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Phase inversion phenomena of EPDM /PP - based TPVs by Electronic Microscopy

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Abstract
Morphology development during phase inversion is a very complex and not well understood process. EPDM/PP -based TPVs were prepared and characterize by different electronic microscopy techniques. Using a low Mw-EPDM, morphology development during phase inversion was successfully followed by scanning electron microscopy with a back scattered electron detector.

Keywords: TPVs, dynamic vulcanization, phase inversion, morphology, BSE

Introduction

Thermoplastics vulcanizated (TPVs) are produced via dynamic vulcanization, which is a process were the rubber is selectively cross-linked while melt mixing with a thermoplastic. Since the morphology changes from an initial thermoplastic-in-rubber dispersed droplet morphology to fine particles of EPDM dispersed in a PP matrix, during dynamic vulcanization phase inversion must take place [1]. As a result of the morphology obtained, TPVs combine the melt processability of the thermoplastics and the mechanical properties of the thermoset rubbers. Although, TPVs are already commercially available from the 1970's and a large number of studies have been published, some fundamental questions related to the morphology development during TPVs production and the final morphology are still not understood. For example, the melt processability of TPVs is explained by a dispersion of cross-linked rubber particles in continuous PP matrix, however the elasticity of TPVs suggests some continuity of the rubber phase [2]. Thus TPVs morphology is a topic of discussion and is far from trivial. This work aims to study TPVs morphology development during dynamic vulcanization using electronic microscopy techniques. TPVs were prepared using a low Mw-EPDM, which allows to slowdown the cross-linking reaction and increase the EPDM domains size.

Materials and Experimental Procedure

TPVs were prepared using PP (MFI=2 and 47 g/10 min, at 230 ºC with 2,16 kg), EPDM (Mw=7,2 and 150 kg/mol) (50/50, w/w) and resol/$SnCl_2$ as vulcanizing agent in a batch mixer at a rotor speed of 80 rpm, a set temperature of 200 ºC and a mixing time of 5 min. Samples collected along the time and at 5 minutes were cryogenically fractured and vapor stained by ruthenium tetroxide during 2 hours. Samples, previously coated with a thin gold layer, were then observed by a secondary electron detector (conventional SEM) and a back scattered electron detector (BSE), using a Leica Scanning and FEI Quanta 400FEG Electron Microscope. Samples were also cryomicrotoming to 100 nm thin sections at -130 ºC and vapour stained by ruthenium tetroxide for 20 minutes for TEM characterization using a Philips CM120 Transmission Electron Microscope.

Results and Discussion

Typical TPV morphology observed by conventional SEM and SEM with BSE detector and TEM are shown in Fig. 1 a), b), c) and d), respectively. As it can be seen in micrographs of Fig. 1 a) and b) the cross-linked rubber particles (white phase) have a small size and seem to be aggregated. More detailed information is given in Fig. c), using higher magnification. In this micrograph, the EPDM particles are dispersed and seem to be "glued" by a thin PP layer (dark phase). However, as can be observed in Fig. 1 d), TEM provides high-resolution images giving more details on the microstructure, which cannot be given by SEM. In this figure the cross-linked EPDM particles (dark phase) show irregular shape and a heterogeneous distribution in domain size, varying between 0.2 - 1.5 µm. Even though TEM seems to be the technique that gives more details on the morphology, SEM was the suitable technique to study phase inversion phenomena. This is related with phase inversion features, very fast process, it has been reported that occurs in less than 1 minute after the addition of the cross-linking system, and rather heterogeneous in the space. In order to slowdown the phase inversion phenomena a low Mw-EPDM was used. Since the cross-linking efficiency of the low M_w EPDM is much lower than for high M_w EPDM, the cross-linking of the EPDM phase is retarded and as a result phase inversion is slowed down. In addition due to the large difference on the viscosity ratio the domains size increases and the morphology development could be followed by SEM using the backscattered detector. Micrographs evidencing phase inversion are depicted in Fig. 2. It can be observed that phase inversion occurs via lamellar structure.

Conclusions

SEM using a BSE detector was successfully used to follow the phase inversion during the production of a TPV.

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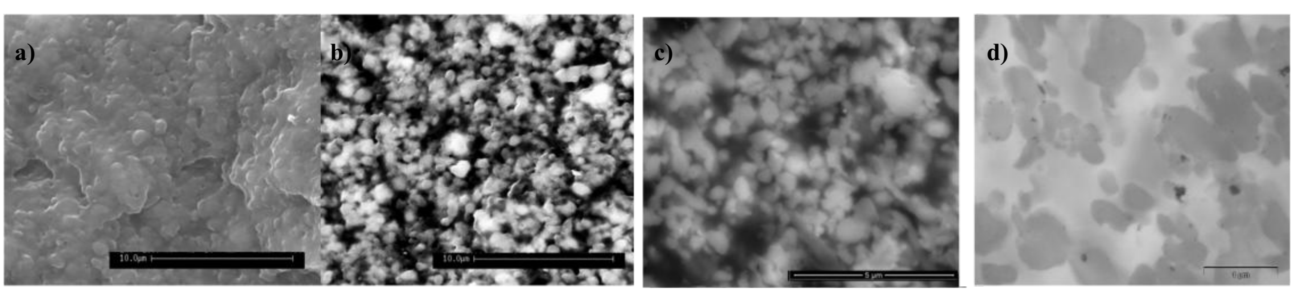

Fig. 1. Micrographs of TPV samples of EPDM (high Mw)/PP (MFI47) collected at 5 min: a) SEM; b) and c) BSE and d) TEM.

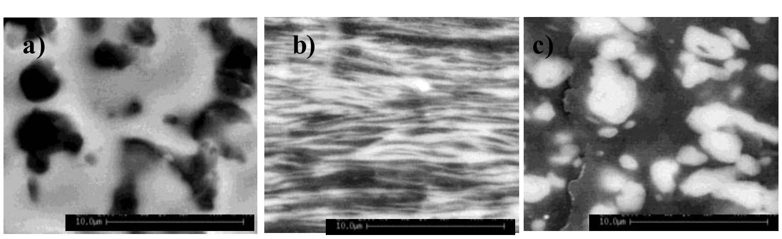

Fig. 2. BSE micrographs of TPV samples (EPDM (low Mw)/PP (MFI 2)): a) 0 s; b) 45 s c) 120 s.

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