

This article was downloaded by:

On: 21 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymer Analysis and Characterization

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646643>

Creep Behavior of PA6/NBR TPVs

Ana C. O. Gomes^a; Bluma G. Soares^a; Marcia G. Oliveira^b; Caio M. Paranhos^c

^a Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil ^b Divisão de Processamento e Caracterização de Materiais, Instituto Nacional de Tecnologia, Rio de Janeiro, Brazil ^c Departamento de Engenharia de Materiais, Universidade Federal de São Carlos, São Carlos, Brazil

Online publication date: 19 July 2010

To cite this Article Gomes, Ana C. O. , Soares, Bluma G. , Oliveira, Marcia G. and Paranhos, Caio M.(2010) 'Creep Behavior of PA6/NBR TPVs', *International Journal of Polymer Analysis and Characterization*, 15: 5, 287 – 297

To link to this Article: DOI: 10.1080/1023666X.2010.493269

URL: <http://dx.doi.org/10.1080/1023666X.2010.493269>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

CREEP BEHAVIOR OF PA6/NBR TPVs

Ana C. O. Gomes,¹ Bluma G. Soares,¹ Marcia G. Oliveira,² and Caio M. Paranhos³

¹Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

²Divisão de Processamento e Caracterização de Materiais, Instituto Nacional de Tecnologia, Rio de Janeiro, Brazil

³Departamento de Engenharia de Materiais, Universidade Federal de São Carlos, São Carlos, Brazil

The influence of compatibilizers and other additives in PA6/NBR blends is evaluated in terms of creep resistance. The results obtained are correlated with density, selective solvent extraction, tensile strength, DMA analysis, and scanning electron microscopy. Our studies show an enhancement of dimensional stability of samples with the presence of EVAMA in the PA6 master batch. On the other hand, better elastomeric behavior is achieved with the compatibilization process, oxazoline-modified NBR being the best compatibilizer. Also, the possibility of evaluating a material in conditions near to final applications, through a shot-time test, with minimal material waste is shown.

Keywords: Creep; Mechanical properties; NBR; PA6; TPV

INTRODUCTION

Thermoplastic elastomer vulcanizates (TPV) are highly promising materials due to their multi-applicability and reprocessability.^[1,2] TPVs unify the processability of thermoplastics and elasticity of elastomers in one unique material. Among the types of TPV, polymer blends have the greatest potential because of the variety of materials that can be combined. The most common way to prepare a TPV is dynamic vulcanization during the blend process, first described by Gessler and Haslett.^[3]

The blend of polyamide (PA) and nitrile rubber (NBR) is expected to have high hot oil resistance and good mechanical strength, especially at high temperatures.^[4,5] Despite this fact, few works have been published about PA/NBR blends, probably due to the low thermal resistance of NBR associated to the high temperature necessary to process PA. In previous works, our research group studied the incorporation

Submitted 22 February 2010; accepted 15 April 2010.

The authors would like to thank CAPES, CNPq, FAPERJ, and FINEP/CNPq for sponsoring this work, and Petroflex, Radici, and Crompton for the supplied materials.

Correspondence: Ana C. O. Gomes, Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, Ilha do Fundão, CEP 21945-598, Rio de Janeiro, Brazil. E-mail: acogomes@gmail.com

of additives with the aim to improve processability and final properties of PA6/NBR blends.^[6]

The creep test is an important characterization due to its good simulation of deformations that occur at final application of the material, being capable of previewing material performance as a function of time.^[7,8] Creep tests are especially useful for studying materials under very low shear rates or frequencies, evaluating not only the material, but also the artifact design.^[9]

Physical aging can be related to creep, i.e., the damage caused due to slow relaxation of polymeric chains. This aging is different from thermal degradation because it is thermodynamically reversible. The test would not be directly related to the physical aging of the material, but a comparison of its behavior can be useful as an evaluation parameter.^[7]

Insufficient knowledge of flow behavior during the solicitation created by the application can lead to mechanical failure of the final product.^[10] Yet creep studies along short time intervals would give information about interfacial interaction in heterogeneous materials such as polymeric blends.^[11] Despite the proved utility of the creep test in reinforced thermoplastics or vulcanized elastomers,^[12] few works apply this characterization test in TPV materials, which unify both properties.

The aim of this work is to evaluate the effect of additives and compatibilization in the creep behavior of PA6/NBR blend TPVs. The results follow the evolution of the material with the objective of obtaining a TPV with dimensional stability and applicability in more severe conditions than commercial products available in the market.

EXPERIMENTAL SECTION

NBR (28% w/w of acrylonitrile, Mooney number = 60, at 100°C), phenolic resin SP 1045 (PR), and carboxylated NBR (XNBR) (28% w/w of acrylonitrile, 12% w/w of carboxyl groups) were kindly supplied by Petroflex Ind e Com. PA6 (Radilon S natural, MFI = 19.6 g/10 min, ASTM 1238D, density 1.14 g/cm³) was kindly supplied by Radici Group. Copolymer of ethylene-co-vinyl acetate modified with maleic anhydride (EVAMA; VA content of 28%, MA content of 0.8% w/w, MFI = 16 g/10 min, density = 0.95 g/cm³) was purchased from Proquimil Produtos Químicos Ltda. Naugard 445, used as antioxidant, was kindly supplied by Crompton Corporation do Brasil. The other antioxidants, Irganox 1010 and Irgafos 168, were acquired from Ciba Corporation do Brasil. Stannous chloride (SnCl₂) was purchased from VETEC Corp. do Brasil, and used as received. NBR-oxazoline (NBROXA) and NBR-epoxy (NBREPO), both with approximately 3 mmol/g of functional groups, were obtained at our laboratory, through chemical modification of NBR, in accordance with the procedures described by Almeida et al.^[13] and Rocha et al.,^[14] respectively.

All blends were prepared by melt mixing in an internal mixer coupled to a Brabender Plasticorder Rheometer with a Banbury rotor at 80 rpm. Master batches of PA6 (PA6 MB) were prepared by processing PA6 alone or with 5 phr of EVAMA at 240°C for 3 min. Separately, a master batch of NBR containing 7.5 phr of Naugard 445 was prepared at 40°C for 3 min. The blends were then prepared by processing the PA6 MB and NBR MB master batches in a proportion of

Table I. Blend composition

Sample code	MB PA6		MB NBR		Compatibilizer		
	PA6 ^b	EVAMA ^b	NBR ^b	Naugard 445 ^b	NBROXA ^b	NBREPO ^b	XNBR ^b
PA6	100	—	—	—	—	—	—
MBPA	100	5	—	—	—	—	—
MBNBR	—	—	100	7.5	—	—	—
Mix 1 ^a	50	—	50	—	—	—	—
Mix 2 ^a	50	5	50	7.5	—	—	—
Mix 3 ^a	50	5	50	7.5	5	—	—
Mix 4 ^a	5	5	50	7.5	—	5	—
Mix 5 ^a	50	5	50	7.5	—	—	5

^aThe blends were cross-linked with RF/SnCl₂ (5: 0.25 phr) system.

^bAll quantities in phr.

50:50 wt.% at 220°C for 3 min. Then, the compatibilizer was added and the mixture was continued for 2 min, followed by the addition of the cross-linking system (RF + SnCl₂) in a proportion of (5:0.25 phr). After 2 min of dynamic vulcanization, an additional amount of Naugard 445 equal to 2.5 phr was added and the mixture was maintained for additional 30 s. The total blending time was 10 min. The blend composition is summarized in Table I.

The blends were ground in appropriate mills and injected in a semi-industrial injection-molding machine (Battenfeld Plus 35) with mold pressure of 110 bar, injection temperature of 240°C, injection pressure of 80 bar, and back pressure of 50 bar. All materials were kept in a vacuum oven at 100°C until constant weight was reached before each processing step.

Creep samples were obtained from compression molded sheets of approximately 0.1 mm in thickness and surface dimensions of 6 mm × 30 mm. Creep tests were realized in DMA Q800, from TA Instruments, in a tension film clamp. The used conditions were: 25°C; instantaneous tension applied of 0.1 MPa; tension sustained during 30 min; applied tension instantaneously removed; strain recovery for 60 min. The time-temperature superposition test was performed at temperatures between 20° and 140°C, with creep time of 5 min, in consecutive cycles, a temperature increment of 10°C at each step, with applied tension of 0.1 MPa. The creep strain curves obtained were used to generate the time-temperature superposition master curve in a temperature reference of 25°C, through the TA TTS Data Analysis program.

Tensile strength was measured on an EMIC DL-2000 universal testing machine, in accordance with DIN 53504 with a speed of 200 mm/min, at room temperature (25°C) and humidity level of 53%.

Selective extraction was performed in a Soxhlet extraction system. Samples of approximately 200 mm³ were evolved in filter paper and exposed to refluxed solvent for 24 h. Toluene was used as a selective solvent to NBR phase, which eventually was not cross-linked by phenolic resin.

Relative density was calculated from weighing samples in air and absolute ethanol, in accordance with ASTM D-297 standard.

Dynamic-mechanical analysis was realized in a Q800 DMA machine, between -60° and 120°C , at 1 Hz frequency, heating rate of $3^{\circ}\text{C}/\text{min}$, with a single cantilever clamp.

Scanning electron microscopy (SEM) was obtained with a JEOL 5610 LV microscope, by applying 30 kV. Samples were cryofractured after 2 h of immersion in liquid nitrogen and stained with osmium tetroxide (OsO_4). Stained samples were covered with carbon and analyzed in a backscattered electron detector.

RESULTS AND DISCUSSION

First of all, it is important to point out that the experiments were realized in nonlinear conditions, applying an initial tension excessively high relative to film dimensions. The choice for nonlinear experiment was mainly based on fact that a real application condition rarely will obey minimal solicitation conditions into the linear viscoelastic strain range.^[8]

The pure PA sample shows peculiar behavior, presenting “negative strain,” which is physically incoherent, as can be seen in Figure 1(a). This behavior can be associated with the dimensional instability of the sample, which would be caused by the “memory effect” of polymeric chains. It is important to remember that the samples are thin films obtained from a thin pressed sheet, i.e., a two-dimensional

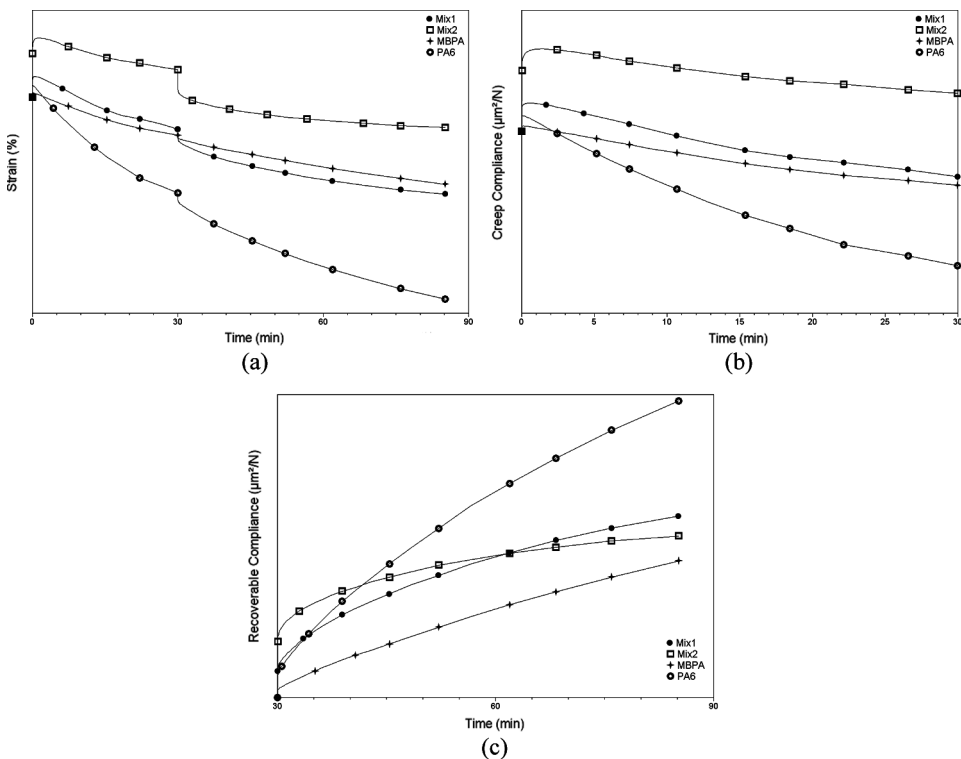


Figure 1. Creep curves for PA6, MBPA, and mixtures: (a) strain, (b) creep compliance, (c) recoverable compliance.

strain molding technique. As can be observed in Figure 1(a), once initial tension is applied, the sample stretches little, but the mobility initiated by the strain allows the chain relaxation, to shrinkage of film dimensions. At the moment where tension is removed (30 min of experiment), the initial strain is recovered, and the film continues to shrink. Indeed, some authors have considered that the amorphous portion of semicrystalline polymers cannot be in a completely relaxed state, even in temperatures next to glass transition, due to a restriction caused by the crystalline domains.^[15]

Influence of Blend and Additives

The relaxation behavior described above is also observed with samples MBPA, Mix 1, and Mix 2. The strain profile of MBPA changes significantly in relation to pure PA6. Besides that, the blend without additives (Mix 1) has more initial deformation, which is expected due to the presence of NBR.^[12] Nevertheless, Mix 1 flows considerably in time, as can be seen in Figure 1(b). The blend with additives (Mix 2) shows higher deformation in initial tension.

A best comparison method can be achieved with a slope value calculated from the last 10 min of creep compliance curves. The obtained values are presented in Table II. It can be noticed that the presence of additives in the PA phase as well as the blend with NBR has a decreasing relaxation effect, the EVAMA addition being more effective. The combination of both, in blends with additives, leads to the lower slope of relaxation among all samples. This behavior can be related to a stabilizer effect of the EVAMA additive in the PA phase. The maleic anhydride functional group in EVAMA is able to react with the amine terminal group of PA6. The reaction is widely described in the literature and frequently associated with increases in mechanical properties of polymeric blends, especially for yield tension.^[15] The molecules generated by the reaction are different than the crystallizable phase of the blend, and tend to be excluded from the organized structure during the crystallization process. If the relaxation phenomenon occurs due to instability of the amorphous phase, as cited before, it is reasonable to suppose that the reaction product between EVAMA and PA6, probably located in the amorphous phase, acts to decrease this effect.

The recoverable compliance decreases with the presence of additives, as can be seen in Figure 1(c). It is possible that the nature of the additive, mainly the EVAMA,

Table II. Slope values on last 10 min of creep compliance curves

Sample	Slope ($\mu\text{m}^2/(\text{N} \cdot \text{min})$)	
	Compliance	TTS (10^{-6})
PA6	-882	—
MBPA	-417	—
Mix 1	-601	—
Mix 2	-390	—
Mix 3	13	1.00
Mix 4	23	2.25
Mix 5	34	1.24

is responsible for this “viscous” behavior. It is important, at this point of the discussion, to separate the stabilization effect of EVAMA in the dimensional relaxation from its influence in recoverable compliance. In the first case, we discuss a phenomenon of steric molecular state, where the macromolecules are not in their “more stable” molecular arrangement and the reaction with EVAMA leading to a more “static” system. In addition, we discuss the rheological effect of a less elastomeric component, such as EVAMA, in the flow behavior of the molecules of the whole blend as one. The same additive acts on the two separated effects.

Influence of Compatibilization

Figure 2(a) presents the strain profile of compatibilized samples. The relaxation effect is completely absent in the compatibilized samples. The Mix 4 sample presents higher deformation, but, nevertheless, good strain recovery. The compliance is comparable for Mix 3 and Mix 5, as can be seen in Figure 2(b). The compliance is lower for these samples, indicating more strain resistance of the blend. NBROXA and XNBR may act as better compatibilizers than NBREPO, leading to a better distribution of NBR domains, and consequently better strain resistance.

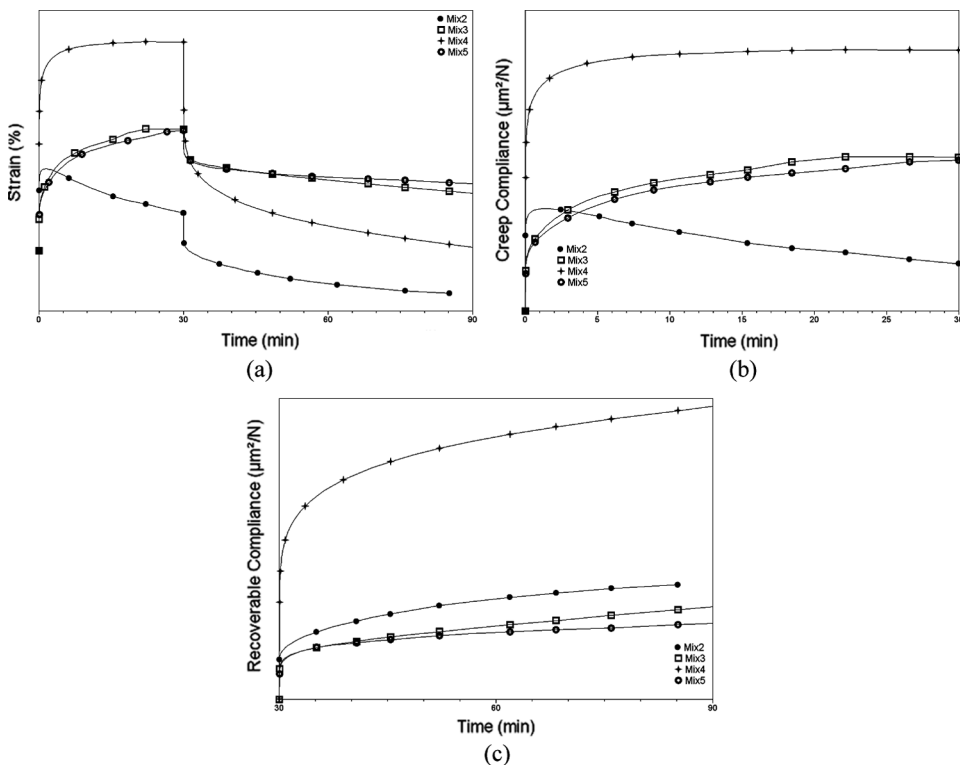


Figure 2. Creep curves for compatibilized samples: (a) strain, (b) creep compliance, (c) recoverable compliance.

The recoverable compliance is comparable for these samples too, as seen in Figure 2(c). Mix 3 and Mix 5 show lower recoverable compliance than Mix 4. The recovery of strain is usually associated with a good interaction between blend phases.^[10,12,15] The compatibilization process does not always produce good interfacial adhesion, leading to good interphase interaction. However, this could not be the only effect considered here, since we are dealing with a complex system, with a large number of components and variables.

The unexpected lower recoverable compliance can be explained by the hypothesis that the compatibilizer system influences the cross-linking process, decreasing the cross-link density and allowing a more viscous behavior. The influence of a compatibilizer in the cross-linking process is cited in the literature.^[16]

Creep TTS

The projection through time of the creep behavior is shown in Figure 3. Mix 4 maintains the higher strain level, with higher relaxation slope. The TTS master curves clarify differences between Mix 3 and Mix 5, too slight to discriminate the samples. Mix 3 shows a higher deformation, with greater slope of steady-state curve portion (after 100 h). Mix 3 is less deformable, showing less strain variation with time (values presented in Table II).

The horizontal shift (*x*-shift) parameter can be associated with thermal activation energy.^[17] The *x*-shift value is lower for Mix 4 at temperatures below 70°C. Above this temperature, the values of *x*-shift are lower for Mix 3 sample instead. The change in behavior occurs in the temperature interval of the glass transition temperature (*T_g*) of the PA phase. This indicates that the presence of oxazoline groups makes the sample more sensitive to changes in the PA phase state. The effect can be the consequence of better compatibilization efficiency. Mix 5 sample has the lowest values of *x*-shift within the whole temperature range, which is in accordance with the higher deformation in time.

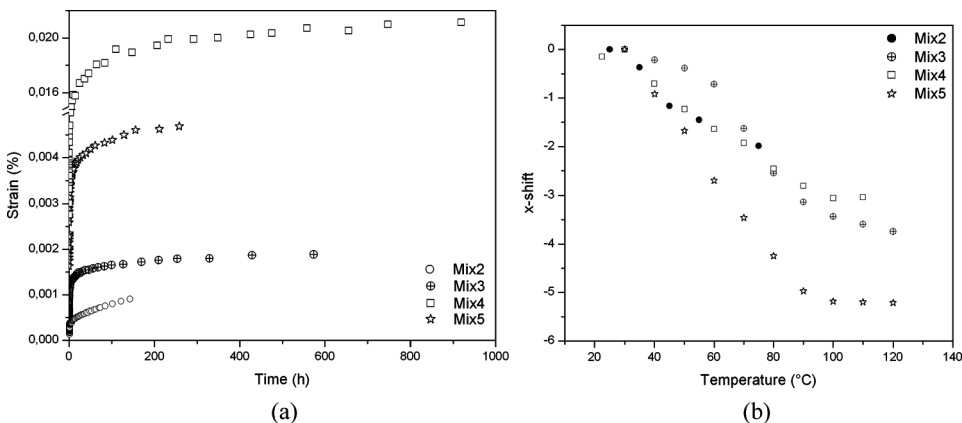


Figure 3. TTS results for Mix 2–5 samples: (a) creep TTS, (b) *x*-shift factors.

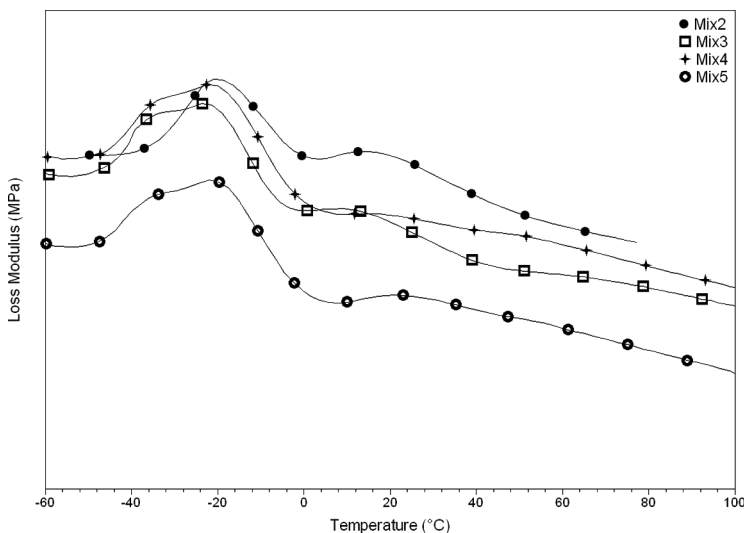


Figure 4. Loss modulus curves for non-compatible and compatible samples.

Correlation with Other Characterization Methods

The hypothesis of a higher interaction of Mix 3 with the PA phase can be corroborated by dynamic mechanical analysis (DMA) curves. The graphic presented in Figure 4 shows a shift in T_g peaks. The non-compatible sample (Mix 2) shows two loss modulus peaks. The first one, at -20°C , is related to the NBR phase of the blend. The second one, at 14°C , is related to the PA6 phase. It is interesting to note that the compatibilization generates an “NBR phase second peak” at lower temperatures. This peak is related to the compatibilizer formed “in situ.” The compatibilization process also changes the PA6 peak shape, decreasing its intensity and broadening it. The width of the peaks, however, is hard to differentiate by the naked eye. Thus the full width at half maxima (fwhm) of the peaks was calculated, and the values are shown in Table III. It can be noticed that all peaks are broader than those of the non-compatible blend. Mix 3 has a T_g peak for the PA phase broader than that of other samples, indicating higher interaction between phases.^[18–20] This interaction would be greatly affected by the mobility of PA phase macromolecules. Above T_g , the molecular mobility increases, decreasing the capacity of compatibilizer phase formed in situ to interact with the PA phase.

Table III. Physicochemical and mechanical properties of compatible samples

	fwhm	Density ($\pm 0.030\text{ g/cm}^3$)	Residual mass of extraction in toluene ($\pm 3\%$)	Tension strength		
				σ (MPa)	ε (%)	E (MPa)
Mix 2	19	1.036	100	15.92 ± 1.24	162 ± 39	212 ± 54
Mix 3	27	1.747	100	13.60 ± 0.30	201 ± 11	234 ± 27
Mix 4	23	0.999	91	12.09 ± 1.77	210 ± 19	276 ± 80
Mix 5	24	1.019	89	12.20 ± 0.80	163 ± 10	306 ± 53

Table III also shows the values of density, residual mass in toluene extraction, and tensile strength of compatibilized samples. Only Mix 3 shows a significant difference in density. This fact can be a consequence of better compatibilization effect or cross-linking efficiency. Toluene is a selective solvent for non-cross-linked NBR. The higher value of residual mass for Mix 3 sample confirms the higher efficiency of the cross-linking process. The residual mass for Mix 4 and Mix 5 is lower than that of the non-compatibilized sample, which corroborates the hypothesis of compatibilizer influence in the cross-linking system cited above.

Since the influence of the oxazoline group in the cross-linking system was excluded by the selective extraction, the lower recoverable compliance for Mix 3 should be correlated to other factors. Sailer and Handge^[21] comment that two opposite effects must be considered in the strain recovery of compatibilized blends. Smaller domains, obtained by the compatibilization process, will stretch less, leading to lower recovery. On the other hand, the increase of compatibilizer content in the interphase of the domain of the same size leads to an increase of recoverable strain. Other authors comment that compatibilization decreases the kinetics of recovery, and the effect is more pronounced when the difference of viscosities of the components is high, as in the discussed case.^[22]

SEM images (Figure 5) were obtained for Mix 2 and Mix 3. The images confirm the better domain dispersion in the compatibilized blend. The PA6 phase appears in the image as the brighter regions. The size of NBR domain changes from approximately 10 μm in the non-compatibilized blend to approximately 4 μm in the compatibilized blend. According to the discussion above, this may be the first factor for recovery decrease. However, the strain resistance demonstrated by the creep compliance is comparable for Mix 3 and Mix 4, indicating that these samples could have similar morphology. In this case, the effects in Mix 3 should be more complex. The oxazoline group shows greater improvement in density and tensile elongation, indicating better interfacial adhesion efficiency. The slowdown of compatibilization in recovery kinetics can explain the similar behavior of Mix 3 and Mix 5. The best compatibilized blend will recover deformation at slower rates. So, in the same time interval, the change in compatibilized blend makes the strain profiles of the two samples appear very similar. This hypothesis can be corroborated by the lower slope value in the master curve of Mix 3 TTS data.

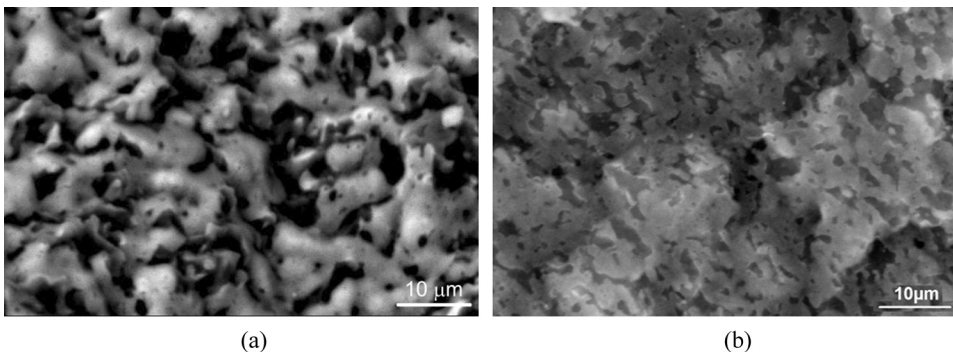


Figure 5. SEM images of (a) Mix 2 and (b) Mix 3 samples.

CONCLUSION

Our work demonstrates that creep test can be a good parameter for evaluating the influence of additives and compatibilization system efficiency in the final properties of TPV material, with good correspondence with other characterizations, like tensile strength, density, and morphology. EVAMA increases the dimensional stability of films. Oxazoline compatibilization has the best conjunction of results, showing good efficiency in increasing strain resistance and low interference in the cross-linking system. The strain recovery results show some incoherence, which was correlated with slower recovery kinetics. The creep test shows itself a fast, easy, and low-cost way to evaluate the TPV performance under conditions similar to a final application, being influenced by all aspects studied by other techniques.

REFERENCES

1. Mehrabzadeh, M., and R. P. Buford. 1996. Effect of crosslinking on polyamide 11/butadiene-acrylonitrile copolymer blends. *J. Appl. Polym. Sci.* 64 (8): 1605–1611.
2. Mehrabzadeh, M., and N. Delfan. 2000. Thermoplastic elastomers of butadiene-acrylonitrile copolymer and polyamide. VI. Dynamic crosslinking by different systems. *J. Appl. Polym. Sci.* 77 (9): 2057–2066.
3. Gessler, A. M., and W. H. Haslett, Jr. 1962. U.S. Patent 3037954.
4. Coran, A. Y., and R. Patel. 1980. Rubber-thermoplastic compositions. Part II. NBR-nylon thermoplastic elastomeric compositions. *Rubber Chem. Technol.* 53 (4): 781–794.
5. Chowhury, R., M. S. Banerji, and K. Shivakumar. 2006. Development of acrylonitrile-butadiene (NBR)/polyamide thermoplastic elastomeric compositions: Effect of carboxylation in the NBR phase. *J. Appl. Polym. Sci.* 100 (2): 1008–1012.
6. Gomes, A. C. O., B. G. Soares, M. G. Oliveira, M. F. L. Oliveira, and C. M. Paranhos. 2009. PA6/NBR blends: Improvement of processability and mechanical properties. *e-Polymers* 106.
7. Bicerano, J. 2002. *Prediction of Polymer Properties*, 3rd ed., ch. 11, (electronic version). New York: Marcel Dekker, pp. 78–82.
8. Kolarik, J., and A. Pegoretti. 2008. Proposal of the Boltzmann-like superposition principle for nonlinear tensile creep of thermoplastics. *Polym. Test.* 27 (5): 596–606.
9. Menard, K. P. 2001. *Dynamic Mechanical Analysis: A Practical Introduction*, ch. 3, Boca Raton, Fla.: CRC Press, p. 39.
10. Osamnaiye, G. J., and K. P. Adewale. 2001. Creep and recovery of EPDM elastomer using a modified sandwich rheometer. *Polym. Test.* 20 (4): 363–370.
11. Yang, J., Z. Zhang, A. K. Schlarb, and K. Friedrich. 2006. On the characterization of tensile creep resistance of polyamide 66 nanocomposites. Part I. Experimental results and general discussions. *Polymer* 47 (5): 2791–2810.
12. El Fray, M., and V. Altstadt. 2003. Fatigue behaviour of multiblock thermoplastic elastomers. 2. Dynamic creep of poly(aliphatic/aromatic-ester) copolymers. *Polymer* 44 (16): 4643–4650.
13. Almeida, M. S. M., B. G. Soares, and P. I. C. Guimarães. 2003. Utilization of NBR modified with 2-oxazoline groups in NBR/EVA blends. *Polim. Ciênc. Tecnol.* 13 (2): 119–124. (in Portuguese)
14. Rocha, L. A. C., R. H. Schuster, M. M. Jacob, and D. Samios. 2004. Study of chemical modification of SBR and BR-like polydienes. *Polim. Ciênc. Tecnol.* 14 (5): 318–321. (in Portuguese)

15. Roguet, E., S. Castagnet, and J. C. Grandidier. 2007. Mechanical features of the rubbery amorphous phase in tension and torsion in a semi-crystalline polymer. *Mech. Mater.* 39 (4): 380–391.
16. Rangaraj, S. V., and L. V. Smith. 1999. The nonlinearly viscoelastic response of a wood-thermoplastic composite. *Mech. Time-Dep. Mater.* 3 (2): 125–139.
17. Le, H. H., Th. Lüpke, T. Pham, and H.-J. Radusch. 2003. Time dependent deformation behavior of thermoplastic elastomers. *Polymer* 44 (16): 4589–4597.
18. Fornes, T. D., and D. R. Paul. 2003. Crystallization behavior of nylon 6 nanocomposites. *Polymer* 44 (14): 3945–3961.
19. Chang, M. C. O., D. A. Thomas, and L. H. Sperling. 1987. Characterization of the area under loss modulus and tan delta-temperature curves: Acrylic polymers and their sequential interpenetrating polymer networks. *J. Appl. Polym. Sci.* 34 (1): 409–422.
20. Lin, M. S., and S. T. Lee. 1997. Mechanical behavior of fully and semi-interpenetrating polymer networks based on epoxy and acrylics. *Polymer* 38 (1): 53–58.
21. Sailer, C., and U. A. Handge. 2008. Reactive blending of polyamide 6 and styrene–acrylonitrile copolymer: Influence of blend composition and compatibilizer concentration on morphology and rheology. *Macromolecules* 41 (12): 4258–4267.
22. Wang, J., and S. Velankar. 2006. Strain recovery of model immiscible blends: Effects of added compatibilizer. *Rheol. Acta* 45 (5): 741–753.