

Study on Nanocomposite Thermoplastic Elastomer Gels

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Introduction

Block copolymers are represent an interesting class of soft polymeric materials, which are produced by covalently linking two or more contiguous linear sequences (blocks) of chemically dissimilar species [1-2]. A common feature of block copolymers is that they can form a variety of self-assembled nanoscale ordered structure, which depends primarily on molecular composition, thermodynamically incompatibility of blocks and monomer of asymmetry. Block copolymers have a number of unique properties resulting from their morphological features. Because of these properties block copolymers have been used in a wide range of applications, for example, thermoplastic elastomer for impact modification, compatibilization and pressure-driven adhesion. One of the most highly investigated copolymer families explored is the commercially available poly[styrene-*b*-ethylene-co-butylene-*b*-styrene] (SEBS) triblock copolymer, which are employed in a diverse range of contemporary technologies. The ability of the SEBS to establish bridges between micelles serve as physical crosslinks sites and the copolymer/solvents solution behaves as physical gels. Since the formation of the micelles is a thermoreversible process, these TPE gels have a unique network behavior providing high elasticity. The temperature where it shows rubber like behavior can be easily adjusted by changing the polymer concentration. Numerous significant researches have been done in understanding the structural morphologies [3-4], viscoelastic and thermal properties [5-10] of these systems in extender oils and *n*-octane. The purpose of the study is to generate nanocomposite thermoplastic elastomer gels consisting of both organic and nanofiller interpenetrating networks with enhance properties. The linear viscoelastic properties of nanocomposites TPE gels were taken for study and investigated as a function of temperature and stress relaxation time. Sol-gel transition and mechanical properties of nanocomposite TPE gels were studied. X-ray was also performed.

Experimental

Poly(styrene-*b*-(ethylene-co-butylene-*b*-styrene), with styrene/rubber ratio of 29/71, number molecular weight of 9,000 and polydispersity of 1.03 and white oil with molecular weight of 500 were used in this study. Different types of nanofiller materials such as graphite were used. The nanocomposite TPE gels were prepared similar to the procedure elsewhere [11]. The ration of white oil to the SEBS was 0.67 and 4 with different amounts of nanofiller materials. The dynamic rheological measurements were conducted on a Rheometric Mechanical Spectrometer (RMS) Stresstech HR model, Rheologica Instruments, USA operated with 25 mm parallel plate geometry and a 1.5 or 2.5 mm gap heights. The tensile strength and elongation at break for ratio of 4 were performed on a Lloyd LR10K tensile testing machine (Farehan Hamsphire, UK) while TPE gels with ratio of 0.67 in a Tensometer 2000 (South Korea). The crosshead speed was 50 mm/min with a load cell of 100 N and a

gauge length of 20 mm. The X-ray diffraction data were taken using a D8 Discover with GADDS, Burker SXS (Germany).

Results and Discussion

One of the most highly investigated copolymer families explored in this area consists of poly[styrene-*b*-ethylene-co-butylene-*b*-styrene] (SEBS) triblock copolymer, which are employed in a diverse range of contemporary technologies. An illustrative transmission electron (TEM) image of a TPE gel composed of 10% SEBS triblock copolymer in 90wt% (EB-selective) aliphatic mineral oil [13] and verifies the micellar morphology anticipated from complimentary small-angle scattering results. A shortcoming of TPE gels on the basis of the SEBS triblock copolymer is an inherently low modulus and a relatively low maximum operating temperature identified as the temperature at which the gel network no longer supports an applied load and the solution flows as the modulus decreases abruptly. Addition of graphite in TPE gels in both ratios of oil/SEBS shows that both moduli (G' & G'') increase slightly with increasing nanofiller content. In all gels, it show G' exceed G'' as a function of temperature. It seems that addition of nanofiller has no significant effect on the sol-gel transition. In X-ray diffraction results that d -value of graphite in TPE gels shifted. Whereas the tensile strength increases as well as the elongation at break.

Conclusion

Addition of different types of nanofiller to a micellar SEBS/oil gels at different amount of oil serves to reinforce the gel as evidenced by an increase in G' . This increase reflects the formation of a secondary network that reinforces the primary network formed by the gel. It was also found that mechanical properties increase at lower nanofiller concentration but tends to decrease when the paraffin oil/SEBS ratio is lower. The sol-gel transition is the same for all nanocomposite TPE gels. At ambient temperature, the nanocomposite TPE gels are more elastic characteristics, i.e loss (G'') is much lower storage modulus (G') indicating physical network being present.

References

- [1] Hashimoto, T, Legge, N.R. Holden, G., Schroeder, H.E (Eds) Thermoplastic Elastomer, 1987 (chapter 12).
- [2] Hamley, I.W., Development in Block Copolymer Science and Technology, Wiley Hoboken, NY 2004.
- [3] Flosenzier, L.S. and Torkelson, J.M., *Macromolecules*, **1992**, 25, 735.
- [4] Kleppinger, R., Reynders, K., Mischenko, N., Overbergh, N., Koch, M.H.J., Mortensen, K, and Reynaers, H., *Macromolecules*, **1997**, 30, 7008.
- [5] Mischenko, N, Reynders, K., Koch, M.H.J., Mortensen, K, Pedersen, J.S. Fontaine, F., Graulus, R., Reynaers, H., *Macromolecules*, **1995**, 28, 2054
- [6] Laurer, J.H., Mulling, J.F., Khan, R.J., Spontak, S.A., Lin, J.S. and Bukovnik J., *Polym. Sci. Part B*, **1998**, 14, 2513
- [7] Soenen, H, Liskova A., Reynaers K., Berghmans, H., Winter, H.H. and Overbergh, N., *Polymer*, **1997**, 38, 22, 5661.
- [8] Quintana, J.R. Diaz, E. Katime, *Macromolecules*, **1997**, 30, 3507
- [9] Kim, J.K, Paglicawan, Lee, S.H, Maridass B., *Journal of Elastomers and Plastics*, in press.
- [10] Kim, J.K, Paglicawan, Maridass B, *Macromolecular Research*, in press.