



Material Characterisation

Raman investigation of thermoplastic vulcanizates based on hydrogenated natural rubber/polypropylene blends



Korn Taksapattanakul ^{a, b, 1}, Tulyapong Tulyapitak ^b, Pranee Phinyocheep ^c, Polphat Ruamcharoen ^d, Jareerat Ruamcharoen ^e, Fabienne Lagarde ^a, Mathieu Edely ^a, Philippe Daniel ^{a, *}

^a Institut des Molécules et des Matériaux du Mans, IMMM –UMR-CNRS 6283, Université du Maine, Avenue Olivier Messiaen, 72085 Le Mans France

^b Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani Campus, 94000 Thailand

^c Department of Chemistry, Faculty of Science, Mahidol University, 10400 Thailand

^d Rubber and Polymer Technology Program, Faculty of Science and Technology, Songkhla Rajabhat University, 90000 Thailand

^e Division of Chemistry, Department of Science, Faculty of Science and Technology, Prince of Songkla University, Pattani Campus, 94000 Thailand

ARTICLE INFO

Article history:

Received 21 July 2016

Received in revised form

30 September 2016

Accepted 11 November 2016

Available online 12 November 2016

Keywords:

Raman spectroscopy

Thermoplastic elastomers

Thermoplastic vulcanizates

Hydrogenated natural rubber

Polymer blends

ABSTRACT

Raman spectroscopy including mapping technique appears as a powerful technique for the characterization of polymer blends like thermoplastic elastomers (TPEs) and thermoplastic vulcanizates (TPVs). The Raman spectra of polymer blends such as natural rubber/polypropylene (NR/PP) and 65% hydrogenated natural rubber/polypropylene (65%HNRR/PP) were identified and the phase distribution was determined. The study was driven for the same type of blends in TPEs state and TPVs state obtained after 2 different processes, either peroxide cure or sulfur cure. The morphology of TPEs and TPVs obtained by Raman spectroscopy were compared and confirmed using scanning electronic microscopy.

Raman mapping shows that the phase morphology of NR/PP, 65%HNRR/PP, were characterized as continuous rubber phase morphology of the thermoplastic elastomers (TPEs) and a fine dispersion of cross-linked rubber phase in a continuous matrix of the thermoplastic vulcanizates (TPVs). Raman spectroscopy is demonstrated to be a reference to determine the content ratio of each component in the TPVs. Moreover, Raman mapping could be used to calculate the phase size of cross-linked rubber phase dispersed in the thermoplastic vulcanizates (TPVs).

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1. Introduction

Thermoplastic vulcanizates (TPVs) constitute a special class of Thermoplastic Elastomers (TPEs) resulting from elastomer cross-linking and generating a fine dispersion of cross-linked elastomer particles in a continuous matrix of thermoplastics. The vulcanization of the elastomer phase has been carried out under dynamic shear during mixing (dynamic vulcanization) by sulfur and accelerator, peroxide vulcanization systems [3]. TPVs offer properties of cross-linked rubber, coupled with the processability of

thermoplastics. There may be several combinations of rubbers, like Ethylene-propylene-diene-rubber (EPDM), natural rubber (NR), with plastics, like PP, to form TPEs and TPVs. Polypropylene (PP) was used because of its high melting point and high crystallinity, resulting in good TPV properties even at high temperatures. EPDM can be also used because of its stability against high temperatures and ozone as same as hydrogenated natural rubber (HNR), thus giving to the corresponding TPVs good heat and ozone resistance. Due to the process of dynamic vulcanization used, the production of TPVs has been carried out under high temperature (melt temperature of plastic). Natural rubber (NR) can be degraded under high temperature due to the unsaturation of C=C double bonds within the isoprene backbone. Hydrogenation of natural rubber helps to improve the thermal and oxidative stability, since the radical-susceptible C=C bonds are replaced by saturated C-C bonds. With almost complete saturation, the backbone structure of natural rubber is changed from *cis*-1,4-polyisoprene to an

* Corresponding author. Institut des Molécules et des Matériaux du Mans, IMMM –UMR CNRS 6283, Université du Maine, Le Mans 72085 France.

E-mail address: philippe.daniel@univ-lemans.fr (P. Daniel).

¹ Permanent address. Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani Campus, 94000 Thailand.

alternating ethylene-propylene copolymer. Therefore, the thermoplastic vulcanizates (TPVs) based on blends of hydrogenated natural rubber (HNR) and polypropylene (PP) were investigated. Hydrogenated natural rubber (HNR) was prepared by the chemical modification of natural rubber via non-catalytic hydrogenation reaction.

Raman mapping techniques can characterize distribution of polymer components in multiphase systems. Actually Raman spectroscopy provides the potential of fast determination with little or no sample preparation and also without the classical use of stains or dyes samples [1,2]. Moreover, Raman spectroscopy has the advantage to produce a strong signal especially in systems with non polar bonds like for instance C=C bond in the case of NR [2]. Additionally Raman spectroscopy is a non-destructive method and a fingerprint technique.

Numerous studies have been done on the Raman mapping of multilayer polymer blends based on polystyrene, polypropylene and poly (styrene-ethylene/propylene) diblock copolymer [4], IR/HNBR blends [5], PET/HDPE polymer blends [6], polypropylene/polyethylene blends [7], thin film of thermoplastic olefin (TPO) of chlorinated Polyolefin (CPO), ethylene-propylene rubber (EPR) and polypropylene (PP) [8], polypropylene/polyethylene/ethene-propenecopolymer, polybutyleneterephthalate/polycarbonate/low density polyethylene, and styrene-co-acrylonitrile/styrene-co-maleicanhydrate/poly-2,6-dimethylphenylene oxide [9], polystyrene/micro-diamonds composite (PS/C) [10].

However, thermoplastic vulcanizates based on hydrogenated natural rubber/polypropylene blends investigated by Raman spectroscopy such as Raman mapping, with calculation of blends ratio, determination of particle size of cross-linked rubber phase dispersed in the thermoplastic vulcanizates (TPVs), has not yet been reported up to our knowledge.

In this work, Raman spectroscopy and Raman mapping were used (1) to characterize the structure of the blends TPEs and TPVs in the 50/50 content ratio, (2) to study the rubber and plastic phase distribution also in the 50/50 content ratio for both blends TPEs and TPVs (3) to determine the content ratio of polypropylene (PP) and natural rubber (NR), hydrogenate natural rubber (65%HNR) in the blends for different ratio contents and finally (4) to calculate the phase size of cross-linked rubber phase dispersed in the thermoplastic vulcanizates (TPVs).

2. Experimental

2.1. Materials

Natural rubber latex (NRL) with 60% dry rubber content (DRC) was purchased from Yala latex Co. Yala, Thailand. Hydrogenated natural rubber (HNR) with a degree of hydrogenation equal to 65% was prepared by using hydrazine monohydrate ($N_2H_4 \cdot H_2O$) (the assay is 35%, commercial grade, Lanxess Deutschland GmbH, Germany) and hydrogen peroxide (H_2O_2) (the assay is 50%, standard, Thai peroxide co. ltd. Thailand) via non-catalytic hydrogenation. Polypropylene was obtained from HP500N, Homopolymer, Lyondell Basell co. USA.

The chemicals for the vulcanization were purchased according to the following: sulfur (vulcanizing agent, Siam Chemicals Co. Ltd. Thailand), Stearic acid (activator, Imperial Chemical Co. Ltd. Thailand), Zinc oxide (activator, Global Chemical Co. Ltd. Thailand), Tetramethylthiuram disulfide (TMTD) (accelerator or as a sulfur donor, Flexsys Co. Ltd. Belgium), 2-mercaptobenzothiazole (MBT) (accelerator, Flexsys American LP Co. Ltd. USA), Dicumyl peroxide (DCP) (curing agent, Wuzhou International Co. Ltd. China), Triallyl cyanurate (TAC) (co-agent, Fluka Chemie, Buchs, Switzerland).

2.2. Preparation of thermoplastic elastomers and thermoplastic vulcanizates

For the preparation of TPEs and TPVs, the grade of PP which was used is characterized by a melt flow rate of 12 g/10 min at 230 °C under 2.16 kg load. Additionally the average molecular weight of this PP grade has been reported in literature to be in the range of 2.38×10^5 – 2.60×10^5 g/mol and polydispersity in the range of 3.3–6.9 [11–14]. The degree of crystallinity of PP HP500N, used in this work, has been previously reported and calculated according to the classical relation:

$$\% \chi C = \Delta H_f / \Delta H_f^0$$

where ΔH_f is an enthalpy of fusion of PP crystals and ΔH_f^0 is the enthalpy of fusion of 100% crystalline PP. These values were then reported in literature to be 45.4%–46.3% and 57.4–58.7% [15–18] depending of the value of ΔH_f^0 used in calculation [19,20].

Note that the blending process probably induce a decreasing in the percentage of crystallinity as it was observed in other blends like PP-thermoplastic polyurethane [18], PP-polyolefine elastomer [21], or also PP-chloroprene rubber [22].

Then for preparing thermoplastic elastomers (TPEs), PP was melt for 3 min in the internal mixer before adding rubber. Two polymers were mixed in the internal mixer (fill factor = 0.8) until the constant torque is obtained. The mixing time for each batch was 10 min at a constant rotor speed of 80 rpm. The temperature setting of the mixer is 180 °C. For the blends without chemicals, they were removed immediately from the mixer and passed through the two-roll mill to get sheets.

The preparation of NR and HNR compounds was performed using an internal mixer (fill factor = 0.8). The mixing was performed at room temperature (30 °C) and at a constant rotor speed of 60 rpm. NR and HNR were masticated for 2 min and then the chemicals were added. The mixing time for each batch took 10 min.

For the vulcanization process peroxide or sulfur were used. The formulation used for the preparation of the rubber compounds is given in Table 1.

For preparing thermoplastic vulcanizates (TPVs), PP was melt for 3 min in the internal mixer before adding rubber compounds. The temperature setting of the mixer is 180 °C. Two polymers were mixed in the internal mixer (fill factor = 0.8) until the constant torque is obtained. The mixing time for each batch took 10 min. The TPVs were removed immediately from the mixer and passed through the two-roll mill to get sheets. TPEs and TPVs samples were pressed for 5 min in a compression molding press at a temperature of 190 °C and at a pressure of 12.5 MPa. Subsequently, the samples were cooled down under pressure to room temperature.

Note that considering the sample preparation method, where compression molding was used with very low shear rate, together with a 1–2 mm samples thickness, a skin-core effect can't be observed.

2.3. Raman spectroscopy and Raman mapping

In this study, Raman spectra of the samples were recorded with a Xplora-Horiba spectrometer. The experiment was performed at room temperature under microscope (Olympus BX 40) using a long distance work objective with a magnification $\times 50$. The simple spectrograph was adjusted with a 1200 lines per mm grating. The samples were illuminated with a laser light at 785 nm. The frequency range studied was 400–3500 cm^{-1} with 50 accumulations and an acquisition time of 2 s per spectrum. The lateral resolution is

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