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In situ compatibilization of polyamide 6/natural rubber blends with maleic anhydride

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Abstract

The rheology, thermal and dynamic-mechanical properties and phase morphology of blends of polyamide 6 with natural rubber (NR) are explored. The objective was to investigate in situ formation of a graft copolymer between NR and polyamide 6 during processing. Addition of maleic anhydride (MA) to the rubber was done prior to blending with polyamide 6. During processing MA can react with both NR and polyamide 6 leading to the graft copolymer formation. Molau test was used to confirm this graft copolymer formation. Rheology and thermal properties as well as dynamic-mechanical analysis also indicated the graftization. Blend morphology analysis showed a significant reduction in particle size as the MA was added to the rubber. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyamide; Natural rubber; Maleic anhydride

1. Introduction

Polyamides are a very attractive class of engineering polymers and have been used for numerous engineering applications because of their excellent tensile properties, chemical and abrasion resistance, high melting point and fatigue resistance. However, polyamides are very notch-sensitive and brittle at low temperatures [1–4]. Blends of polyamide with rubber have been extensively studied in order to obtain new materials with good impact properties [5–22]. Some requirements to achieve toughening include: (i) an appropriate range of rubber particle size and interparticle distance; and (ii) an uniform distribution of the rubber particles. Both requisites can be obtained by controlling the level of interfacial adhesion between the phases [22]. To fulfill those requirements, existing rubbers can be chemically and/or physically modified prior to blending with polyamide. Maleated rubbers are a successful example of these modifications. The maleic anhydride (MA) groups of these rubbers can react with polyamide amine end group and form a graft copolymer at rubber–matrix interface, which reduces interfacial tension and retards particle coalescence during mixing. The resulting particles can present suitable sizes uniformly distributed for effective toughening [5–11].

For non-functionalized rubbers, addition of a compatibilizer can be an alternative to improve toughness [12–22], because it can react with one phase and physically interact with the other improving the adhesion between the rubber and polyamide phases.

The purpose of this paper is to investigate an effective method to compatibilize rubber–polyamide blends. The rubber particles are formed from natural rubber (NR) and the matrix phase is polyamide 6. Compatibilization was done by adding MA to the rubber in a roll mill at room temperature prior to blending with polyamide 6. During processing at high temperature (240°C), two different reactions can take place [23–27]. The first one is the grafting of the MA onto NR chains (ene reaction) as shown in Fig. 1. This ene reaction occurs only at temperatures above 200°C, even in the absence of any free radical initiator. Addition of peroxides increases the efficiency of this reaction, however a high degree of reticulation can be obtained [23]. The other possible reaction is the formation of the graft copolymer between NR and polyamide 6 (NR-*g*-PA6), through the reaction between already maleated NR and polyamide matrix (Fig. 1). The question of interest in this work is whether this graft copolymer (NR-*g*-PA6) was generated during processing. Rheology, thermal properties, dynamic-mechanical analysis and morphology of these blends were analyzed.

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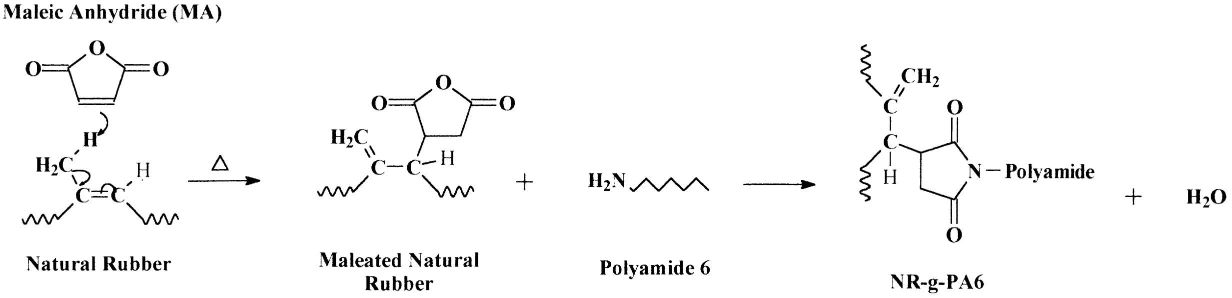

Fig. 1. Possible reactions among MA, polyamide 6 and NR that can take place during processing.

2. Experimental

2.1. Materials

The matrix was polyamide 6, obtained from Petronyl Ind. Com. Poliamidas S.A. The weight average molecular weight, M_w, of the polyamide 6 was calculated from the results of intrinsic viscosity analysis. The solution viscosity of the polyamide was measured with an Ubbelhode viscometer using formic acid/water 85/15 as solvent. The empirical relationship employed to correlate viscosity with molecular weight is given in Eq. (1):

$$[\eta] = KM_w^a \quad (1)$$

where $[\eta]$ is the intrinsic viscosity. The Mark–Houwink coefficients for this solvent system are $K = 2.26 \times 10^{-4}$ dl g^{-1} and $a = 0.82$ [28–30]. The M_w value obtained from Eq. (1) was $M_w = 85\,000$ g mol^{-1}. The elastomer was NR (commercial designation: GEB1), obtained from Fragon Prod. Ind. de Borracha Ltd. MA was obtained from Aldrich Chemical Co.

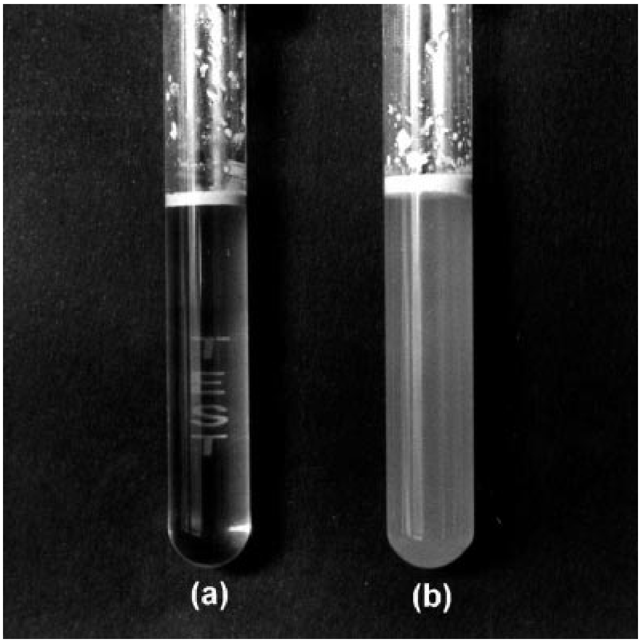

Fig. 2. Molau test solutions in formic acid of blends of 75/25: (a) polyamide 6/NR; and (b) polyamide 6/(NR 3 wt% MA) after 30 days.

2.2. Blend preparation and torque rheology

Prior to all melt processing steps, the polyamide was dried in a vacuum oven at 80°C for at least 12 h. Blends of different compositions were prepared in a Haake Torque Rheometer outfitted with a 50 ml mixing bowl and standard rotors at 240°C and 60 rpm. Mixtures of NR and 3% of MA were prepared in a roll mill at room temperature. This NR with MA was also mixed with polyamide 6 at different compositions in the mixing bowl. After mixing, blends were immediately quenched in cold water and dried in air. The blocks were ground and compression molded at 240°C to obtain films of approximately 200 μm thickness. Torque was measured continuously during mixing.

2.3. Thermal analysis

Selected materials were subjected to thermogravimetric analysis using a DuPont TA Instruments-TGA 2050 equipment at a heating rate of 10°C min^{-1} under Argon flow. The storage modulus and loss factor of the films

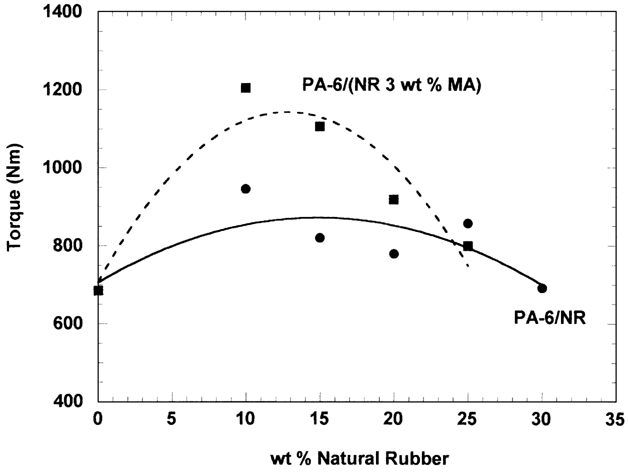

Fig. 3. Haake torque of polyamide 6/NR (●) and polyamide 6/(NR 3 wt% MA) (■) as a function of NR content. Torque readings were taken after 6 min at 240°C and 60 rpm.

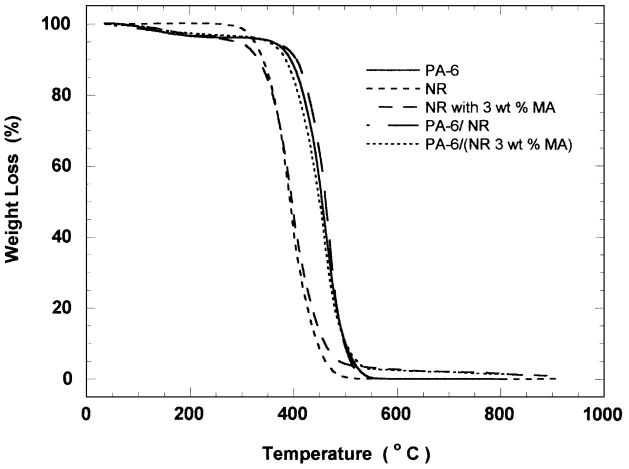

Fig. 4. Weight loss as a function of the temperature for polyamide 6, NR, NR with 3 wt% MA, polyamide 6/NR 85/15 and polyamide 6/(NR 3 wt% MA) 85/15, obtained from thermogravimetric analysis.

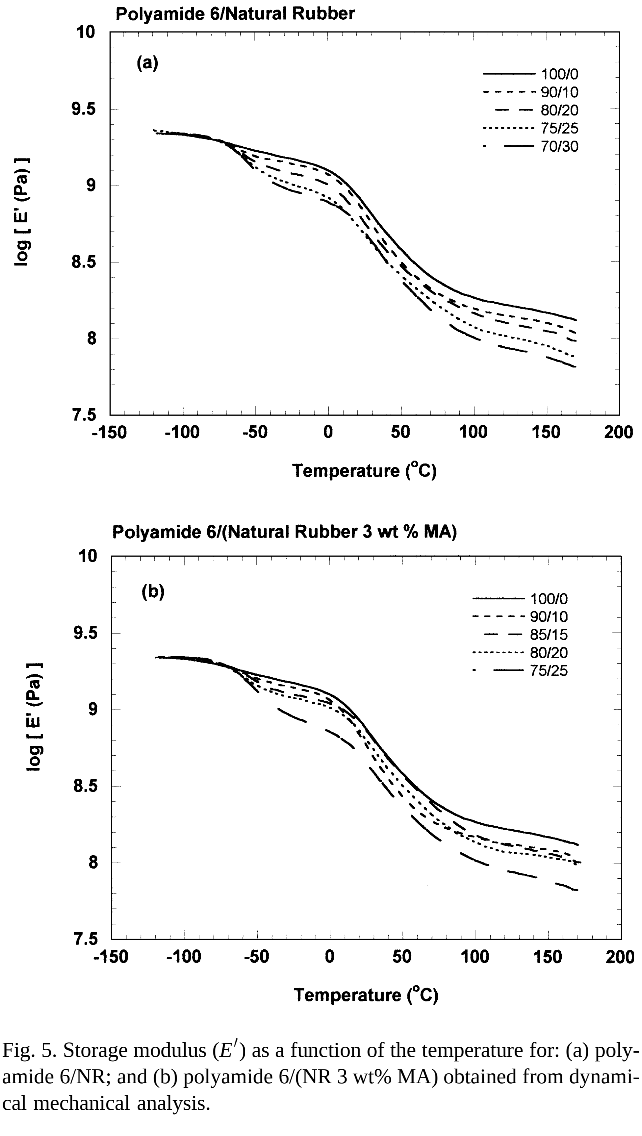

Fig. 5. Storage modulus (E') as a function of the temperature for: (a) polyamide 6/NR; and (b) polyamide 6/(NR 3 wt% MA) obtained from dynamical mechanical analysis.

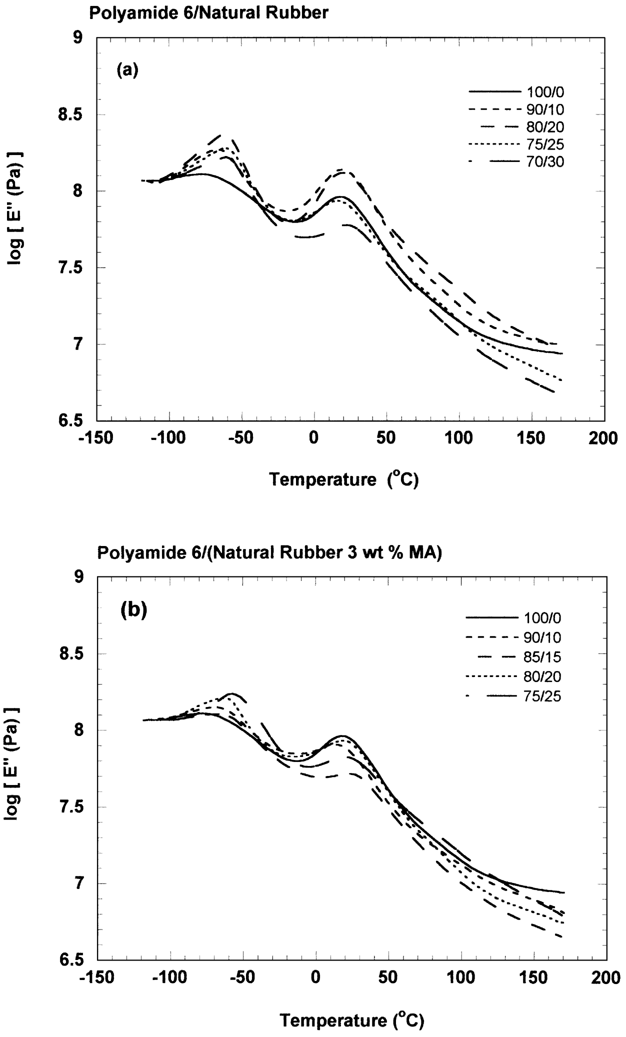

Fig. 6. Loss modulus (E'') as a function of the temperature for: (a) polyamide 6/NR and (b) polyamide 6/(NR 3 wt% MA) obtained from dynamical mechanical analysis.

were measured as a function of temperature in a DuPont TA Instruments-DMA 983 dynamic mechanical analyzer with frequency fixed at 1 Hz and scanning rate of 5°C min^{-1}. The range of temperature was −120°C to 170°C and the displacement amplitude was 0.2 mm.

2.4. Molau test

Molau test was conducted [8,9,33] by mixing about 0.1 g of both graftized and non-graftized blends and formic acid in a test tube. The mixture was shaken vigorously and left alone for a long time.

2.5. Morphology

Blend morphologies were determined using a Zeiss CEM-902 transmission electron microscope (TEM). The films were microtomed under cryogenic conditions (−50°C) to obtain ultrathin sections (ca. 30 nm). Phase contrast between the blend components was achieved by

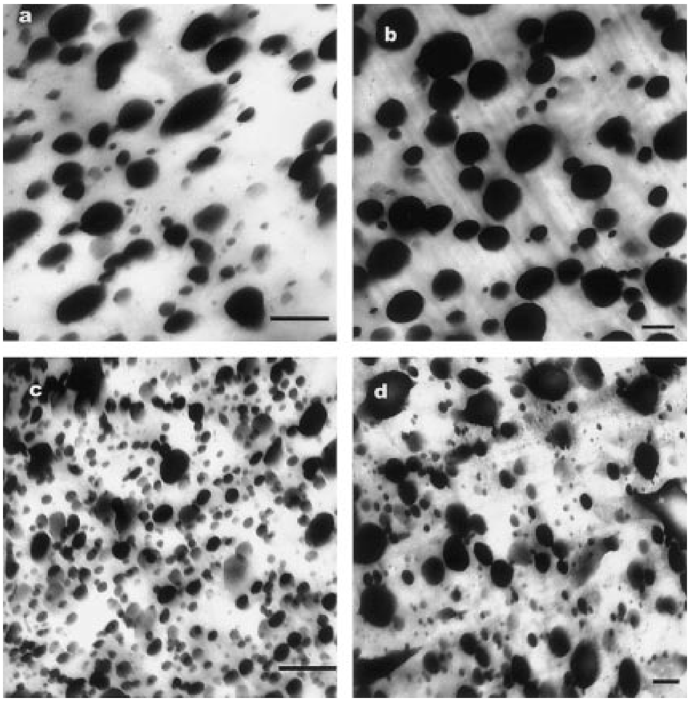

Fig. 7. TEM photomicrographs of blends of polyamide 6/NR: (a) 85/15; and (b) 75/25, and blends of polyamide 6/(NR 3 wt% MA): (c) 85/15; and (d) 75/25. Rubber particles are stained dark by OSO_4. Scaling bars correspond to 1 μm.

exposing the samples to vapors of OsO_4 for a period of 3 h. The rubber phase is stained darker than the polyamide. Photomicrographs of selected blends were employed for particle size analysis by a digital analysis technique based on IMAGE PRO PLUS® software. The particle size distribution as well as the weight average particle diameters, $\bar{d}_w$, were computed from these results.

3. Results and discussion

The subsequent sections describe the formation of the graft copolymer at the interface of polyamide 6 and NR and also the effects of varying the NR and NR (3 wt% MA) concentrations in blends with polyamide 6 on rheology, thermal behavior and morphology of these materials.

3.1. Molau test

Molau [31] and Illing [32], working with emulsions consisting of two immiscible polymer solutions and a graft copolymer, proposed that the formation of a white, colloidal suspension indicates the emulsifying action of the graft copolymer. The Molau test was conducted in this work in order to confirm the formation of graft copolymer between the polyamide 6 matrix and the NR particles. Polyamide 6/NR blends with or without MA were mixed with formic acid and both formed white suspensions just after vigorous mixing.

The polyamide phase is in principle soluble in formic acid whereas the rubber phase is insoluble. As seen in Fig. 2, polyamide 6/NR blends showed phase separation 30 days after mixing, while turbidity persisted in the solution containing the polyamide 6/(NR 3% MA) blend. The higher stability of solutions of MA-containing blends is undoubtedly attributed to the emulsifying effect of the graft copolymer formed between polyamide 6 and NR during melt blending. Han and Chuang [33] observed the same behavior for blends of polyamide 6/ethylene-based multifunctional polymer.

The formation of the graft copolymer influenced some other properties which will be discussed later in this paper.

3.2. Torque rheology

Haake torque rheometry was used to characterize the melt behavior of these materials. Fig. 3 shows characteristic torque values of binary polyamide 6/NR and polyamide 6/(NR 3 wt% MA) blends obtained after 6 min of mixing. It is clear that MA-containing blends have much higher melt viscosity than polyamide 6/NR blends. These higher torque values can indicate the occurrence of polyamide 6/NR grafting and also rubber crosslinking.

3.3. Thermogravimetric analysis

Fig. 4 shows weight loss as a function of the temperature for polyamide 6, NR, NR with 3 wt% of MA and for blends of polyamide 6/NR and polyamide 6/(NR 3 wt% MA) containing 15% of rubber phase. All tested polyamide-containing materials, presented weight loss of approximately 3 wt% at around 100°C due to loss of water; and

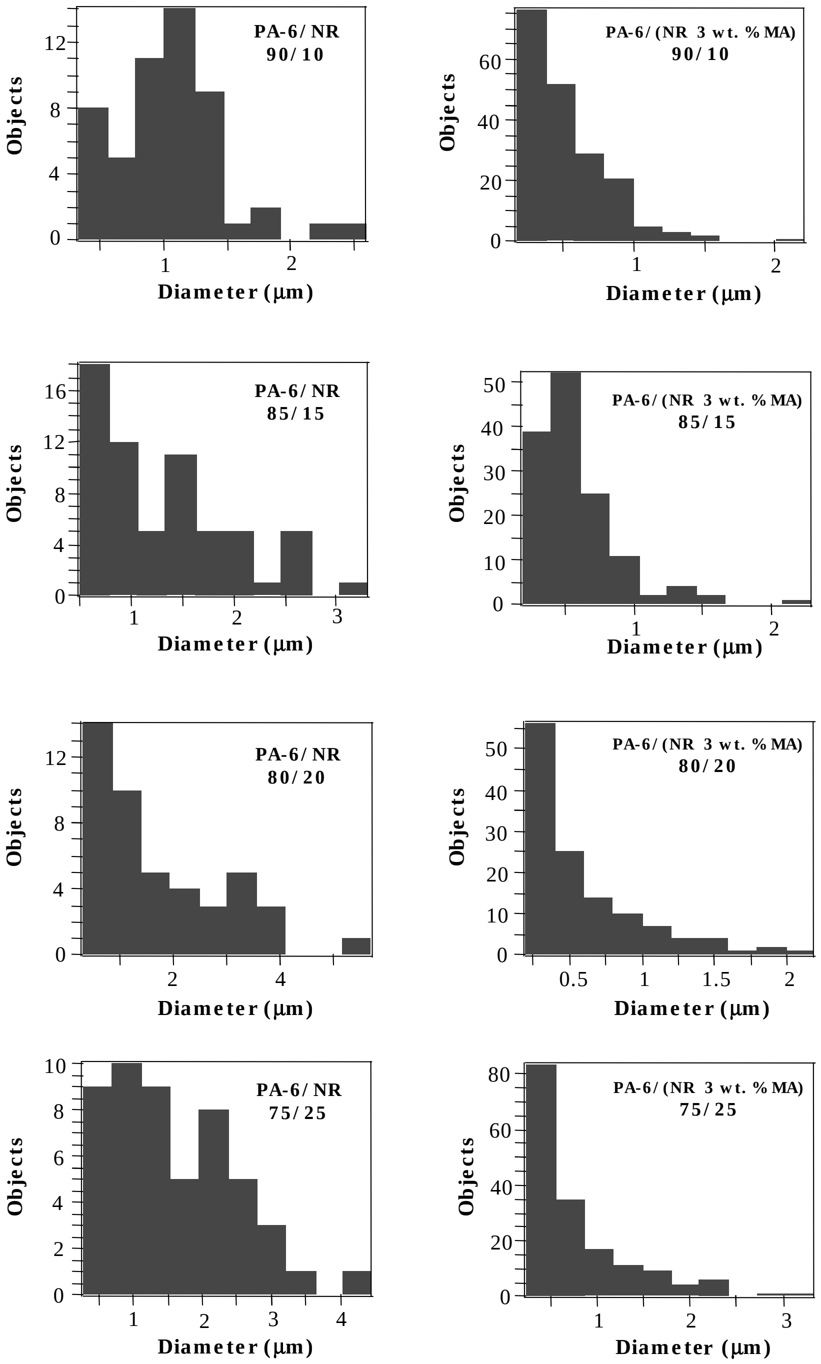

Fig. 8. Rubber particle size distributions obtained from TEM micrographs of selected blends.

MA-containing materials presented weight loss due to free MA anhydride sublimation at approximately 200°C. Natural rubber (with or without MA) showed weight loss due to degradation at around 400°C, whereas all polyamide-containing materials showed degradation weight loss at higher temperatures (around 500°C).

It is interesting to note that after polymer degradation (above 500°C), only MA-containing materials showed residual material up to 800°C. This evidence indicates that reactions took place during processing and caused the formation of both gel and graft copolymer. Gel material is formed during processing of NR with MA as can be seen in the literature [23–27]. In the blend of polyamide 6/(NR 3 wt% MA), rubber reticulation also took place, however, the 15 wt% rubber blend showed the same residual amount as the neat NR with 3 wt% MA (Fig. 4). This allows one to conclude that besides rubber crosslinking, the NR-*g*-PA6 graft copolymer was also formed since the same amount of residual material was obtained.

3.4. Dynamical mechanical analysis

Storage Modulus (E') and loss modulus (E'') curves of the blends as a function of the temperature is showed in the Figs. 5 and 6. As seen in Figs. 5 and 6, two main peaks can be observed. A prominent sub-T_g relaxation peak, which is associated with local modes of polyamide main-chain motion [12,13,34] can be seen at about −70°C. The T_g of NR also occurs at the same region. The other peak, about 30°C, is related to the T_g of polyamide 6.

As the rubber content increased, an increase in the −70°C peak was observed, as already expected. Higher polyamide main chain mobility was also expected due to the presence of the rubber particles. This higher mobility is also expected to contribute to the increase of the −70°C peak intensity. On the other hand, grafting reduces the intensity of this peak due to the reduction in chain mobility [34]. Comparing Fig. 6(a) and (b), MA-containing materials showed lower peaks at this region, relative to the same NR composition but without MA. This also suggests the occurrence of grafting reactions.

3.5. Morphology

Fig. 7 shows the morphologies of some blends of polyamide 6/NR and polyamide 6/(NR 3 wt% MA) containing 15 and 25 wt% of rubber. The rubber particles are dark because of the staining response. Comparing the micrographs of the blends it is clear that MA addition caused a strong decrease in particle size, which also confirms the formation of the graft copolymer proposed in the Fig. 1. The formation of this graft copolymer at rubber–matrix interface reduced interfacial tension and retarded particle coalescence during mixing leading to smaller particles.

As seen in Fig. 7, the rubber particle shapes are very complex, which make determination of an average size difficult; nevertheless a quantitative measure of the micrographs of the blends prepared was done. The diameter calculated from each particle is an average of a number of different dimensions measured at different possible axes of the particle. Fig. 8 shows the histograms for such analysis in each of the micrographs. All blends showed a large number of small particles; but it is clear that the MA-containing blends showed smaller particle sizes compared to the corresponding composition without MA. The weight average diameter of the rubber particles of each blend composition was also calculated by image analysis of the TEM micrographs, and the results are summarized in Fig. 9. Both blends with or without MA showed the same trend, but the MA-containing blends clearly showed smaller particles.

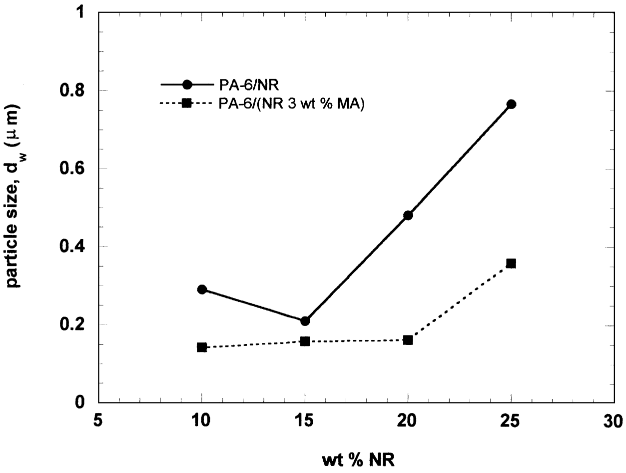

Fig. 9. Weight average diameter of the rubber particles calculated from the TEM micrographs

4. Conclusions

Polyamide 6 and NR blends were examined. Addition of MA to NR at room temperature prior to blending with polyamide 6 led to an in situ graft copolymer formation. Maleic anhydride molecules reacted with both rubber and polyamide 6 matrix during processing. This graftization reaction reduced particle size dramatically, as observed by TEM. Other graftization evidences were verified by Molau test, torque rheometry, themogravimetry and dynamic mechanical analysis.

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