temperatures (140,170 and 200°C), screw speeds (100,200 and 300 rpm) and throughputs (2,5,5 and 10 kg/h) were used

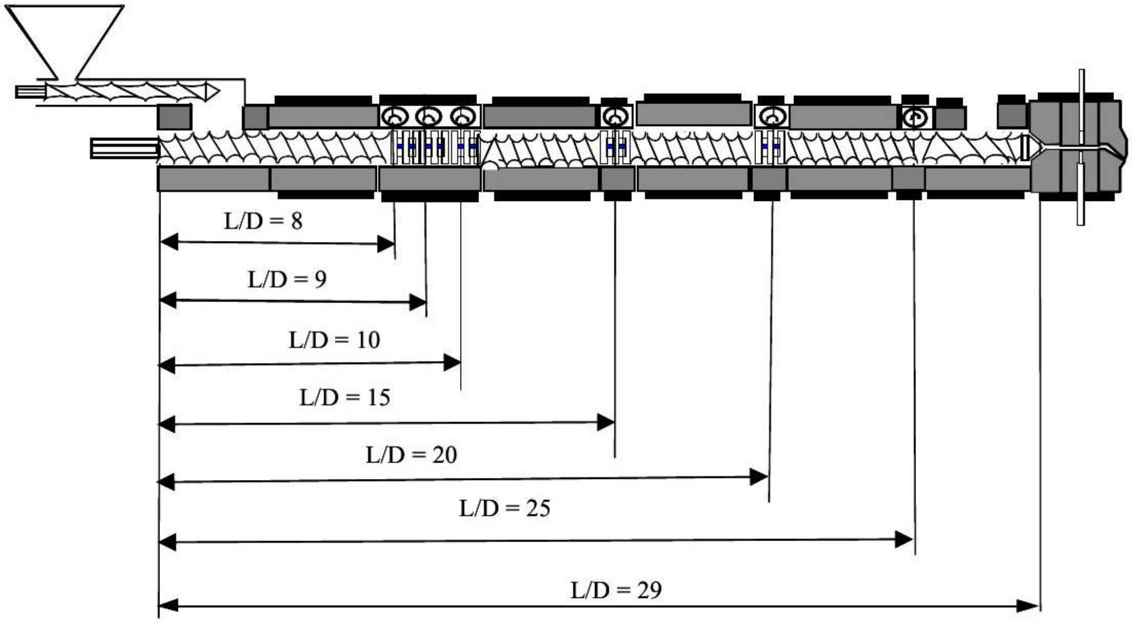

Fig. 1 - Extruder lay-out with positions of the sampling devices. Samples were taken along the screw axis using a series of sampling devices at L/D is 8,9,10,15, 20, 25 and 30 (extrudate) (Figure 1), which allowed rapid sampling (~ 5sec.) of sufficient melt sample (~ 2 g) for further characterisation. Melt samples for further characterisation were collected along the screw axis and from the extrudate and then quenched in liquid nitrogen in order to freeze the morphology and stop the crosslinking reaction.

Characterization Extractions using cyclohexane were used to determine the EPDM content as a measure for the crosslink density of the EPDM phase. Approximately 2 g of the sample was stirred in 100 ml cyclohexane (Riedel) for 48 hours (the cyclohexane was refreshed after 24 hours) at room temperature. The EPDM gel content was calculated with the assumption that the EPDM residue consisted of PE and crosslinked EPDM only. Swelling experiments were used to determine the network density by weighing a sample ($50 \times 25 \times 1$ mm) and immersing it in cyclohexane for 48 h while gently stirring. Cyclohexane was refreshed after 24 h . The swelling was calculated by the ratio of the weight of the samples after and before being immersed in cyclohexane. The mechanical properties were characterized using tensile tests, which were carried out in an INSTRON 4505 with a speed of 50 mm/min and a distance of 80 mm between grips.

Results and Discussion

Since a significant amount of results were obtained in this study and the number of pages allowed for this paper is limited, only some results of one type of processing conditions will be presented and discussed here. The other results will be presented and discussed in a future publication.
The EPDM gel content was used in this study as a measure for the degree of crosslinking of the EPDM phase. It was shown that the EPDM dissolves fully in cyclohexane at room temperature, whereas the PE did not dissolve at all. It was noted that, in some cases, the EPDM gel content was well above 100%, which is not possible from a theoretical point of view. This was probably due to linking of the resol to the rubber and incomplete extraction

of the extender oil from the rubber network.

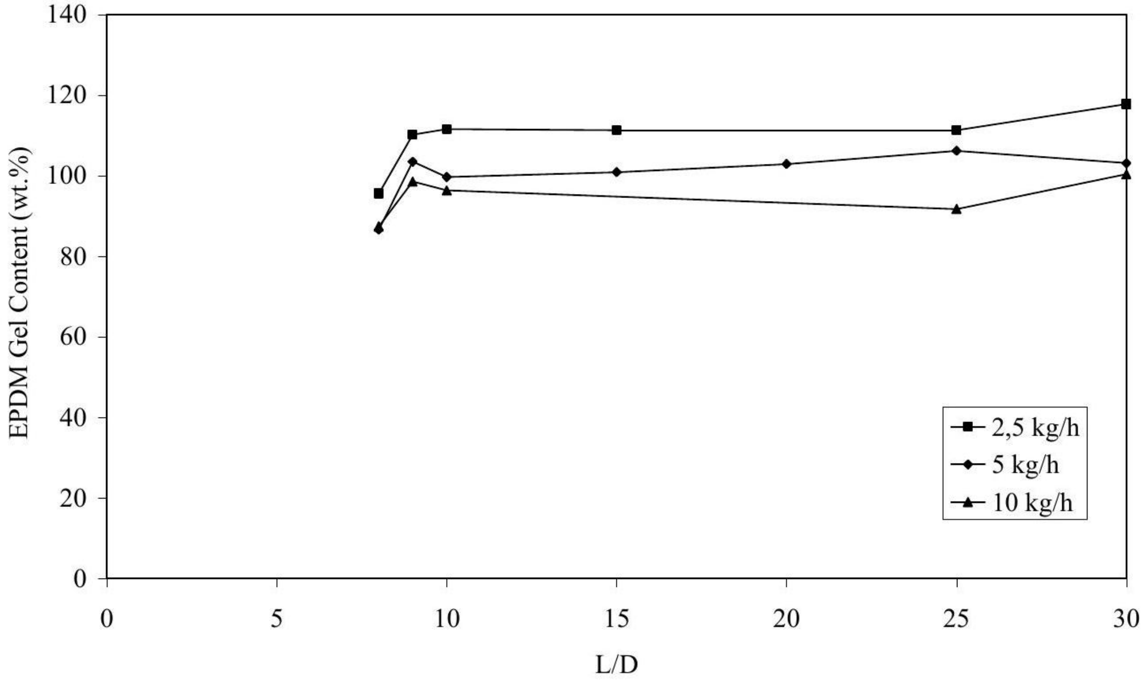

Fig. 2 - EPDM gel content of TPVs as a function of screw length processed using different throughput.

Figure 2 shows the EPDM gel content, as a function of screw length, of the TPVs processed using different throughput. For all cases, the gel content was approximately 100% along the screw axis and the shape of the curves were similar. This shows that all EPDM chains are already part of a crosslinked 3D rubber network at L/D = 9, i.e., the crosslinking reaction was very fast under the processing conditions used. It is noteworthy to mention that these results do not indicate that the crosslinking reaction was already completed at L/D = 9, since the EPDM gel content is not sensitive to variations in the degree of crosslinking at high degrees of crosslinking. However, it was possible to observe the differences in EPDM gel content along the extruder between the three conditions used. The differences among the results of the gel content along the extruder can be explained by the differences occurring during processing, namely the use of dissimilar throughput. The various throughputs influenced the residence time and the flow inside the extruder, which had an effect on the chemical reaction. Using lower throughput, the local and total residence time inside the extruder increased and also the amount of material in the screw sections was also higher. In fact, along fully filled kneading blocks the average residence time is simply determined by V/Q, where V and Q are the local volume and volumetric feed rate, respectively, i.e., residence time is independent of screw speed. Therefore, a decrease in Q produces a linear increase in the local time for reaction. Given that, higher gel content would be expected for the lower throughput, while a decrease in gel content would be expected as the throughput increases. Figure 3 depicts the results of the swelling experiences, which were used to determine the network density. Low values of swelling signify high network density. Thus, gel content and swelling results are in agreement. The network density increased in the first part of the extruder until a plateau was reached and depended on the throughput, being higher for lower throughput.

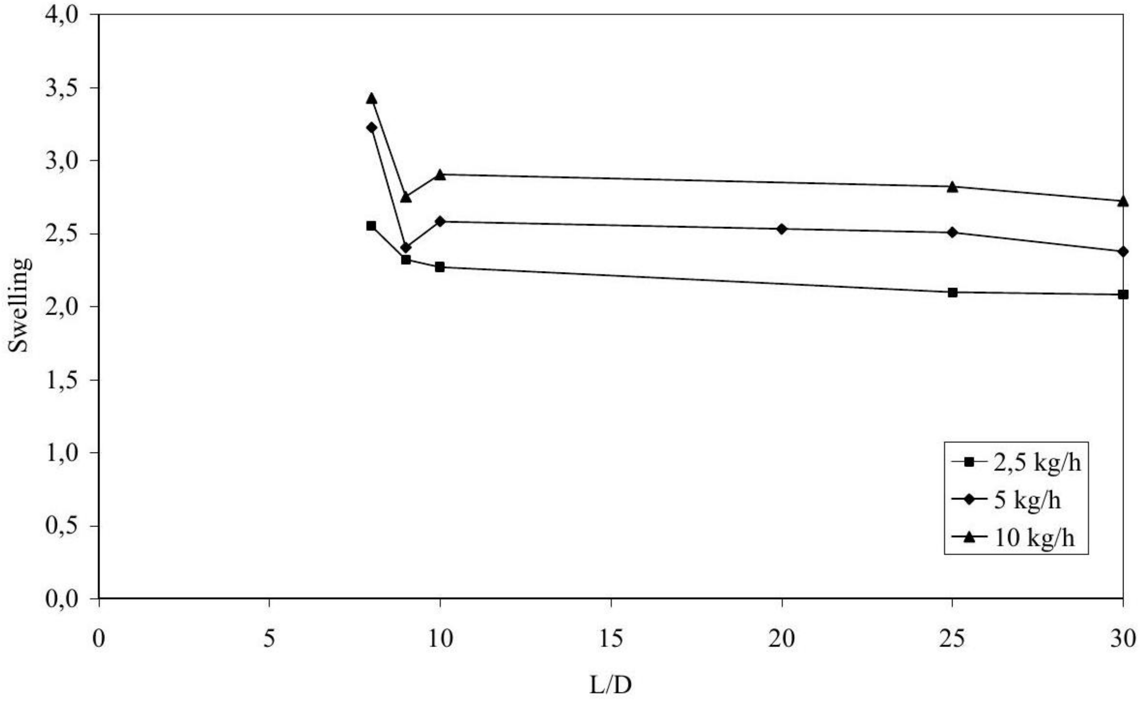

Fig. 3 - Swelling of TPVs as a function of screw length processed using different throughput.

Hardness and stress at break are mechanical properties which are very sensitive to crosslinking density. For these reason, they were selected in order to check the effect of gel content. The differences in gel content of each extrudate material were clearly related to the mechanical properties. As is reflected in Figure 4, hardness of the extrudate decreases as the throughput increases. The same effect is clearly illustrated in Figure 5, stress at break decreases as the gel content decreases.

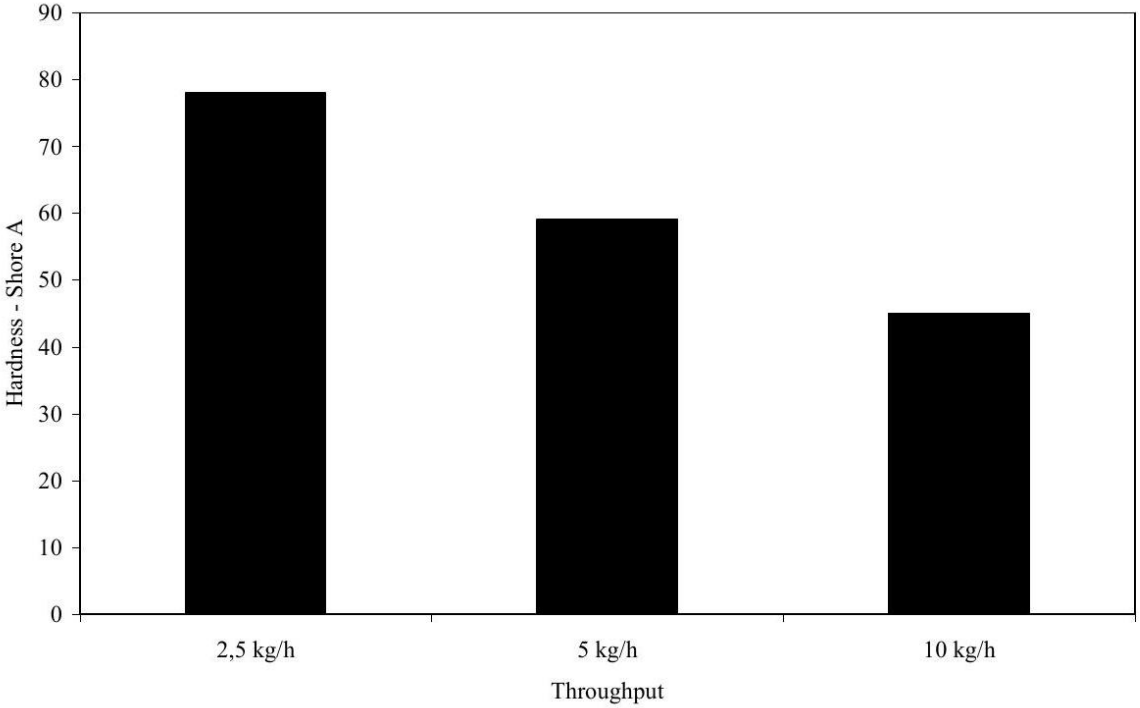

Fig. 4 - Hardness of TPVs processed under different throughput.

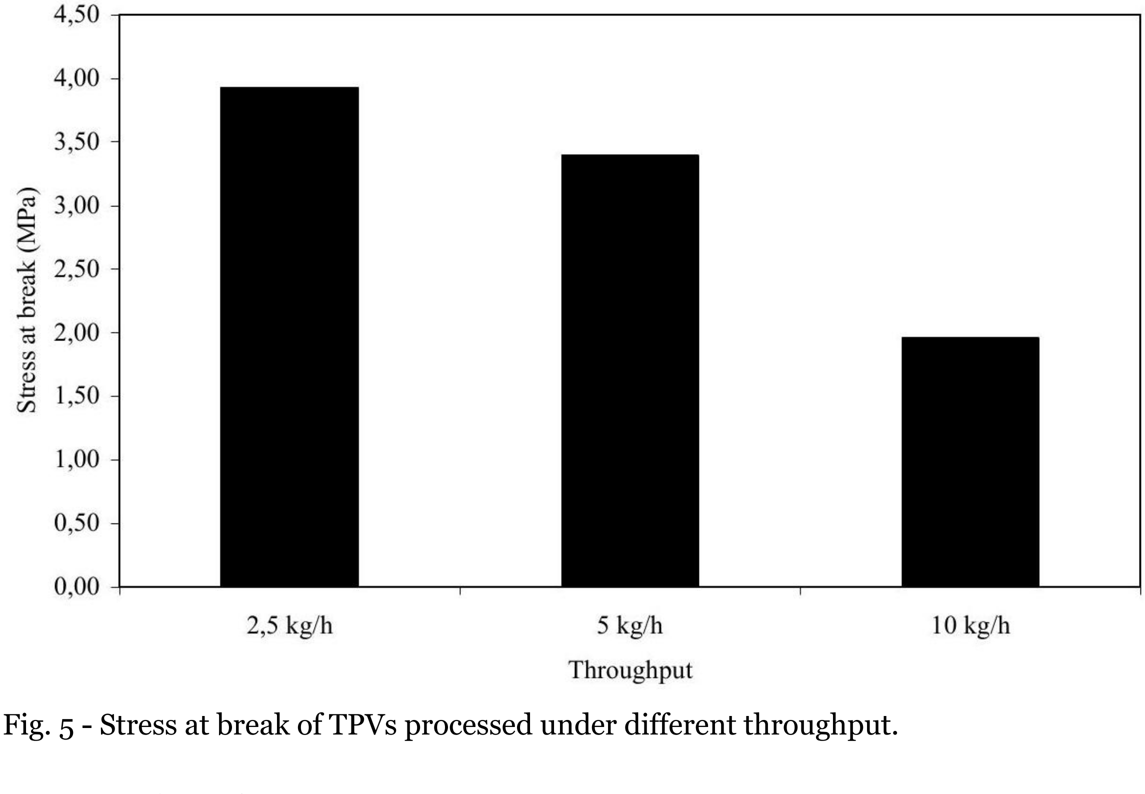

Fig. 5 - Stress at break of TPVs processed under different throughput.

Conclusion

As a general conclusion, using dynamic vulcanisation during melt-blending opens a new route for the preparation of novel high performance engineering thermoplastic vulcanisates based on polyolefin/rubber blends.
During dynamic vulcanization of PE/EPDM blends using the resol/SnCl2 system it was shown that crosslinking of the EPDM phase takes place mostly in the first kneading zone. The gel content increases with a decrease in the throughput, until a plateau is reached. The mechanical properties of the extrudate, hardness and stress at break, are very sensitive to the crosslinking density of the EPDM.

References

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