

Poly(dimethylaminoethyl methacrylate) grafted natural rubber from seeded emulsion polymerization

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Abstract

The grafting efficiency of dimethylaminoethylmethacrylate (DMAEMA) on to natural rubber (NR) has been studied. Grafting was by ‘topology-controlled’ emulsion polymerization, whereby polymerization is initiated by a redox couple where one component (tetraethylene pentamine) is hydrophilic and the other (cumene hydroperoxide) is hydrophobic. This should promote grafting at the interface between hydrophobic natural rubber particles and the hydrophilic DMAEMA. The effects of different amounts of monomer were examined, with NMR to obtain the percent branching, transmission electron microscopy to obtain information on morphology, gel fraction measurement and dynamic mechanical analysis to obtain information on mechanical properties. Although there will be significant amounts of ungrafted polyDMAEMA present, there is good evidence for the formation of graft copolymers of NR with core-shell morphology, and significant amounts of grafting, at high concentrations of monomer.

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1. Introduction

Natural rubber (NR), largely *cis*-polyisoprene, has advantageous physical properties, including high resilience, strength, and fatigue resistance. However, most of its industrial applications (automotive tyres, load bearing, pads, silent blocks) require the use of particulate fillers to obtain the desired reinforcement (increase of the modulus, wear resistance, and ultimate properties) [1,2]. Interactions between NR and filler can be augmented by ‘topology-controlled’ emulsion polymerization [3,4], whereby polymerization is initiated by a redox couple where one component (tetraethylene pentamine) is hydrophilic and the other (cumene hydroperoxide) is hydrophobic. This should promote grafting at the interface between

hydrophobic natural rubber particles and the hydrophilic DMAEMA. It has been shown that this process results in significant amounts of both grafted and ungrafted poly (DMAEMA) [5]. There should be sufficient grafted polyDMAEMA formed so as to provide strong interactions with inorganic fillers. This provides an alternative route to modify NR, instead of the more conventional method of modifying a filler surface, and has potential applications for rubber-based modification of inorganic fillers. This paper explores the synthesis and characterization of modified natural rubber latex (MNRL) with different amounts of DMAEMA.

2. Experimental

2.1. Materials

Natural rubber latex (NRL) with a solid content of 60%

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was kindly donated by LATEX PLAN-HEVEA Ind. Comércio Ltda, Brazil. DMAEMA 98%, CHP tech grade, TEPA tech. grade, deuterated chloroform and osmium tetroxide (all from Aldrich) and toluene (EM Science) were used as supplied.

2.2. Preparation of modified natural rubber latex

Modified NRL was made by using the hydrophilic monomer DMAEMA at different concentrations (10, 20 and 30 wt% of solid NR), by seeded emulsion polymerization, as described elsewhere [3]. The reactions were carried out in a 300 mL jacketed glass reactor at 2 °C under a nitrogen atmosphere. A low temperature was chosen to reduce branching and cross-linking. The pH was maintained at 9.0 by adding 1.5 vol% of ammonium hydroxide solution. The mixture was continually stirred at 400 rpm with an anchor-like impeller.

The polymerization procedure was as follows. The NRL was diluted with distilled water and NH₄OH solution at 10 °C. DMAEMA was then added followed by the CHP. After 30 min, the reaction medium was cooled to 2 °C and then TEPA was added at a rate of 0.04 mL min⁻¹ over 8 h. The reactions were allowed to proceed under agitation for two more hours. Table 1 lists the reaction conditions.

2.3. Degree of swelling

Polymer networks can be characterized by measuring the degree of swelling in a solvent under well-specified conditions; particular care needs to be taken with NRL because the results of gel-fraction measurements can be technique-dependent. Swelling measurements of films were performed with toluene, which is a good solvent for NR, using the method described by Lee et al. [6].

2.4. Gel fraction

After film forming the reaction products were submitted to Soxhlet extraction to evaluate the gel content. Extraction was into toluene for a period of 24 h. After each extraction, the gel fractions were dried at room temperature. This procedure was only used to prepare the samples to be analyzed by ¹H NMR.

2.5. ¹H NMR

The grafting reaction efficiency has been evaluated by ¹H NMR. The dried samples of each gel fraction were swollen for 1 h in deuterated chloroform and analyzed by ¹H NMR in a 300 MHz spectrometer (Varian, Mercury 300) at 22 °C. Details are given in Section 3.2.

2.6. Transmission electron microscopy (TEM)

TEM of rubbery particles requires the particles to be stained and embedded in a resin before ultramicrotoming and examination under an electron microscope. The samples were prepared based on chemical fixation technique using the procedure described by Subramanian et al. [7]. TEM micrographs were obtained on a Phillips EM-400 operating at 100 kV.

2.7. Dynamic mechanical analysis (DMA)

The materials obtained from modified latexes after film-forming in a silicon mould at 40 °C were characterized by dynamic mechanical experiments at a frequency of 0.1 Hz in the range –100 to 100 °C, using a DMA from Metravib Instruments in torsion mode, with parallelepiped samples with 2×6×14 mm³ dimensions.

2.8. Tensile tests

Tensile tests were performed on a MTS 1/ME machine at ambient temperature and with a constant crosshead speed corresponding to an initial strain rate of $d\varepsilon/dt = 2.1 \times 10^{-2} \text{ s}^{-1}$.

3. Results and discussion

3.1. Gel fraction

The results obtained from gel fraction and swelling ratio of NR and DMAEMA-modified NR latexes are given in Fig. 1. Both gel fraction and swelling ratio with toluene are indicators of the amount of cross-linking, but the two properties are not necessarily directly correlated. This is because the presence of polyDMAEMA as a new phase makes samples of

Table 1

Reaction conditions for seeded emulsion polymerization of DMAEMA onto NRL at 2 °C with the redox couple CHP and TEPA

Ingredients	Reaction 1	Reaction 2	Reaction 3	Reaction 4
NRL (g)	100	100	100	100
DMAEMA (g)	–	6.0	12.0	18.0
CHP (g)	0.30	0.30	0.30	0.30
TEPA (g)	0.40	0.40	0.40	0.40
Distilled water (mL)	100	100	100	100
NH ₄ OH 1.5% (mL)	50	50	50	50

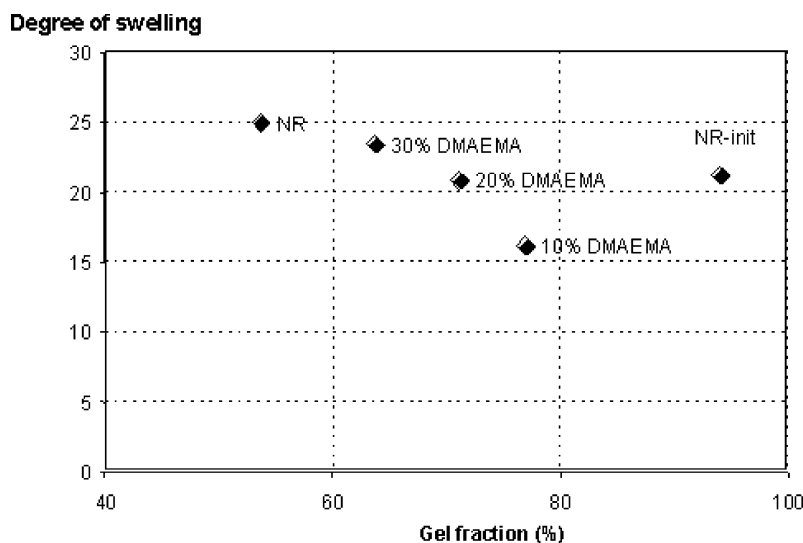


Fig. 1. Gel fraction and swelling ratio for cast films of NR, NR subjected to initiator without addition of monomer (NR-initiator) and NR-g-PDMAEMA with the percent of DMAEMA as indicated. Degree of swelling = (final volume/initial volume).

modified NRL chemically distinct from both pure NR and NR that has been exposed to radicals ('NR-init'). One sees that exposing NR to radicals leads to a large increase in gel fraction, as expected if there is a significant increase in cross-linking caused by these radicals. The relatively small decrease in degree of swelling in NR-initiator compared to NR is also consistent with increased cross-linking.

The effect of polymerizing DMAEMA is to decrease the gel fraction, and increase the degree of swelling, with increasing amount of DMAEMA. Both results are consistent with the capture of radicals by DMAEMA which would otherwise lead to crosslinking of the NR caused by the flux of radicals. As stated, the observation that NR exposed to radicals in the absence of DMAEMA does not fit the trends with decreasing DMAEMA can be ascribed to the chemically distinct nature of the two systems.

3.2. NMR

The products from Soxhlet extractions were similar in character as tough, rubbery and non-tacky materials for any concentration of the monomer used in the reactions. Figs. 2 and 3 show the ^1H NMR spectra of NR and NR modified with 30 wt% of DMAEMA.

For NR (Fig. 2) the following ^1H NMR (300 MHz, CDCl_3) peaks were assigned: δ 5.15 (1H, =CH), δ 2.10 (4H, $(\text{CH}_2)_2$), δ 1.70 (3H, CH_3). For NR-g-PDMAEMA 30% (Fig. 3): δ 5.15 (1H, =CH), δ 4.05 (2H, OCH_2 from DMAEMA), δ 2.10 (4H, $(\text{CH}_2)_2$), δ 1.70 (3H, CH_3).

Average copolymer compositions were determined from ^1H NMR spectrum (Fig. 3) using [8]:

$$\text{mol\% of DMAEMA} = \frac{\left(\frac{S_1}{2}\right)}{\left(S_0 + \frac{S_1}{2}\right)} \quad (1)$$

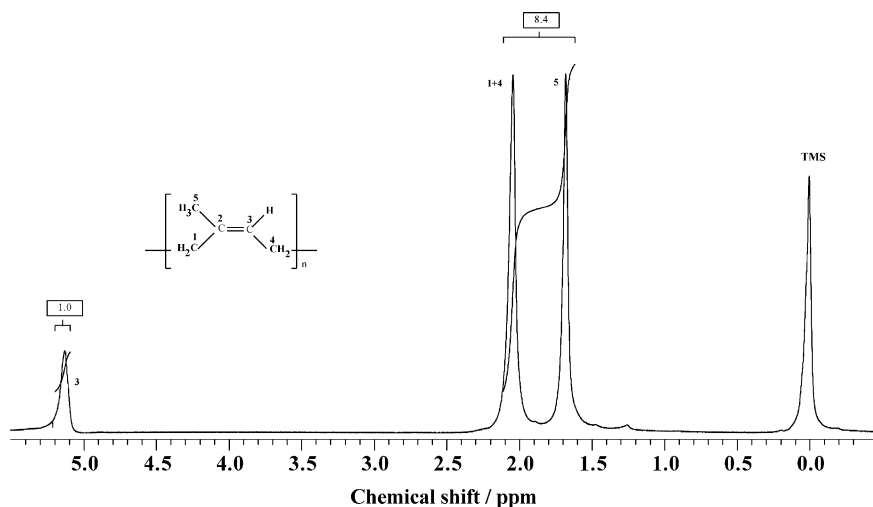


Fig. 2. ^1H NMR spectrum of natural rubber.

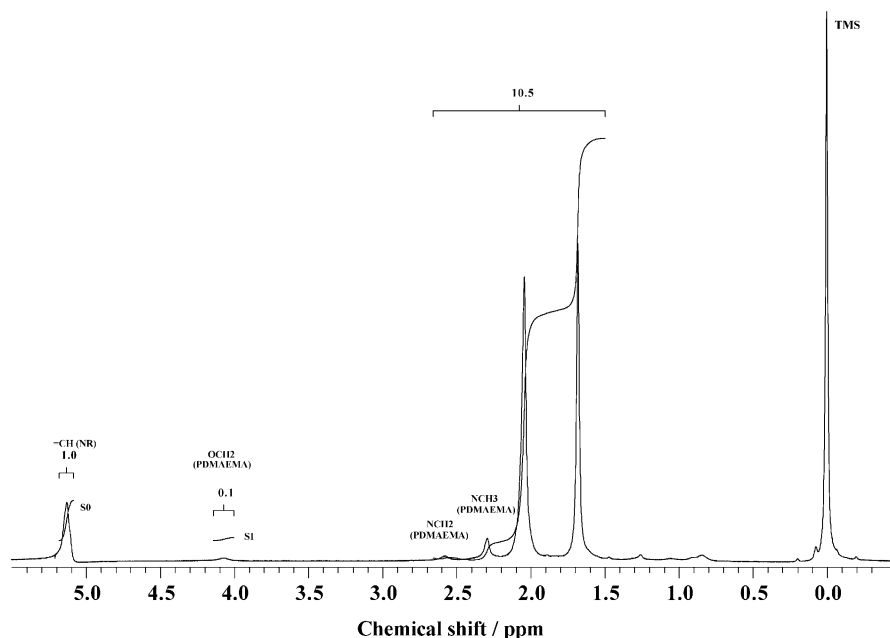


Fig. 3. ^1H NMR spectrum of NR grafted with 30% DMAEMA (reaction 4, Table 1).

where S_0 and S_1 are the peak areas corresponding respectively to NR and DMAEMA (Fig. 3). Results are given in Table 2, and show that no detectable grafting between NR and DMAEMA occurred when 10 wt% of DMAEMA were used, and this increases to a significant amount of grafting with 30% DMAEMA.

It is noted that the Soxhlet technique could cause some degradation of the films and extraction of some grafted polymers in the NR backbone with ungrafted molecules. Nevertheless, the trends are clear, and the results are consistent with the inferences of a rate study on a similar system [5].

3.3. Transmission electron microscopy

Figs. 4 and 5 show transmission electron micrographs of OsO_4 -stained ultrathin sections of NR and of NR modified with 30 wt% of DMAEMA.

Fig. 5 and other micrographs of this sample show distinct core-shell structures for many particles, particularly smaller ones. This is interpreted as a polyDMAEMA shell surrounding a NR core. This morphology was not observed for NRL samples modified with 10 and 20 wt% of

DMAEMA, consistent with the low grafting levels found for these latexes by ^1H NMR analysis (Table 2). While there will also be an appreciable amount of ungrafted polyDMAEMA present in these systems [5], the samples were subjected to several cycles of centrifugation and re-suspension in water and alcohol, as part of preparation for TEM. This should remove much of the ungrafted polyDMAEMA. The observation that such a distinct shell is not observed for larger particles is consistent with greater amounts of grafting per unit particle surface area occurring with smaller particles, which have a higher surface area per particle. Nevertheless, we cannot exclude a possible interaction between polyDMAEMA and the proteins at the particle surface that could change the extension of the shell and could result in the difference of the thickness and of the density of the shell.

3.4. Dynamic mechanical properties

Fig. 6 gives the results of dynamic mechanical analysis of the films of NR, NR with initiator alone and NR grafted with polyDMAEMA, all at a frequency of 0.1 Hz. It is apparent that the initiation process leads to an increase of the modulus of the material in the rubbery domain. This is due to crosslinking. However, the slow decrease of this modulus with temperature suggests that this crosslinking is only partial and heterogeneous. This is consistent with the swelling data (Fig. 1).

The modification by DMAEMA leads for the storage modulus to the occurrence of a second plateau between -40°C and room temperature followed by a drop of this modulus down to the level of the NR modulus. The high level of this second plateau cannot be ascribed to a

Table 2

Copolymer composition based on mol% of DMAEMA in the gel fraction of the films of NRL modified with DMAEMA

Copolymer	S_0	S_1	mol % DMAEMA
NR-g-PDMAEMA 10%	1	0	0
NR-g-PDMAEMA 20%	1	0.02	1.0
NR-g-PDMAEMA 30%	1	0.09	4.3

S_0 and S_1 are the peak areas corresponding respectively to NR and DMAEMA (Fig. 3).

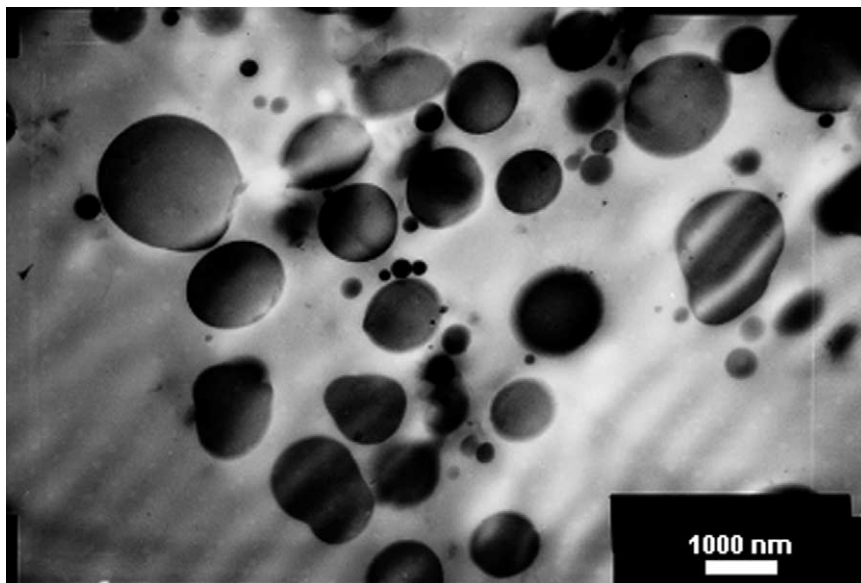


Fig. 4. TEM micrograph of OsO₄-stained ultramicrotome sections of NR particles.

supplementary crosslinking of NR by the grafting reaction: indeed, its value is in the range of the modulus of an epoxy resin above its glass transition temperature [9]. In other words, such an explanation would mean that the NR has been crosslinked as much as a thermoset, which is totally unrealistic. Moreover, the modulus decreases after this plateau at a temperature which corresponds to the glass transition temperature of polyDMAEMA [10]. If the polyDMAEMA were dispersed as particles in the NR phase, the reinforcement level, measured in the temperature range of this second plateau, would be comparable to that obtained with fillers. The modulus predicted by mechanical modelling, for instance the Eilers/van Dijk equation [11],

predicts an increase of modulus by a factor 2.2 with 25 vol% (the volume fraction of DMAEMA added to the NR) of filler: this is much below the reinforcement level measured with our sample. All this suggests the presence of a core-shell type morphology of the NR particle with a *cis*-polyisoprene core and a poly-DMAEMA layer. The film-forming temperature is high enough (40 °C) for the grafted DMAEMA chains to coalesce and create a co-continuous phase in the material. This was confirmed by the impossibility of being able to form a coherent film at room temperature. Moreover, a simple parallel model predicts, taking a reasonable modulus value for the DMAEMA phase of 1.5 GPa, a maximum composite

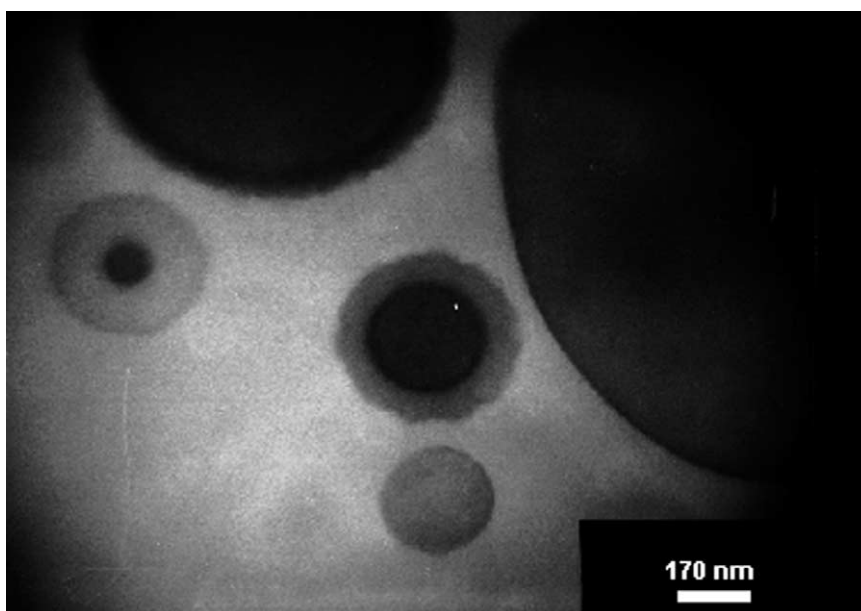


Fig. 5. TEM micrograph of OsO₄-stained ultramicrotome sections of NR grafted with polyDMAEMA (NR-g-PDMAEMA 30%).

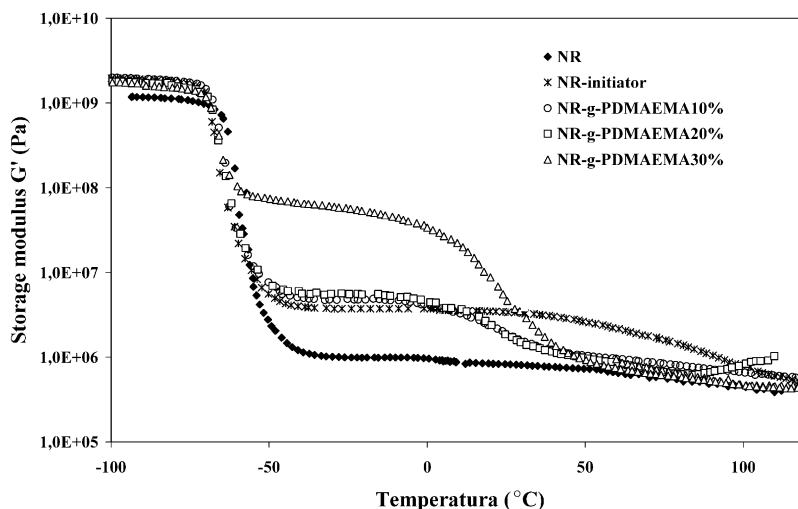


Fig. 6. Storage modulus at 0.1 Hz from DMA on NR films, NR modified with initiator, and NR films grafted with the indicated amounts of DMAEMA.

modulus equal to 0.33 GPa, which is in the range of the measured modulus [12]. There is however a gap between the NR-g-PDMAEMA (30%) sample and the other ones, which indicates a threshold below which the layer is not important enough for the formation of this co-continuous phase.

3.5. Tensile tests

Fig. 7 presents the tensile stress–strain curve of the different samples. The initial modulus deduced from these curves are coherent with those measured at the same temperature by DMA. The NR sample shows a stress level below that of the grafted NR. Moreover, the NR modified by the presence of the initiator shows a hardening much higher than in the case of NR. This can be related to the increase of the crosslinking density generated by the initiator, as already mentioned. This effect might be enhanced by the crystallization of the NR during the stretching, which is known to depend on the crosslink density and to increase the stress level at large deformation [13]. The samples of

grafted NR with 10 and 20% of DMAEMA have behaviour at low deformation similar to that of the NR-initiator sample, except that the hardening part is less steep. The latter effect can be explained by a decrease of the crosslinking effect of the initiator in presence of DMAEMA, as already suggested by the DMA curve which shows a modulus level at high temperature below the modulus of the NR-initiator sample. The NR-g-PDMAEMA 30% shows a different behaviour. The hardening part of its stress–strain curve is still comparable to that of the NR-g-DMAEMA10% and NR-g-DMAEMA20% samples, but a yield stress is visible at low deformation, leading to a global higher stress level. The mechanical response of this material during a tensile test might be a combination of the plastic response of the grafted DMAEMA chains forming a co-continuous phase and of the elastic response of the NR. The results obtained from these tests are in agreement with those from mechanical spectrometry and support the assumption of the formation of core-shell type particles with a core made of natural rubber and a shell made of polyDMAEMA chains.

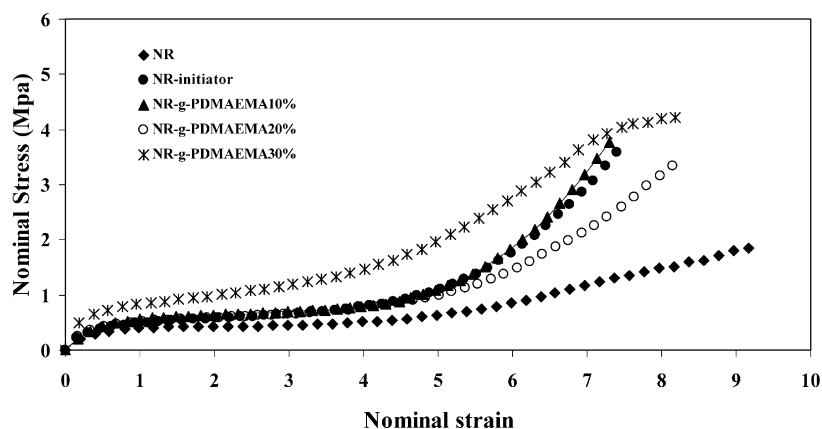


Fig. 7. Strain curves of NR, NR modified by the initiator and NR grafted with different amounts of DMAEMA.

4. Conclusions

An examination of latexes formed by polymerization of DMAEMA in the presence of natural rubber latex as seed particles, using ‘topology-controlled’ emulsion polymerization to maximize grafting, leads to the following inferences. Modifying the NRL by exposure to radicals from the redox initiator in the absence of monomer leads, not surprisingly, to increased cross-linking. In the presence of DMAEMA, there is a competition between crosslinking, homogeneous aqueous-phase polymerization and grafting, and leads to less crosslinking for the same radical flux. Analysis of the amount of grafting from ^1H NMR spectroscopy shows the presence of significant grafting at relatively high levels of DMAEMA (20–30 wt%). Swollen based NMR spectroscopy has been proven to be a more reliable technique to analyze the copolymer composition allowing to obtaining very clean spectra for all analyzed samples. Microtoming transmission electron microscopy suggests that the grafted layer in these high-DMAEMA samples is a shell around the natural rubber core.

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References

- [1] Park S-J, Cho K-S. *J Coll Interf Sci* 2003;267:86.
- [2] Robert AD. *Natural rubber science and technology*. Oxford: Oxford University Press; 1988.
- [3] Lamb D, Anstey JF, Fellows CM, Monteiro JM, Gilbert RG. *Biomacromolecules* 2001;2:518.
- [4] Lamb D, Anstey JF, Lee DY, Fellows CM, Monteiro MJ, Gilbert RG. *Macromol Symp* 2001;174:13.
- [5] Kangwansupamonkon W, Fellows CM, Lamb DJ, Gilbert RG, Kiatkamjornwong S. *Polymer* 2004;45:5775.
- [6] Lee D-Y, Subramaniam N, Fellows CM, Gilbert RG. *Polymer* 2002; 40:809.
- [7] Subramaniam N, Simpson A, Monteiro MJ, Shaffer O, Fellows CM, Gilbert RG. *Microsc Res Tech* 2004;63:111.
- [8] Llauro-Darricades MF, Pichot C, Guillot J, Rios GL, Cruz EMA, Guzman CC. *Polymer* 1986;27:889.
- [9] Sasuga T, Udagawa A. *Polymer* 1991;32:402.
- [10] Martin-Gomis L, Cuervo-Rodriguez R, Fernandez-Monreal MC, Madruga EL, Fernandez-Garcia M. *J Polym Sci Part A-Polymer Chem* 2003;41:2659.
- [11] Ferry JD. *Viscoelastic properties of polymers*. 2nd ed. New York: Wiley-Interscience; 1980.
- [12] Bornert M, Breteau T, Gilormini P. *Homogeneisation en mécanique des matériaux 1 matériaux aléatoires élastiques et milieux périodiques*. Paris: Hermes; 2001.
- [13] Bokobza L, Rapoport O. *J Appl Polym Sci* 2002;85:2301.