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Enhancement of rheological and mechanical properties of bitumen using styrene acrylonitrile copolymer

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ABSTRACT: In this research, styrene acrylonitrile copolymer as a novel additive is used to modify rheological, mechanical and thermal properties of the base bitumen 70 penetration grade. Styrene acrylonitrile copolymer combines the rigidity of polystyrene with the hardness and thermal resistance of polyacrylonitrile to enhance viscoelastic property of the bitumen. To investigate the performance of the proposed mixture, shear complex module, phase angle, penetration, softening point, and reversibility of prepared samples are measured at different additive content and compared with the base bitumen. The results show that softening point of the base and modified samples are 49–86°C, respectively. The rheological properties of the base bitumen and modified samples are measured by a dynamic shear rheometer (DSR). The phase angle as elasticity measure decreases from 55° to 35° in the modified bitumen compared to the base bitumen. Generally, the experimental results showed that styrene acrylonitrile copolymer makes bitumen to be more stable at high temperatures and more flexible at low temperatures. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41875.

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INTRODUCTION

Bitumen as a mixture of hydrocarbons is a black, amorphous and viscoelastic material that is found in different forms, such as natural bitumen, rock asphalt, tar, and petroleum bitumen. The chemistry of bitumen is very complex, so the properties of bitumen are closely related to the source and the processing method. Bitumen is widely used as a binder for granular materials in the construction of road, highways, and runways due to thermoplastic and reversible property. Since bitumen is a deformable material and forms a continuous matrix in asphalt, it controls the final properties of the asphalt.[1] In the recent years, because of increasing demand for road building materials, researchers have focused on production of improved bitumen.[2] There is a narrow temperature range in which base bitumen exhibits suitable rheological and mechanical property.[3,4] There are two general methods to modify characteristics of the base bitumen. The first method is adding plastomer components, such as polyolefin, to the bitumen so that the viscous property of the bitumen is improved. Plastomer components are used to decrease permanent deformation or rutting in bitumen. The limited improvement in elasticity and potential storage stability of the plastomer-modified bitumen restrict the application of these materials as a bitumen modifier. The second method is increasing the elastomer components, which directly influences the elastic property of bitumen.

Since 1980, polymer modified bitumen has been utilized to decrease bitumen susceptibility at high and low temperatures, reduce damages caused by humidity and reduction in common failure mechanisms as rutting and cracking.[5] Many researchers have focused on polymeric modification of bitumen to reduce processing cost and enhance mechanical, rheological, and thermal characteristics of the conventional bitumen. In the past, styrene-butadiene-styrene (SBS) and ethylene-vinyl acetate copolymers were used to improve the performance of base bitumen.[6,7] Zhu *et al.*[8] presented a good review about advances and challenges in the field of bitumen polymer modification during the last 40 years. Bahia[9] investigated the effect of polymer modification using scanning electron microscope images. The experimental results showed that the modified asphalt presents the better binder-aggregate adhesion. Polymer modification affects the binder's flexibility as well as increasing the fatigue resistance and viscosity of the asphalt binder, which improves the tensile and the compressive strengths of the mixtures. Da Silva *et al.*[10] showed that modified bitumen improves the performance of asphalt in terms of resistance to permanent deformation and fatigue cracking. Sengoz and Isikyakar[11] investigated the performance of modified bitumen containing SBS copolymer. The results indicated that SBS improves the penetration, softening point and the mechanical properties of the base bitumen. It was concluded that the polymer particles are homogenously dispersed in a continuous bitumen phase at low polymer content, and continuous polymer phase can be observed at high polymer content. Çelik and Atiş[12] noted that polymer based modifiers improve continuity of bitumen and showed that the board temperature and elasticity have a significant effect on performance of modified bitumen. Pérez-Lepe *et al.*[13] proved that high-density polyethylene modified bitumen shows a remarkable enhancement in the mechanical properties compared to those modified with low-density polyethylene, ethylene propylene diene-monomer and SBS. Yu *et al.*[14] showed that the adding MMT to SBS modified bitumen increases softening point and viscosity. Proposed modified bitumen composites exhibited higher complex modulus, lower phase angle, and higher rutting resistance. Markanday *et al.*[15] used EVA–organoclay nanocomposite to enhance rheological property of the base bitumen. Munera and Ossa investigated the effect of polyethylene wax, SBS copolymer, and crumb rubber on the properties of bitumen 80 penetration grade. The optimum content of modifier in the base bitumen was found using an experimental design procedure.[16]

In this research, the styrene acrylonitrile copolymer is used to improve the thermal, mechanical and rheological properties of bitumen 70 penetration grade produced in Bandar Abbas Refinery (Iran). Styrene acrylonitrile copolymer is a rigid and transparent plastic produced by the copolymerization of styrene and acrylonitrile. It combines the clarity and rigidity of polystyrene with the hardness, strength, and heat and solvent resistance of polyacrylonitrile. In this study, to investigate the performance of the prepared bitumen, fatigue resistance, phase angle degree, penetration, reversibility, and softening point of samples are compared with the base bitumen. The rheological properties of the base bitumen and modified samples are measured by a dynamic shear rheometer (DSR).

MATERIALS AND TEST METHOD

Bitumen 70 penetration grade, provided from Bandar Abbas Refinery in Iran, was used as the base material. At the first, conventional bitumen was heated up to 160°C and styrene acrylonitrile copolymer was added to the bitumen samples at different weight ratios of 3%, 5%, 7%, and 10%. Then, the prepared sample was placed in a mixer with rotation speed of 500 rpm for 30 min, followed 60 min at 4000 rpm to create a homogeneous mixture. During operation, sample's top was covered with a nonstick paper. Then four small steel sheets with thickness of 1–2 mm were placed on the nonstick paper. Then bitumen was heated and put between steel sheets. The upper steel plate was pressed to obtain a uniform thickness, and then bitumen plates were solidified at 10°C. Finally, fatigue resistance, rheological properties, penetration and phase angle degree of samples were measured to compare the performance of modified bitumen with the blank sample. The penetration degree represents the consistency and stability of bitumen, which is defined as the number of penetration units of standard vertical needle in a bitumen sample at a specified temperature and time. ASTM-D5 standard test was used to measure penetration degree of the samples. The softening point, ductility (elasticity) and elastic recovery of samples were measured based on ASTM D-36, D-113 and D-6084 test methods, respectively. The viscoelastic behavior of the base and modified samples were measured by a DSR at a wide range of temperature, stress rate, and frequency. The DSR is a common tool used to study the rheology of binders.

Table I. Specifications of Basic and Modified Bitumen

No	SAN %	Penetration (dmm)	Reversibility	Softening point (°C)	Elasticity (cm)
1	0	63	13	49	100
2	3	58	45	51.4	100
3	5	52	49	53	100
4	7	44	96	64	100
5	10	43	99	86	83
Error	–	1	1%	0.5	1%

RESULTS AND DISCUSSION

In this section, the rheological properties and fatigue resistance test results are presented for the modified and blank samples. The testing framework is selected to study effect of styrene acrylonitrile copolymer on bitumen properties at various additive weight percents and different temperatures and loading frequencies. Table I represents the experimental results for penetration, reversibility, softening point, and elasticity of the modified and blank samples. Although penetration and reversibility are improved increasing additive concentration, difference between penetration and reversibility in Samples 4 and 5 are negligible. These changes are linearly dependent on the polymer weight percent in the samples, particularly in samples with lower polymer content. In the bitumen industry, the penetration test is used to assess bitumen consistency. The experimental results show that the increasing styrene acrylonitrile copolymer in the base bitumen makes the modified bitumen harder and more consistent and it improves the rutting resistance of the mixture. Softening point as a main criterion to investigate the performance of bitumen is improved and higher softening point can be appeared in the sample containing 10% additive. Although no noticeable change is seen in the softening point at low additive concentrations, at higher additive concentrations change is easily noticed. Softening point indicates the tendency of material to flow at high temperature. Therefore, higher softening point results in higher resistance of the prepared modified bitumen to flow at high temperature. The modified bitumen samples present a reduced permeability and higher softening point and elastic recovery that indicate an improvement in the bitumen stiffness and flexibility.

The rheological properties of the base and prepared modified samples are measured by a DSR. In DSR test method, the sample is placed between two parallel plates, one standing and one oscillatory. The oscillating plate is rotated and procedure involves determining the complex shear modulus and phase angle of binders over a wide range of stress rates, loading frequencies and temperatures. Measured complex shear modulus and phase angle are used to characterize both viscous and elastic behavior of the prepared bitumen. Figure 1 presents the complex shear modules of the blank and modified bitumen

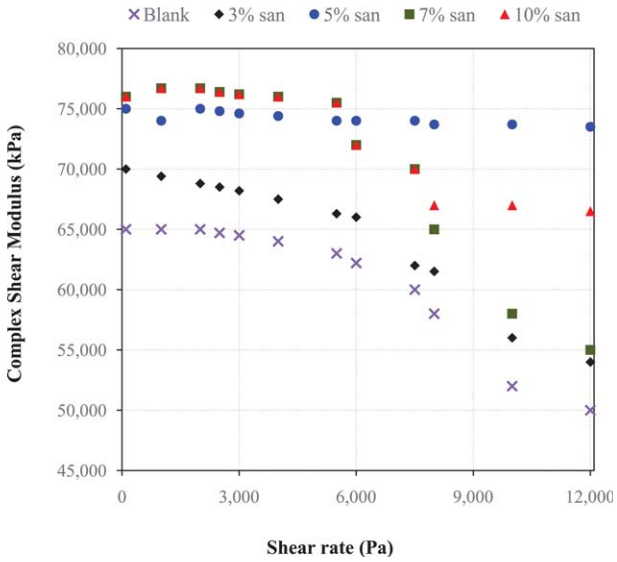

Figure 1. Complex shear modulus versus stress in modified sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

samples against applied stress rate at different additive concentrations. The complex shear module is defined as the ratio of maximum shear stress to maximum strain and represents the material resistance to deformation when subjected to shear loading. Tests are performed at 30°C with a shear stress range 100–12,000 Pa. Mixtures containing stiffer binders, higher amounts of fines, and lower voids present higher complex shear modulus values. In general, mixtures with higher complex shear modulus at a specific temperature exhibit lower permanent deformation compared to the similar mixtures with lower shear modulus. This figure shows that increasing additive concentration enhances complex shear modules at low shear rates and the sample containing 10% additive shows a higher shear modulus and resistance to deformation. The samples present different shear modulus behaviors at high stress rates. The shear modulus decreases at high stress rates and the minimum change is appeared in sample containing 5% styrene acrylonitrile copolymer, which is justified by the strength of bonds in bitumen structure. Generally, increasing polymer content in the modified bitumen can cause heterogeneity. Thus, sample containing 5% additive exhibits lower permanent deformation compared to other samples and presents proper property. In addition, the linear range of complex shear modulus lies between 100 Pa and 5000 Pa, except sample containing 5% additive that lies between 100 Pa and 12,000 Pa.

The frequency sweep test is used to obtain complex shear modulus and phase angle degree. In this test, the range of loading frequency was selected based on the traffic condition. The highest loading frequency was considered to simulate highway traffic speeds, and the lowest one was considered to simulate loading in slow moving traffic conditions. Figure 2 depicts the complex shear modulus at various loading frequencies for modified bitumen samples. The complex shear modulus has similar profile in all samples. Generally, increasing the amount of styrene acrylonitrile copolymer in the modified samples reduces the fraction of low molecular weight components and creates a three dimensional polymeric network structure between polymer and base bitumen, and therefore rheological properties of the modified bitumen are improved. Increasing the concentration of styrene acrylonitrile mass increases the complex shear modulus at a specific frequency, particularly in the samples contains 7% and 10% additive. At low additive content samples, 3% and 5%, the shear modulus of the modified binders remains close to that of the base bitumen due to low network structure between polymer and base bitumen. The complex shear modulus is improved about 50% and 29.3% in sample containing 10% additive compared to base bitumen at low and high frequency loads, respectively.

Figure 3 shows the phase angle degree of the modified bitumen samples versus frequency. The complex shear modulus and the phase angle degree are defined as the resistance of binder to shear deformation in the linear viscoelastic region. In other word, the phase angle is the phase lag between the applied shear stress and the shear strain. A purely viscous liquid and an ideal elastic solid demonstrate phase angle degree of 90° and 0°, respectively. Bitumen composition strongly influences the rheological property of bitumen such as phase angle and shear complex modulus.[17] The molecular compounds in bitumen are divided into polar and nonpolar material. Polar compounds create elastic properties in bitumen, while nonpolar compounds such as the maltene fractions result viscous behavior. The experimental results indicate that samples show viscous property at low loading frequencies and behave like an elastic solid at high loading frequencies. At low frequency, the dynamic storage modulus [$G^*\cos(\delta)$] decreases and samples behave as a viscous fluid. As frequency increases, the dynamic loss modulus [$G^*\sin(\delta)$] decreases and the samples behave like an elastic solid. Therefore, samples with higher loss modulus present ability to resist deformation, and prepared samples with higher

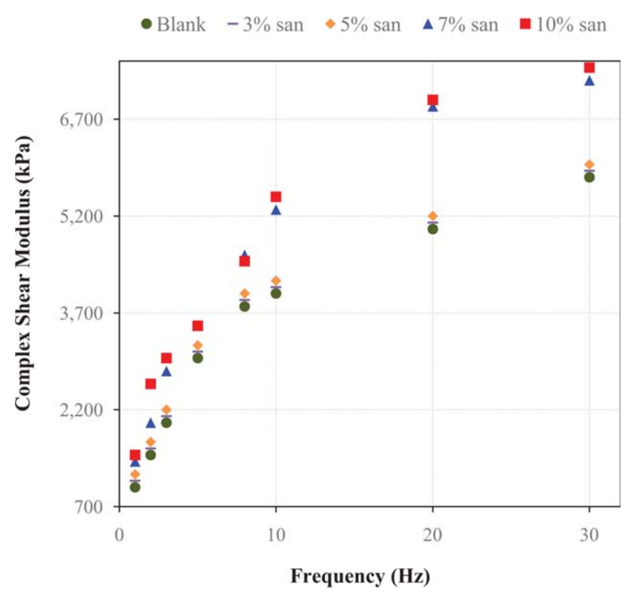

Figure 2. Complex shear module versus loading frequency. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

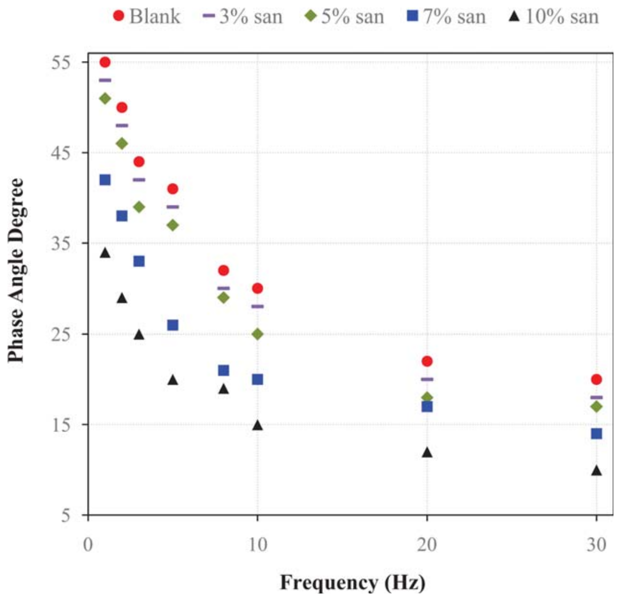

Figure 3. Phase angle of modified bitumen versus loading frequency. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

storage modulus have greater elasticity against deformation at prescribed frequency. In the base bitumen, dynamic loss modulus and dynamic storage modulus are 818.98 kPa and 574 kPa at the lowest frequency, while approach toward 1982.8 kPa and 5450.6 kPa at the highest frequency. Increasing the copolymer content in the bitumen causes a significant phase angle drop, which influence directly binder elastic recovery properties and helps bitumen to reshape to its initial state after removing the stress. In the sample contains 10% additive, dynamic loss modulus and dynamic storage modulus are 726.98 kPa and 1243.8 kPa at the lowest frequency and approach toward 1301.78 kPa and 7386.2 kPa at the highest frequency. The sample contains 10% additive shows a predominantly elastic behavior in all frequencies. Since styrene acrylonitrile copolymer is a high molecular weight compound, a three dimensional polymeric network structure is created between polymer and base bitumen that enhances bitumen elasticity. Styrene acrylonitrile copolymer combines the rigidity of polystyrene with the hardness, strength, and thermal resistance of polyacrylonitrile to enhance viscoelastic property of the base bitumen. Generally, increasing complex modulus and decreasing phase angle degree of the bitumen indicate higher resistance to deformation compared to the base bitumen and leads to produce hard and elastic bitumen.

The number of cycles to failure, as main criteria to investigate the fatigue failure of binders, occurs after the crack initiation point and before the crack propagation point. Figure 4 shows the phase angle degree versus number of required cycles to failure. It is clear that the number of load cycles increases when the phase angle decreases. The results show that there is a relationship between phase angle and the frequency of the applied mass, which leads to destruction of bitumen. Phase angles in the base bitumen and samples containing 5% and 10% styrene acrylonitrile copolymer was about 40.5°, 36.5°, and 34° and the number of cycles are 1900, 2400, and 2700, respectively. The results show that sample containing 10% additive has the lowest phase angle and highest number of required cycles to failure compared to the base bitumen. This figure illustrates that there is a little difference between the rheological properties of base bitumen and modified bitumen containing 3% styrene acrylonitrile copolymer.

Figure 5 presents results of complex shear modulus against test temperature. Test temperature has a significant effect on complex shear modulus in all samples and the increasing test temperature decreases the complex shear modulus. Although there is negligible difference between the rheological properties of samples containing 3% and 5% copolymer at high temperatures, as the modifier content increases the rheological properties are improved particularly in samples containing 7% and 10% additive. In this study, a significant improvement in the rheological property of the base bitumen is observed when the copolymer content is increased from 5% to 7%. The results show that as temperature increases, complex shear modulus of samples decrease and approach toward a constant value. Generally, the sample containing 10% styrene acrylonitrile has a greater resistance to deformation at high temperatures compared to the base bitumen. The styrene acrylonitrile copolymer influences the bitumen property by creating an interconnecting matrix between long chain molecules and the bitumen. This matrix modifies the stability and physical properties of the bitumen and increases the complex shear modulus and elasticity, which results greater stiffness at higher temperature and high flexibility at low temperatures.

The results shows that sample containing 5% additive presents a steady performance over the considered shear rates while other samples experience a dramatic decrease in shear modulus especially at high shear rates. However, the sample containing 10% additive has the lowest phase angle, highest number of required

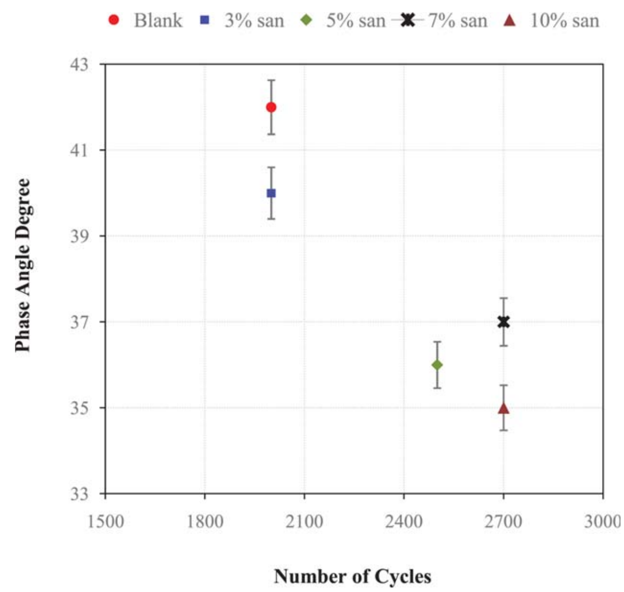

Figure 4. Phase angle of modified bitumen versus number of required cycles to failure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

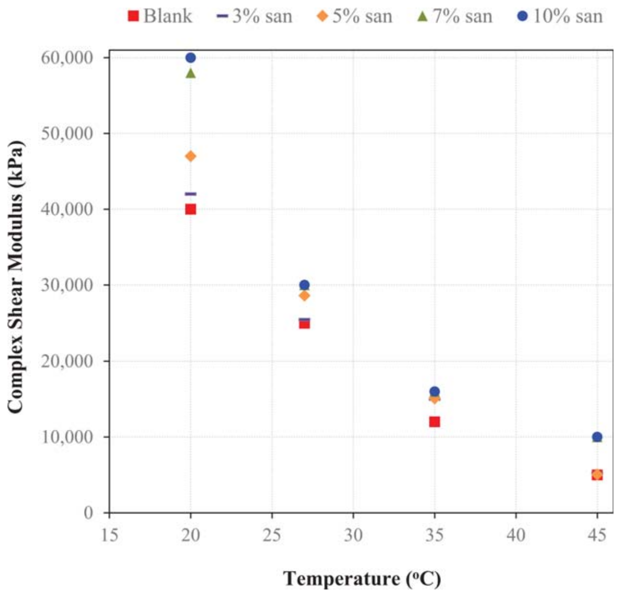

Figure 5. Complex shear modulus of modified bitumen versus temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cycles to failure and complex shear modulus versus frequency compared to the base bitumen, which results higher elasticity and resistance to deformation. Therefore, sample contains 10% additive can be selected as the best one among all samples.

CONCLUSIONS

The main goal of this research was to characterize the mechanical, rheological, and thermal properties of the modified bitumen by styrene acrylonitrile copolymer. Softening point, reversibility and penetration in sample containing 10% styrene acrylonitrile was optimum and desirable. The experimental results showed that the modified bitumen is more elastic, and phase angle decreases about 38.2% and 50% in the modified bitumen containing 10% additive compared to the base bitumen at low and high frequency loads, respectively. The experimental results showed that complex shear modulus is improved about 50% and 29.3% in sample containing 10% additive compared to base bitumen at low and high frequency loads, respectively. In the sample containing 10% additive, dynamic loss modulus and dynamic storage modulus were 726.9 kPa and 1243.8 kPa at the lowest frequency and approached toward 1301.7 kPa and 7386.2 kPa at the highest frequency. Phase angle in the base bitumen and sample containing 10% additive were about 40.5° and 34°, and number of required cycles were obtained 1900 and 2700, respectively. Bitumen contains 10% styrene acrylonitrile presented a greater resistance against deformation at high temperatures compared to base bitumen. Therefore, the sample contains 10% modifiers could be selected as the best one among all samples due to higher elasticity and resistance to deformation.

REFERENCES

1. Adedeji, A.; Grunfelder, T.; Bates, F. S.; Macosko, C. W.; Stroup-Gardiner, M.; Newcomb, D. E. *Polym. Eng. Sci.* **1994**, *36*, 1707.
2. Isacsson, U.; Zeng, H. Y. *Constr. Build. Mater.* **1977**, *11*, 83.
3. Ait-Kadi, A.; Brahimi, B.; Bousmina, M. *Polym. Eng. Sci.* **1996**, *36*, 1724.
4. Xiaohu, L.; Ulf, I. *J. Appl. Polym. Sci.* **2000**, *76*, 1811.
5. Morrison, G. R.; Hedmark, H. *J. Mater. Sci.* **1994**, *272*, 375.
6. Polacco, G.; Stastna, J.; Biondi, D.; Zanzotto, L. *Curr. Opi. Coll. Int. Sci.* **2006**, *11*, 230.
7. Airey, G. D. *Const. Build. Mater.* **2002**, *16*, 473.
8. Zhu, J.; Birgisson, B.; Kringos, N. *Eur. Polym. J.* **2014**, *54*, 18.
9. Bahia, H. A. Critical Evaluation of Asphalt Modification Using Strategic Highway Research Program Concepts; Transportation Research Record: Washington, DC, **1995**.
10. Da Silva, L. S.; De Camargo, M. M.; Vignol, L. D. A.; Cardozo, N. S. M. *J. Mater. Sci.* **2004**, *39*, 539.
11. Sengoz, B.; Isikyakar, G. *J. Hazard. Mater.* **2008**, *150*, 424.
12. Çelik, O. N.; Atiş, C. D. *Construction and Building Materials* **2008**, *22*, 1143.
13. Pérez-Lepe, A.; Martínez-Boza, F. J.; Gallegos, C. *J. Appl. Polym. Sci.* **2007**, *103*, 1166.
14. Yu, J.; Wang, L.; Zeng, X.; Wu, S.; Li, B. *Polym. Eng. Sci.* **2007**, *47*, 1289.
15. Markanday, S. S.; Stastna, J.; Polacco, G.; Filippi, S.; Kazatchkov, L.; Zanzotto, L. *J. Appl. Polym. Sci.* **2010**, *118*, 557.
16. Munera, J. C.; Ossa, E. A. *Mater. Des.* **2014**, *62*, 91.
17. Wen, G.; Zhang, Y.; Zhang, Y. X. *Polym. Eng. Sci.* **2002**, *42*, 1070.