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Morphology development by reactive compatibilisation and dynamic vulcanisation of nylon6/EPDM blends with a high rubber fraction

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Abstract

Binary nylon6/rubber blends with 50 or 60 weight percent of an EPDM rubber exhibit co-continuous morphologies and thereby relatively poor mechanical properties. This paper describes methods to develop nylon6/EPDM blends with a high amount of finely dispersed rubber particles embedded in a nylon matrix. Using a suitable compatibiliser and by slightly crosslinking the rubber phase during melt-mixing, it was possible to disperse up to 60 wt% rubber in the nylon matrix and to improve the mechanical properties markedly. These materials are called thermoplastic vulcanisates and exhibit good elastic properties with a thermoplastic processability. The influence of the compatibiliser, the crosslinking agent and the viscosity ratio rubber/thermoplastic on the blend phase morphology is investigated using transmission electron microscopy. It was found that the viscosity ratio rubber/nylon plays a crucial role in order to achieve a nylon6/rubber TPV with a fine rubber dispersion. The viscosity of the nylon phase should be low enough to shift the phase inversion towards higher rubber content. On the other hand, if the viscosity of the nylon is too low, a coarse blend morphology was achieved resulting in poor mechanical properties.

Keywords: Thermoplastic vulcanisate; Morphology development; Nylon6

1. Introduction

Thermoplastic vulcanisates (TPVs) are a relatively new class of materials, which combine the excellent processing characteristics of thermoplastics with the elastic properties of elastomers. The elastic properties of this type of blends are similar to the more conventional class of thermoplastic elastomers based on hard segment and soft segment block copolymers [1,2]. The ideal morphology is a fine dispersion of the elastomer in a relatively small amount of the thermoplastic polymer. The dispersed elastomer particles have to be crosslinked in order to promote elasticity.

The best way to prepare TPVs is by melt-mixing of a semi-crystalline thermoplastic and a rubber, followed by the simultaneous vulcanisation of the rubber phase during mixing. The crosslinking of the rubber phase during melt-blending with the thermoplastic is called dynamic vulcanisation. The original investigations on the dynamic vulcanisation of TPVs were performed on polypropylene and different rubber compositions, and were initiated by Fisher [3] and Coran et al. [4]. A well-known commercial example of dynamically vulcanised thermoplastic-elastomer compositions are blends of polypropylene (PP) and ethylene–polypropylene–diene terpolymer rubber (EPDM) [2]. These TPVs are prepared by first melt-mixing PP with EPDM whereby a co-continuous phase morphology is formed. Subsequently a vulcanisation agent (peroxide or phenolic resin) is added to crosslink the EPDM rubber phase, and hereby the rubber phase is not able anymore to coalesce into a continuous phase. At the end of the melt-mixing process, the rubber phase will be finely dispersed in the thermoplastic matrix. The phase morphology formation in dynamically vulcanised PP/EPDM blends has been examined in detail by Radusch et al. [5].

During the melt-processing of polymer blends the final morphology is determined by composition, viscosity and elasticity ratio, and interfacial tension between the components. If two components of a blend have the same viscosity, the component with the lowest volume fraction will form the dispersed phase. When the amount of the dispersed phase is increased, the particles will become larger due to increased coalescence. Finally, the amount of dispersed phase will reach a maximum, and subsequently the blend morphology will become co-continuous and phase inversion

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will occur. Avgeropoulus [6] observed on EPDM/BR blends (50/50 vol%) that it is possible to shift the phase inversion by lowering the viscosity of one of the components. Jordhamo et al. [7] developed an empirical model based on the melt-viscosity ratio, $\eta_\mathrm{d}/\eta_\mathrm{m}$, and the volume fractions ϕ, of each phase for predicting the phase inversion region in immiscible polymer blends. According to this model, phase inversion should occur when the following equation holds:

$$\frac{\eta_\mathrm{m}}{\eta_\mathrm{d}}\frac{\phi_\mathrm{d}}{\phi_\mathrm{m} = 1}. \qquad (1)$$

Jordhamo's model however is limited to low shear rates, and does not take into account the effect of the interfacial tension between the components. Nevertheless, this equation gives a good indication how to shift the phase inversion of a polymer blend. In the case of thermoplastic/rubber blends this would mean that if the viscosity of the thermoplastic is reduced, a higher amount of rubber can be dispersed before the phase inversion is reached. Conversely, increasing the viscosity of the rubber can also shift the phase inversion. Different viscosities can be obtained by using polymers with different molecular weights.

The interfacial tension between the components should be relatively low to achieve a good and fine dispersion of the rubber phase. The interfacial tension between PP and EPDM is relatively low. Therefore, this blend does not require compatibilisation with a block or graft copolymer in order to generate a finely dispersed rubber phase and a good interfacial adhesion between the two phases. Furthermore, as a result of the vulcanisation process, the crosslinked rubber particles are relatively resistant towards coalescence upon further melt-processing. In the case of thermoplastic/rubber combinations with a high interfacial tension between the components, it is necessary to compatibilise the blend in order to generate a fine dispersion of the rubber phase. Compatibilisation is usually achieved by using a thermoplastic and a rubber with functional groups that can react with each other during melt-mixing to form a block or graft copolymer at the interface between the phases [2,8].

This paper describes methods to develop nylon6/EPDM TPVs with a high amount of rubber. A lot of literature is available about PP/rubber TPVs; concerning TPVs in which the thermoplastic is an engineering polymer (polyamide or polyester), no information is available. The difficulty to prepare such TPV's is due to the high interfacial energy between the two components. By using a suitable compatibiliser and dynamic vulcanisation, it will be possible to develop nylon6/rubber TPVs, whereby the rubber phase will be finely dispersed in the nylon matrix. The influence of the viscosity ratio rubber/thermoplastic on the blend phase morphology and the mechanical properties will be investigated by changing the molecular weight of nylon6. The morphology development as a function of the mixing time, and also the thermal properties of the nylon6/rubber TPVs are examined.

2. Experimental

2.1. Materials

For the blend systems studied in this work a low, low/medium and high molar mass nylon6 was used ($M_\mathrm{w} \approx$ 18.500, 25.000 and 47.000 g mol^{-1}, respectively, and density $\rho = 1.14$ g ml^{-1}). All nylons (tradename Akulon) were kindly supplied by DSM.

For the rubber phase two different EPDM rubbers and two different modified EPDM rubbers were used, all having a high molecular weight and density $\rho = 0.88$ g ml^{-1}. The two EPDM rubbers differ in the ethylene–propylene ratio: 75/25 and 45/55 wt%. These rubbers were kindly supplied by DSM, tradename Keltan. The two modified rubbers that have been used were: a maleic anhydride (MA) modified ethylene–propylene (75/25 wt%) diene terpolymer (0.5 wt% MA), type Royaltuf 465A and a MA modified ethylene–propylene (50/50 wt%) diene terpolymer (1 wt% MA), type Royaltuf 465. These rubbers were kindly supplied by Uniroyal.

Also two MA modified EPM rubbers (0.7 wt% MA) were used, both having a relatively low molecular weight. The two modified EPM rubbers differ in the ethylene–propylene ratio; 75/25 and 50/50 wt%. These rubbers were kindly supplied by Exxon Chemical, trade name Exxelor.

2.2. Blend preparation

Prior to the melt-mixing operations, all materials were dried under vacuum at 120 °C overnight. The components were then melt-mixed and dynamically vulcanised in a mini-extruder (DSM Research, The Netherlands), which is a conical co-rotating fully intermeshing twin-screw extruder with a capacity of about 4 cm^3. A recirculation channel allows varying of the blending time. All blends were prepared under nitrogen atmosphere to prevent oxidative degradation. The blending conditions were chosen carefully by variation of rotor speed, blending temperature and mixing time; the optimal blending conditions result in a mixing time, temperature and rotor speed of 6 min, 260 °C and 80 rpm, respectively. The peroxide (0.25 wt%), used as crosslinking agent, was first dissolved in mineral oil (2 wt%) and subsequently premixed with the rubber in a Haake 69 cm^3 batch kneader before the nylon/rubber blend was compounded in the mini-extruder. The peroxide was dissolved in mineral oil in order to achieve a better dispersion in the rubber.

2.3. Viscosity measurements

The melt-viscosity of all the materials under processing conditions was measured using a high pressure capillary rheometer Rheograph 2002 (Göttfert) with a capillary die of 1 mm diameter and a L/D ratio of 30. Measurements were performed at 260 °C over a shear rate range, $\dot{\gamma}$, between 10 and 300 s^{-1}. Measurements for the Bagley correction have been performed with capillary dies having a L/D ratio of 30/1, 20/1 and 10/1. For the shear rate used to calculate the viscosity ratios ($\dot{\gamma} = 80\ \mathrm{s}^{-1}$), the Rabinowitch correction factor was negligible for the lower viscosity materials and became more important for the more viscous materials.

2.4. Morphological analysis

The phase morphology of the blends was examined on the extruded strands (perpendicular to the extrusion direction) with a Transmission Electron Microscope (TEM), Philips CM10. In order to examine the phase morphology by TEM, slices of 80 nm were cut with a diamond knife, using a Leica Ultracut ULT microtome, equipped with liquid nitrogen cooling unit. The specimen temperature during microtoming was −100 °C and the knife temperature was −55 °C. The samples were stained with an osmiumtetroxide/formaldehyde solution for 24 h.

2.5. Material testing

The specimens ($l_0 \times b \times d = 20 \times 6 \times 0.1\ \mathrm{mm}^3$) for mechanical testing were cut from a moulded film. To meet this requirement an extruded strand of the blend was placed between two teflon sheets and compression moulded at a temperature of 250 °C and a pressure of 50 kN for 5 min. Subsequently the moulded film was cooled to room temperature with cold water. The specimens were stretched at a constant rate of 4 mm min^{-1} (20% min^{-1}) on a mini-stretching device (FSK, Load cell = 100 N) until failure. The strain recovery tests were performed at the same strain rate (20% min^{-1}) until 100% strain, after which the strain was reversed while the strain rate remained the same, until zero stress was reached.

2.6. Thermal analysis

The thermal properties of the blends were analysed under dynamic conditions in a nitrogen atmosphere using a heating rate of 10 °C min^{-1} The experiments were carried out in a Perkin–Elmer Pyris 1 differential scanning calorimeter (DSC). Several heating and cooling cycles were performed in the temperature range between 0 and 250 °C. The samples were firstly heated till 250 °C. After this melting scan a cooling step from 250 to 0 °C was performed, followed by a second heating scan. The sample weight was approximately 6 mg and the peak temperatures were taken as the transition temperatures. The crystallinity level of the nylon6 phase, (X_c), was determined from the cooling curve by using the following relation:

$$X_\mathrm{c} = \frac{\Delta H_\mathrm{N6}}{\Delta H_\mathrm{N6,100\%} w_\mathrm{N6}} \tag{2}$$

where ΔH_N6 is the apparent enthalpy of crystallisation of nylon6, w_N6 is the weight fraction of nylon6 in the blends and $\Delta H_\mathrm{N6,100\%}$ is the extrapolated value of the enthalpy of crystallisation corresponding to a 100% crystalline sample.

Nylon6 can exhibit two different polymorphic forms (α and γ) [9–14]. The crystalline unit cell for the α form is monoclinic and for the γ form pseudohexagonal. Several values are proposed in literature for the $\Delta H_\mathrm{N6100\%}$ values [9–12]. Wunderlich [10] reported 230 J g^{-1} as the most probable value for the completely crystalline α form. Illners [11] reported 239 J g^{-1} for the γ form. Upon slowly cooling from the melt (10 °C min^{-1}), nylon6 crystallises mostly in the more stable α form and less in the γ form [9,13–14]. For that reason the value of 230 J g^{-1} has been chosen in this paper.

3. Results and discussion

3.1. Melt-viscosity of the blend components

In order to calculate the viscosity ratio, p, of the blend components corresponding to the applied processing conditions, capillary rheometry measurements were performed at the blending temperature of 260 °C. Because the melt-mixing in the mini-extruder has been performed at a constant screw speed of 80 rpm, the rheological behaviour of each component is best reflected by its melt-viscosity measured at a constant shear rate. Wu [15] stated that for his co-rotating twin-screw extruder, the shear rate, expressed in reciprocal seconds, has the same numerical value as the screw revolution per unit time (rpm). Although our twin-screw extruder specifications do not meet the one of Wu [15], we assume that the applied screw speed of 80 rpm for our experimental extruder coincides with a shear rate of 80 s^{-1}. The melt-viscosity of all components as a function of the shear rate is presented in Fig. 1. In Table 1 the melt-viscosity determined at 260 °C and 80 s^{-1} is given.

The curves for the nylons and rubbers may be roughly expressed by the power law:

$$\eta = \eta_0 \dot{\gamma}^{\beta}$$

where η is the melt-viscosity, $\dot{\gamma}$ the shear rate, and η_0 and β are constants. The β values for the different components are listed in Table 1. Newtonian behaviour corresponds to $\beta = 0$, and shear-thinning behaviour corresponds to $0 < \beta < 1$. Using the β values as a guide, it can be seen that the three nylon6 polymers exhibit a more Newtonian and less shear-thinning behaviour than the rubbers which are more shear-thinning and less Newtonian. Also the molecular weight has an influence on the shear-thinning behaviour of these polymers; a high molecular weight polymer behaves more shear-thinning compared to a low molecular weight polymer.

3.2. Phase morphology of nylon6/rubber blends with a high amount of rubber

3.2.1. Phase morphology of reactively compatibilised nylon6/rubber blends

In order to study the development of a nylon/rubber TPV,

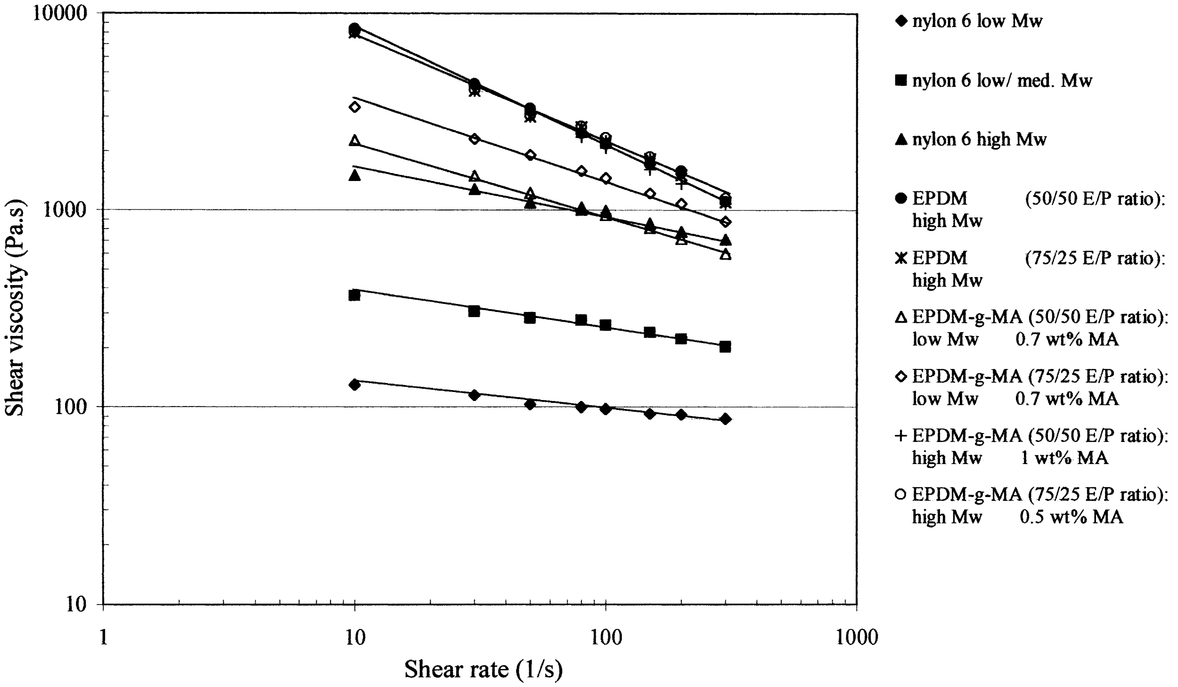

Fig. 1. Melt-viscosity of the materials, measured at 260 °C, as a function of shear rate.

we applied the model of Jordhamo Eq. (1)) by selecting EPDM rubbers with a high melt-viscosity (2355 and 2650 Pa s) and a nylon6 with a relatively low melt-viscosity (k123, 275 Pa s). On account of the much lower viscosity of the nylon phase, it will tend to form the matrix. Nylon6/EPDM blends consisting of 50 wt% rubber display a morphology which is made up of large rubber particles and which has a tendency to be co-continuous. This can be seen from the TEM micrograph in Fig. 2(a) for a nylon6/EPDM blend in which the rubber has an E/P ratio of 50/50 and a viscosity of 2355 Pa s. In this TEM micrograph the dark area represents the nylon phase.

By using MA modified EPDM rubbers with a similar high viscosity, it was possible to disperse 50 wt% rubber in the nylon matrix on account of reactive compatibilisation. In Fig. 2(b) a TEM micrograph is presented in which the rubber has an E/P ratio of 50/50 and a viscosity of 2395 Pa s. In this micrograph, the dark phase represents again the nylon phase. The principle of reactive compatibilisation is that the maleic anhydride groups of the modified rubber react in the melt with the amino-endgroups of PA6 leading to the formation of EPDM-*g*-PA6 graft copolymers. This graft copolymer will be preferentially situated between the nylon and the rubber phase. Hereby the interfacial tension between the phases is lowered and coalescence of the droplets is suppressed by steric hindrance [2,15–18]. As a result, the phase inversion point is shifted and a very fine rubber dispersion is obtained. This binary nylon6/EPDM-*g*-MA blend with 50 wt% rubber shows excellent mechanical properties (Table 2). Inside the rubber particles some nylon subinclusions can be observed (Fig. 2(b)); these occlusions most probably arise from the steric stabilisation effect of the EPDM-*g*-PA6 which, if it encapsulates the nylon droplets, effectively prevents their coalescence with the nylon continuous phase.

The influence of the amount of MA in the EPDM rubber

Table 1
Melt-viscosity of the blend compositions, at 260 °C for a shear rate of 80 s^{-1}

Material	E/P ratio	M_w	η (Pa s), at 260 °C, 80 s^{-1}	β
Nylon6 (k120)	–	Low	100	0.1
Nylon6 (k123)	–	Low/medium	275	0.19
Nylon6 (k136)	–	High	1005	0.26
EPDM	50/50	High	2355	0.6
EPDM	75/25	High	2650	0.55
EPDM-*g*-MA, 1 wt% MA	50/50	High	2395	0.6
EPDM-*g*-MA, 0.5 wt% MA	75/25	High	2670	0.57
EPM-*g*-MA, 0.7 wt% MA	50/50	Low	1034	0.39
EPM-*g*-MA, 0.7 wt% MA	75/25	Low	1589	0.42

Table 2
Mechanical properties of uncompatibilised and compatibilised nylon6/EPDM blends

	σ_b (MPa), tensile stress at break	ϵ_b (%), strain at break
Nylon6/EPDM (50/50 wt%)	8	10
Nylon6/EPDM-*g*-MA (50/50 wt%)	35	200

phase on the phase morphology and phase inversion region of nylon/rubber blends with 50 wt% rubber was investigated by changing the concentration of MA in the rubber phase from 1 to 0 wt% (steps of 0.2 wt% MA). This was done by pre-mixing EPDM with a MA modified EPDM rubber (1 wt% MA) with the same E/P ratio (50/50) and viscositiy (approximately 2400 Pa s), before the nylon/rubber blend was compounded. TEM micrographs revealed that phase inversion was taking place by increasing the amount of MA till 0.4 wt%, and smaller rubber particles were formed by increasing the concentration of MA from 0.4 to 1 wt% MA (Fig. 3). It can be concluded that only a small amount of MA is needed to disperse 50 wt% of rubber in the nylon matrix.

The viscosity ratio rubber/nylon plays a crucial role in shifting the phase inversion of nylon/rubber blends. In Table 3 the morphology is given for nylon6/EPDM-*g*-MA blends with 50 wt% rubber with different viscosity ratios for the rubber/nylon phases. It is possible to shift the phase inversion region and to disperse the rubber finely in the nylon matrix if the viscosity ratio between the rubber and nylon phase is high enough.

3.2.2. Phase morphology of reactively compatibilised and dynamically vulcanised nylon6/rubber blends

Using MA modified EPDM rubbers with a high viscosity and a relatively low viscosity nylon, it is possible to disperse 50 wt% rubber in the nylon matrix on account of reactive compatibilisation (Table 3). By increasing the amount of rubber to 60 wt%, phase inversion takes place. The phase morphology of binary nylon6/EPDM-*g*-MA blends with 60 wt% rubber, having an E/P ratio of 50/50 and 75/25, are presented in Fig. 4(a) and (b), respectively. In these TEM micrographs, the light area represents the rubber phase and the stained darker area the nylon phase. Phase inversion has taken place for the nylon/rubber blend in which the rubber has an E/P ratio of 50/50 and contains 0.5 wt% MA (Fig. 4(a)). A co-continuous morphology was formed for the blend in which the rubber has an E/P ratio of 75/25 and contains 1 wt% MA (Fig. 4(b)). This difference in phase morphology between the two MA modified EPDM rubbers can be due to the difference in MA concentration.

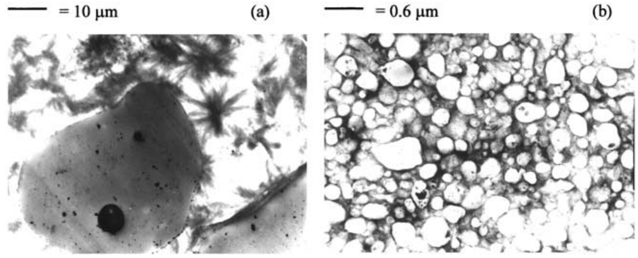

Fig. 2. (a) Nylon6/EPDM 50/50 wt%, (b) Nylon6/EPDM-*g*-MA 50/50 wt%.

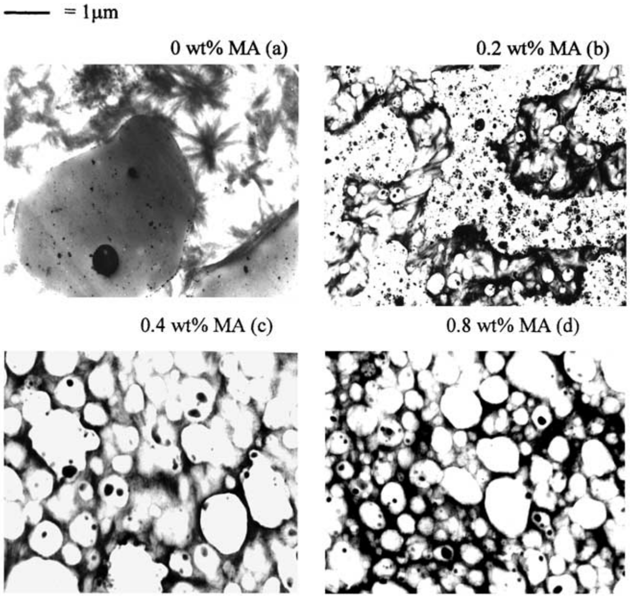

Fig. 3. Influence of MA concentration in the EPDM rubber on the phase morphology of nylon6/rubber blends with 50 wt% rubber.

To shift the phase inversion we added a second extrusion step. In the second extrusion step the reactively compatibilised nylon6/EPDM-*g*-MA blend was dynamically vulcanised with a small amount of vulcanisation agent to crosslink the rubber phase. An example of a suitable vulcanisation agent for EPDM is a peroxide such as 2.5-dimethyl-2,5-bis(t-butylperoxy) hexyne which upon melt-extrusion generates free radicals on the EPDM chains which then combine to form chemical crosslinks. The well-known TPVs of PP and EPDM are prepared in this way, by first

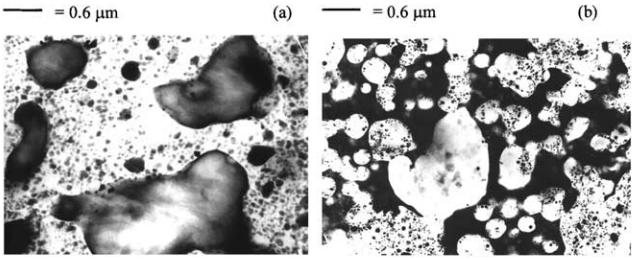

Fig. 4. Phase morphology of nylon6/EPDM-*g*-MA blends with 60 wt% rubber: (a) blend with a high viscosity MA modified EPDM with an E/P ratio of 50/50 and (b) with an E/P ratio of 75/25.

Table 3
Influence of the viscosity ratio rubber/nylon on the blend phase morphology

Rubber	E/P ratio	$\eta_{\text{rub.}}$ (Pa s)	η ratio ($\eta_{\text{rub.}}/\eta_{\text{nyl.}}$)	Phase morphology	Diameter (μm)
EPDM-*g*-MA, 0.7 wt% MA	50/50	1034	3.8	Co-continuous	
EPDM-*g*-MA, 0.7 wt% MA	75/25	1589	5.8	Co-continuous	
EPDM-*g*-MA, 1.0 wt% MA	50/50	2395	8.7	Rubber dispersion	0.2–0.8
EPDM-*g*-MA, 0.5 wt% MA	75/25	2670	10.7	Rubber dispersion	0.2–1

melt-mixing PP with EPDM whereby a co-continuous phase morphology is generated. Subsequently, a vulcanisation agent for EPDM is added to crosslink the rubber phase, and hereby the rubber phase is not able anymore to coalesce into a continuous phase. At the end of the melt-mixing process the rubber phase will be finely dispersed in the thermoplastic matrix [2,5].

In our work different peroxide concentrations were used to shift the phase inversion region of the nylon6/EPDM-*g*-MA blends by dynamic vulcanisation. But due to the compatibilisation reaction between EPDM-*g*-MA and nylon6, the phase inversion region could not be shifted. For that reason the peroxide was premixed with the rubber before the nylon/rubber blend was compounded. The peroxide (0.25 wt%) was dissolved in mineral oil (2 wt%) at a temperature of 120 °C to achieve a better dispersion of the peroxide in the rubber. The phase morphology of the dynamically vulcanised nylon6/EPDM-*g*-MA blends with 60 wt% rubber, having an E/P ratio of 50/50 and 75/25, are presented in Fig. 5(a) and (b), respectively.

From these TEM micrographs it can be concluded that by slightly crosslinking the rubber phase during melt-blending, the rubber phase can be finely dispersed in the nylon matrix. This is the desired morphology for this type of blends, called TPVs, because only a continuous nylon phase provides these blends with important properties such as melt processability as well as good heat and solvent resistance, while the crosslinked rubber particles lead to a high strain recovery. The development of the morphology as a function of mixing time will be discussed in Section 3.4.

From the TEM micrographs of the dynamically vulcanised nylon6/rubber blends with 60 wt% rubber, stacks of lamellae can be observed which are mostly oriented tangential to the rubber particles. These stacks of lamellae were not able to form spherulites due to the lack of space between the rubber particles (Fig. 6).

By increasing the rubber content to 70 wt%, phase inversion takes place for the nylon6/rubber blend with an E/P ratio of 50/50, and an intermediate morphology is formed for the nylon6/rubber blend with an E/P ratio of 75/25 for the rubber phase. The phase morphology of the dynamically vulcanised nylon6/EPDM-*g*-MA blends with 70 wt% rubber is represented in Fig. 7(a) and (b), respectively. Numerous small and a few large nylon particles are formed in the rubber phase, where the small particles still have the tendency to encapsulate the rubber phase.

3.3. Thermal properties of nylon/rubber TPVs

The thermal analysis of nylon6/EPDM-*g*-MA blends using differential scanning calorimetry (DSC) was performed as a function of the composition. The nylon6/rubber TPVs consist of a low/medium molecular weight nylon6 (k123) and two different high viscosity MA modified EPDM rubbers (as in Section 3.2). The DSC peak temperatures were taken as the transition temperatures. The crystallinity level of the nylon6 phase (X_c) was determined from the cooling curve according to Eq. (2). In Fig. 8 the cooling curves are represented for the dynamically vulcanised nylon6/rubber blends. The crystallisation temperature (T_c), melting temperature (T_m) and crystallinity level (X_c) of the nylon6 phase for the different blend compositions are given in Table 4.

The DSC analysis of pure nylon6 was performed on a pre-extruded sample in order to have the same thermal history as that of the nylon/rubber blends. The crystallisation temperature (T_c) of the nylon phase does not seem to be affected by

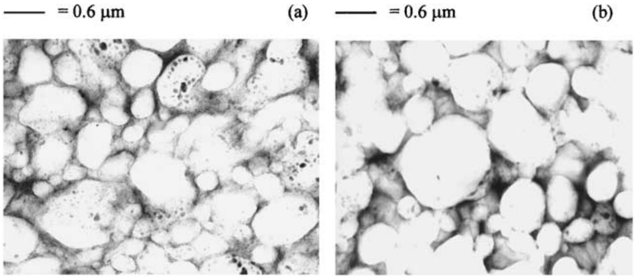

Fig. 5. Phase morphology of dynamically vulcanised nylon6/EPDM-*g*-MA blends with 60 wt% rubber: (a) blend with a high viscosity MA modified EPDM with an E/P ratio of 50/50 and (b) with an E/P ratio of 75/25.

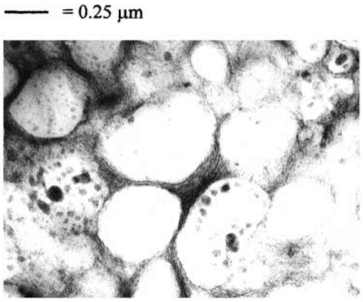

Fig. 6. Crystalline morphology of a dynamically vulcanised nylon6/EPDM-*g*-MA blend, 40/60 wt%, 0.25 wt% peroxide.

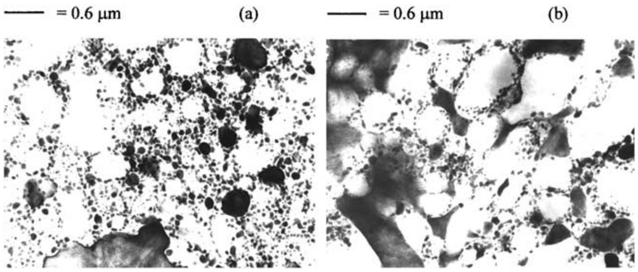

Fig. 7. Phase morphology of dynamically vulcanised nylon6/EPDM-*g*-MA blends with 70 wt% rubber: (a) blend with a high viscosity MA modified EPDM with an E/P ratio of 50/50 and (b) with an E/P ratio of 75/25.

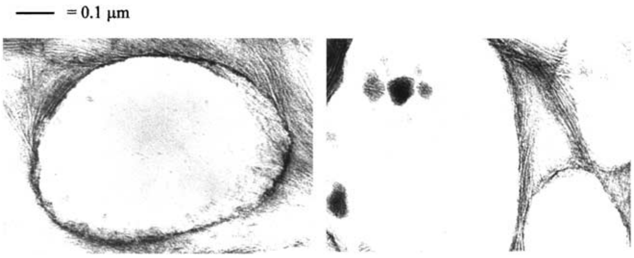

Fig. 9. Interphase of rubber particles in a nylon6/EPDM-*g*-MA TPV with 50 wt% rubber.

the rubber phase and the rubber concentration, although TEM micrographs from the nylon6/EPDM-*g*-MA TPVs (Figs. 6 and 9) seem to indicate that nucleation starts at the interface, in contrast to the non-compatibilised nylon/rubber blends where the nucleation starts in the nylon phase (see Fig. 2(a)). From literature Ref. [13] it is known that the extrusion of pure nylon6 increases the crystallisation temperature from around 170 to 185 °C. This phenomenom has been ascribed to the fact that after melt-extrusion oriented molecules, or even small crystalline entities, still exist in the nylon melt even far above the melting temperature, which can subsequently act as nucleating centres for crystallisation.

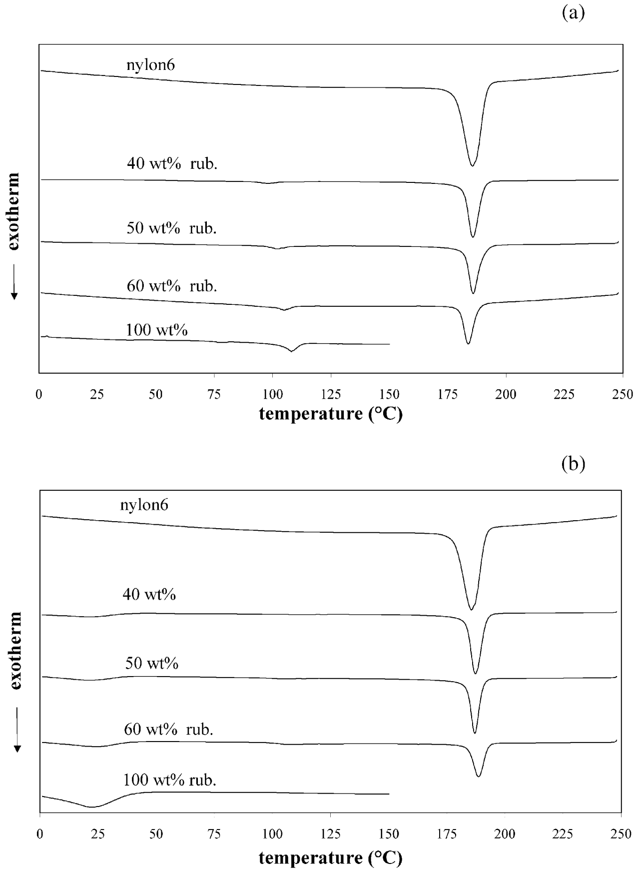

Fig. 8. D.S.C. cooling curves for nylon6/EPDM-*g*-MA TPVs with different compositions, for a high viscosity MA modified EPDM rubber with (a) an E/P ratio of 50/50 and (b) an E/P ratio of 75/25.

The overall crystallinity of the nylon6 phase in the nylon6/EPDM-*g*-MA TPVs decreases with increasing rubber content (Table 4). The reason for this decrease in crystallinity can be due to the crystallisation in confined spaces between rubber particles. This limits the mobility of the chains and hereby the growth of the crystalline lamella into a more spherulitic structure, especially for the nylon/rubber TPVs with a high amount of rubber (see Fig. 6).

The DSC analysis of the two types of TPVs studied (EPDM with E/P ratio of 50/50 and 75/25) also reveals the occurrence of a crystallisation peak at lower temperatures. For the nylon6/EPDM-*g*-MA TPV with an E/P ratio of 50/50, this peak is located at about 110 °C (Fig. 8(a)). The occurrence of this peak can be explained by the characteristic crystallisation of the ethylene sequences in the EPDM rubber. This MA modified EPDM rubber seems to have an amount of ethylene blocks, which are long enough to crystallise in a usual manner. The DSC thermogram of the pure EPDM-*g*-MA with an E/P ratio of 50/50 also displays this crystallisation peak at a temperature of 110 °C (Fig. 8(a)). In contrast, the nylon6/EPDM-*g*-MA TPV with an E/P ratio of 75/25 displays a crystallisation peak at about 25 °C (Fig. 8(b)); this crystallisation peak seems to be characteristic for the rubber component as such. The ethylene sequences of this EPDM-*g*-MA rubber are too short to be able to crystallise in the usual way; this leads to a significant decrease of the crystallisation temperature to 25 °C, which is also noted for the pure component (Fig. 8(b)).

The ability of the rubber to crystallise improves the strain recovery of the blends. These so-called physical crosslinks disappear when the temperature reaches the final melting temperature of the crystallites. The final melting temperatures are 35 and 120 °C for the used rubbers with an E/P ratio of 75/25 and 50/50, respectively.

3.4. Morphology development in nylon6/rubber TPVs as a function of mixing time

For the well-known PP/EPDM TPVs the morphology development as a function of the mixing time starts from

Table 4
Crystallisation and melting temperatures, and crystallinity value for (x) cooling cycle (y) 2nd heating cycle

(a) E/P ratio 50/50				(b) E/P ratio 75/25			
Blend composition nylon6/rubber	T_c^x (°C)	T_m^y (°C)	X_c	Blend composition nylon6/rubber	T_c^x (°C)	T_m^y (°C)	X_c
100/0	185.5	222	35	100/0	185.5	222	35
80/20	187.5	220	32.5	80/20	188.0	220.5	31.5
60/40	185.5	220	28	60/40	187.5	220	30
50/50	186	220	27.5	50/50	186	220	29
40/60	184	220.5	26.5	40/60	188.5	220.5	28

a co-continuous phase morphology to a finely dispersed rubber phase in the polypropylene matrix. During the dynamic vulcanisation process the rubber phase is crosslinked by the crosslinking agent under shear and elongation stresses. In the initial stages of the dynamic curing process the degree of crosslinking advances during mixing and the co-continuous rubber phase breaks up into polymer droplets. The high degree of crosslinking in the rubber particles suppresses the coalescence of these particles, which would otherwise lead to a co-continuous morphology. Also the viscosity of the rubber phase increases during the vulcanisation which will increase the initial rubber/plastic viscosity ratio leaving the thermoplastic phase to form the matrix [6]. The rubber particles, which are formed become trapped in the thermoplastic matrix and due to the crosslinking are not able to coalescence into a continuous phase. Thus, dynamic vulcanisation stabilises the phase morphology and allows the rubber phase to disperse in very fine particles.

As discussed in Section 3.2.2, phase inversion did not take place upon addition of peroxide into the nylon6/EPDM-*g*-MA blends during melt-mixing. The nylon particles are really stacked inside the rubber matrix due to reactive compatibilisation. For this reason the peroxide (0.25 wt%) was pre-mixed with the rubber, before the nylon/rubber blend was compounded. The phase morphology development as a function of time for a nylon6/EPDM-MA TPV with 60 wt% rubber is shown in Fig. 10(a) and (b), respectively. A recirculating channel in the batch type mini-extruder allows variation of the mixing time.

Fig. 10(a) shows the morphology after 15 s of mixing. The low viscosity nylon phase already forms the matrix at the beginning of the melt-mixing operation, on account of the slightly crosslinked rubber phase. Due to crosslinking in the rubber phase, at the beginning of the dynamic vulcanisation process the initial rubber/nylon viscosity ratio increases, which will favour the rubber forming the dispersed phase. After 30 s of mixing the rubber phase starts to disperse in fine particles (Fig. 10(b)), and after 4 min a very fine and stable rubber dispersion is achieved. In the work of Grace [19] a full quantification of the deformation and break-up under flow of a droplet in Newtonian system has been performed both in simple shear and in elongational flow. It was found that elongational flow is capable of breaking a droplet even at viscosity ratios higher than 4. Wu [15] reported, based on nylon/EPM blends (15 wt% rubber), that viscoelastic drops can break-up during extrusion even for viscosity ratios $(p) > 4$ due to the presence of an elongational flow field in the extruder. In our blend system, droplets even break-up for a viscosity ratio of more than 8. Due to the decrease in interfacial tension between the phases and suppression of coalescence by reactive compatibilisation and dynamic vulcanisation, it is possible to disperse a high amount of rubber finely in the nylon matrix.

By increasing the concentration of the peroxide in order to increase the crosslink density of the rubber phase, it becomes too difficult for the relatively low viscosity nylon matrix to break-up the crosslinked EPDM rubber. At a later stage of the melt-mixing operation, the rubber phase can be more crosslinked by adding an additional amount of vulcanisation agent.

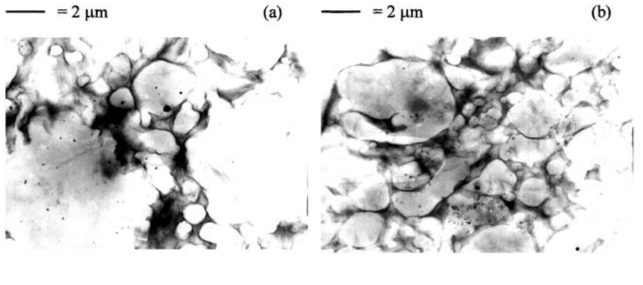

Fig. 10. Morphology development of a nylon6/EPDM-*g*-MA TPV with 60 wt% rubber, after (a) 15 s and (b) 30 s mixing.

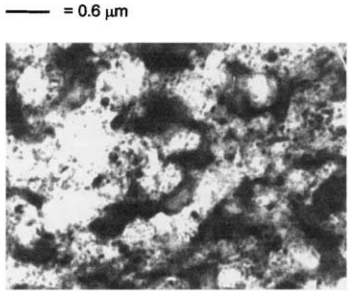

Fig. 11. Nylon6/EPDM-*g*-MA 40/60 wt%, high molecular weight nylon.

Table 5
Mechanical properties of the different nylon6/rubber TPVs with 60 wt% rubber

Nylon6, type	Viscosity, of nylon6	Morphology of rubber phase	σ_b (MPa), tensile stress at break	ϵ_b (%), strain at break	Recovery[a] (%) strain
Akulon k120	Low	Coarse dispersed	20	150	30
Akulon k123	Low/medium	Finely dispersed	25	175	45
Akulon k136	High	Co-continuous	10	25	–

[a] Reversed strain after 100% deformation.

3.5. Influence of the molecular weight of nylon6 on the morphology development of nylon6/rubber TPVs with 60 wt% rubber

As discussed in Section 3.2, the viscosity ratio rubber/thermoplastic is very important when attempting to disperse a high amount of rubber in the thermoplastic matrix. In this section the influence of the molecular weight of the nylon phase on the morphology development and mechanical properties of nylon/rubber TPVs with 60 wt% rubber will be examined. A low, low/medium and a high molecular weight nylon6, were used (Table 1). A high viscosity MA modified EPDM rubber was used, with an E/P ratio of 50/50 and 1 wt% MA.

It was not possible to disperse 60 wt% of rubber in a high molecular weight nylon6 by dynamic vulcanisation. The blend morphology is co-continuous (Fig. 11) and this material shows poor mechanical properties (Table 5). The phase inversion region was shifted when a low/medium molecular weight nylon6 was used. The phase morphology of this blend is shown in Fig. 12; this morphology gave rise to excellent mechanical properties for a nylon/rubber TPV (Table 5).

The viscosity of the nylon phase should also not be too low. The morphology of a nylon/rubber blend with 60 wt% rubber using a very low molecular weight nylon exhibits a coarse morphology (Fig. 13). Even when the visosity ratio (p) between the rubber and the nylon phase is larger than 23, it is still possible to disperse the rubber in the nylon phase on account of reactive compatibilisation and vulcanisation. This blend with a coarse morphology shows inferior mechanical properties compared to the blend with a fine morphology (Fig. 12).

Fig. 14 presents the stress–strain recovery behaviour of the two blends with the fine (Fig. 12) and the coarse morphology (Fig. 13), respectively. The elastic behaviour of a fine rubber dispersion within the nylon matrix is much better compared to a coarsely dispersed rubber phase. Note the typical stress–strain behaviour of these TPVs; an initial E-modulus, which is lower than expected from a simple composite model with dispersed rubber and a broad yield 'region' followed by a constant modulus. The elastic properties of these so-called engineering TPVs are less good compared to the well-known PP/EPDM TPVs. This is due to the high glass-transition temperature (T_g) of the nylon phase ($T_g \approx 60$ °C) compared to polypropylene ($T_g \approx 0$ °C) giving less mobility to the polymer chains of the thermoplastic matrix phase.

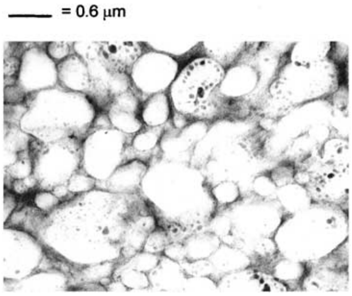

Fig. 12. Nylon6/EPDM-*g*-MA 40/60 wt%, low/medium molecular weight nylon.

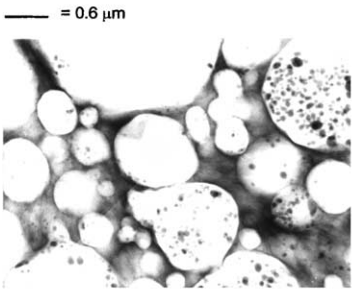

Fig. 13. Nylon6/EPDM-*g*-MA 40/60 wt%, low molecular weight nylon.

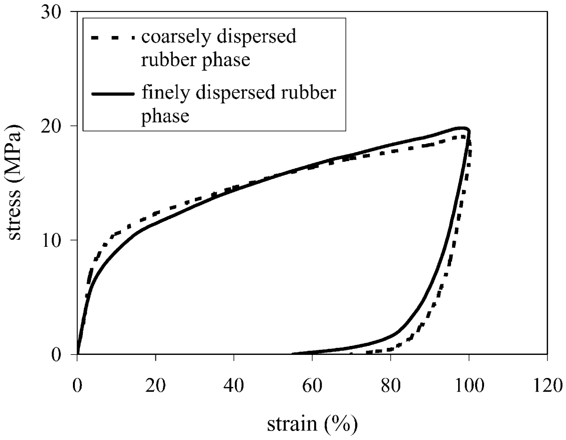

Fig. 14. Influence of the morphology on the recovery behaviour of nylon6/EPDM-*g*-MA TPVs with 60 wt% rubber.

4. Conclusions

Nylon6/rubber TPVs with a high amount of dispersed rubber, displaying good strain recovery and mechanical properties, can be prepared using both reactive compatibilisation and dynamic vulcanisation. By slightly crosslinking the rubber phase during melt-mixing, it is possible to finely disperse 60 wt% rubber in the nylon matrix. The viscosity ratio rubber/nylon plays a crucial role in order to achieve a nylon/rubber TPV with a fine rubber dispersion. The viscosity of the nylon phase should be low enough to shift the phase inversion point towards higher rubber contents, whereby the nylon phase already forms the matrix in the beginning of the melt-mixing operation, on account of the slightly crosslinked rubber phase. In our blend system droplets even break-up for a viscosity ratio (rubber/nylon) of more than 8, due to the decrease in interfacial tension between the phases and suppression of coalescence by reactive compatibilisation and dynamic vulcanisation. On the other hand, the viscosity of the nylon should also not to be too low; this leads to a coarse blend morphology resulting in a deterioration of the mechanical properties and poor elasticity behaviour.

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