

Effect of Filler Loading on the Mechanical Properties of Crosslinked 1,2,3-Triazole Polymers

Alan R. Katritzky,¹ Rajeev Sakhuja,¹ Longchuan Huang,¹ Reena Gyanda,¹ Ling Wang,² David Carnaby Jackson,³ David A. Ciaramitaro,⁴ Clifford D. Bedford,⁴ Randolph S. Duran²

¹Department of Chemistry, Center for Heterocyclic Compounds, University of Florida, Florida, Gainesville 32611-7200

²Department of Chemistry, Polymer Research Laboratory, University of Florida, Gainesville, Florida, 32611-7200

³Department of Material Science and Engineering, University of Florida, Florida, Gainesville 32611-7200

⁴Office of Naval Research, Virginia, Arlington 22203

Received 24 November 2009; accepted 11 February 2010

DOI 10.1002/app.32257

Published online 14 May 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effect of filler loading on the mechanical properties of crosslinked triazole polymers obtained by polymerization of E300 dipropiolate (**1**) with diazide (**2**) obtained from tetraethylene glycol using tetraacetylene functionalized crosslinker (**3**) was studied systematically. Aluminum (10–14 μm) was used as the primary filler during the formulations; the effect of secondary fillers such as aluminum (<75 μm), NaCl (45–50 and 83–105 μm) was studied with the increase in the total filler loading. The modulus of the aluminum-filled crosslinked triazole polymers increases with the increase in the filler content while using either particle sized aluminum powder. The use of Al (particle size <75 μm) and NaCl (particle size 45–50 μm and 83–105 μm) as secondary or

additional fillers while using aluminum (10–14 μm) as the main filler, has a diminishing effect on the modulus and strain of the crosslinked triazole polymers. Triazole polymers described herein have the ability to wet and adhere to large quantities of these inorganic salts and thus maintain mechanical properties of the composite comparable to typical polyurethane elastomeric matrices, regardless of the chemistry of the particulate filler, which imparts an important and necessary binder characteristic for energetic composites. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 121–127, 2010

Key words: mechanical properties; strain; modulus; fillers; composites

INTRODUCTION

1,2,3-Triazole-polymers prepared by the utilization of “Click Chemistry”^{1–3} are novel binders for high-energy explosive and propellant materials, with advantages in terms of lower tensile stress and modulus compared to the polyurethanes used extensively as rocket propellant binders.^{4–6} Reed’s group synthesized crosslinked triazoles polymer as energetic binders with improved mechanical properties and stability.⁶ Crosslinker effects on the mechanical properties of conventional rubbers have been studied for many years and are well understood.⁷ We have recently studied the effect of crosslinker type and concentration on the mechanical properties of unfilled and filled crosslinked 1,2,3-triazole polymers.^{8,9}

The inclusion of particulate fillers in polymeric materials is an established industrial practice which typically is performed to enhance polymer properties such as modulus, fracture resistance and tough-

ness while reducing the overall component cost.¹⁰ A composite material is more rigid than a pure polymer and the addition of metal particles to polymer during injection reduces the internal stresses in injection-molded components.¹¹ Metal-filled polymers are widely used for electromagnetic interference shields, their advantages over metals being lighter weight and lower cost; specific applications include easy discharge of static electricity, heat conduction, electrical heating and conversion of mechanical signals to electrical signals.¹¹

The mechanical properties of a composite material depend strongly on particle-matrix interface adhesion, particle size and particle loading.¹² Landon et al. studied the importance of adhesion between filler and the matrix phase in explaining the mechanical behavior of the composite.¹⁰ The dependence of filler particle size on mechanical properties have also been studied on carbonate-filled PP models.¹³ Bhattacharyya et al. examined the effect of particle size ratios of the polymer to metal particles on the mechanical properties of PVC-Cu composites.¹⁴ Significant improvements in the mechanical properties were achieved by incorporating a low weight percent of inorganic exfoliated clay minerals consisting of layered silicate into polymer matrices.^{15–17}

The effects of using different weight percentages of fillers such as carbon black, silica, aluminum

Correspondence to: A. R. Katritzky (Katritzky@chem.ufl.edu).

Contract grant sponsor: Office of Naval Research; contract grant number: N00014-06-1-0211.

oxide, zirconium oxide,¹⁸ metal or metal clad fillers,¹⁹ carbon nanotubes,²⁰ glass-ceramic,²¹ soda lime glass particles,²² and sodium sulfate,²³ on the thermal and mechanical properties of elastomers have been reported in detail by several groups. Aluminum powder is a commonly used filler that improves mechanical, electrical and thermal properties of polythiourethane-modified epoxy adhesives,²⁴ low density polyethylene (LDPE)²⁵ and high density polyethylenes (HDPE) composites,¹¹ natural rubber (NR) composites,²⁶ polymethylmethacrylate (PMMA)²⁷ and ethylene-propylene-diene terpolymer (EPDM) composites.²⁸

The fillers in energetic composites are primarily added for performance enhancement, although a strong, tough composite is required nonetheless. The polymeric binder component must tolerate a large proportion of energetic filler ingredients and still be processible by cast-cure production methods, curable at relatively low temperatures and inert to internal and external degradation reactions over long periods of ambient storage.

A large proportion of the filler in a solid rocket motor will be an inorganic oxidizing salt, typically ammonium perchlorate (AP). The surface interaction between the binder polymer and an inorganic oxidizer can range from a weak association, easily released under stress which can weaken the composite, to a strong association which may include a slight solubility and disproportionation of the oxidizer. This condition can degrade the formulation's aging behavior, i.e., the mechanical properties and combustion characteristics over time. A binder system must possess the proper compatibility with such ingredients to maintain this tensile strength over a service life that may span decades.

Our earlier studies on triazole polymers emphasized that with the use of 43 wt % aluminum filler in a crosslinked triazole polymerization process, the polymer has good processability and better modulus as compared to unfilled triazole polymers.⁸ The effect of fillers loading on the mechanical properties of triazole polymers has not been studied yet. Ozkar systematically studied the effect of the use of auxiliary fillers in addition to the main filler, for improving the thermal, rheological and tensile properties of polyurethane elastomers.¹⁸ However, no such studies on the use of mixed fillers on the mechanical properties of triazole polymers have been conducted to date. Herein, we report the results of our studies on the effect of use of two different particle sizes of aluminum fillers and of mixtures of different particle sized aluminum and sodium chloride fillers, on the mechanical properties of crosslinked triazole polymers. These experiments are intended to evaluate the degree to which the triazole-cured binder candidates can tolerate increases in the loadings of vari-

ous solids (especially that of the sodium chloride, the model for inorganic oxidizing salts in general) and still maintain good stress and a reasonable strain capability.

EXPERIMENTAL

General

Commercially obtained reagents were used without further purification. E300 dipropiolate (**1**), diazide (**2**) derived from tetra ethylene glycol and the tetra-functional crosslinker 3-(propioloyloxy)-2,2-bis[(propioloyloxy)methyl]propyl propiolate (**3**) were prepared following reported procedures.^{4,8} In view of the stringent stoichiometry requirements for step polymerization, the monomers were systematically dried by azeotropic distillation and lyophilization. The uniaxial test specimen was a standard microtensile dog bone with dimensions of 0.88" × 0.19" × 0.13".²⁹ Strain (percentage elongation at break) and elastic modulus (Young's modulus) were measured by an Instron universal tensile testing machine (model number 4301) with a strain rate of 50 mm/min.. Aluminum (10–14 μm and <75 μm) were purchased from Aldrich. Anhydrous sodium chloride was ground and passed through a series of sieves of different pore sizes to obtain NaCl in 45–50 μm and 83–105 μm monodisperse particle sizes. Each data entry in the Tables I–VIII is an average of at least three measurements.

General procedures for preparation of crosslinked triazole polymers

E300 Dipropiolate (**1**) and crosslinker (**3**) were weighed into an aluminum pan, and stirred until homogeneous. The time for dissolving the crosslinker varied from 15 to 30 min. Diazide (**2**) was added with stirring to give a homogeneous mixture. The reactions were carried on a total scale of 2 g (comprising the three reactants for each dogbone sample) in aluminum pans by taking 100 mol % of **1** and calculating the concentrations of **2** and the crosslinker **3**, keeping the overall end group stoichiometric ratios 1 : 1. (Scheme 1) The filler (or mixture of

TABLE I
Comparison of the Strain and Modulus of Unfilled and Filled Crosslinked Triazole Polymers

Entry	Crosslinker concentration (mol %)	Filler wt % (Al: 10–14 μm)	Strain (%)	Modulus (MPa)
1	6	0	683	0.04
2	6	43	441	0.27
3	8	0	338	0.17
4	8	43	171	0.90

TABLE II
Effect of Filler Loading (Al: 10–14 μm) on Strain and Modulus of Crosslinked Triazole Polymers

Entry	Crosslinker concentration (mol %)	Filler wt % (Al: 10–14 μm)	Strain (%)	Modulus (MPa)
1	8	34.2	205.4	0.64
2	8	43.0	171.0	0.90
3	8	58.1	97.5	2.33
4	8	67.5	48.3	5.06
5	8	71.7	29.6	11.31
6	8	74.2	18.7	13.68

fillers) was then added to the homogeneous mixture and mixed uniformly by hand for about 45 min. The mixtures were cast into a dogbone molds, degassed under vacuum at room temperature for 15 min and then cured in an oven at 55°C for 72 h. The dogbone samples were carefully removed from the molds. After cooling, they were tested at ambient temperature using a Universal Tensile Test Machine with a 22 lb load cell and 50 mm/min test speed.

RESULTS AND DISCUSSION

Our earlier studies on the development of triazole polymers as potential rocket propellant binders emphasized that with the use of 43 wt % aluminum filler in a crosslinked triazole polymerization process, the polymer had good processability and a better modulus compared to unfilled triazole polymers⁸. In continuation of this work, we now report the effects of filler type, content and concentration on the mechanical properties of the crosslinked triazole polymers obtained by mixing E300 dipropiolate **1**, tetrafunctionalized crosslinker **3** and diazide **2** obtained from tetra ethylene glycol in stoichiometric ratios.

To select an optimum percentage of the crosslinker that could be used and set constant for the synthesis of the filled crosslinked triazole polymers throughout our present studies, some preliminary experiments based on our earlier experience in the

TABLE III
Effect of Filler Loading (Al: < 75 μm) on Strain and Modulus of Crosslinked Triazole Polymers

Entry	Crosslinker concentration (mol %)	Filler wt % (Al: < 75 μm)	Strain (%)	Modulus (MPa)
1	8	34.2	108.1	0.88
2	8	43.0	93.7	1.68
3	8	58.1	41.0	4.70
4	8	67.5	33.1	9.72
5	8	71.7	10.7	25.39
6	8	74.2	9.2	32.07

TABLE IV
Effect of Filler Loading (NaCl: 45–50 μm) on Strain and Modulus of Mechanical Properties of Crosslinked Triazole Polymers

Entry	Crosslinker concentration (mol %)	Filler wt % (NaCl: 45–50 μm)	Strain (%)	Modulus (MPa)
1	8	34.2	237.6	0.38
2	8	43.0	208.9	0.44
3	8	58.0	60.4	1.49
4	8	67.5	41.3	1.65

preparation of crosslinked triazole polymers were required. We used 4 mol % of the crosslinker with freshly prepared monomers: the polymers were obtained by the reaction of E300 dipropiolate **1** and diazide **2** with 4 mol % crosslinker **3**, keeping the end group stoichiometry 1 : 1 and the samples cured both without filler and with 43 wt % aluminum filler (10–14 μm particle size). Upon curing, these samples were tacky and soft and testing via Instron Machine was difficult. However, these results were somewhat different from those obtained in our earlier studies. This may be explained by the use of a different batch of starting monomer, more specifically E300 dipropiolate, since E300 polyol itself is not a single compound. Our further triazole polymerization reactions were carried using 6 and 8 mol % of the crosslinker both with and without 43 wt % of the aluminum (10–14 μm). The mechanical properties of the cured, crosslinked triazole polymers are summarized in Table I.

The physical nature of the polymers and the modulus and strain values suggested that 8 mol % crosslinker should be used to study the effect of different filler loadings on the mechanical properties of the resulting triazole polymers.

The content of the aluminium filler with particle sizes of 10–14 μm and <75 μm was systematically increased separately (Scheme 1) from 34.18 to 74.14 wt % (Tables II and III) resulting in two separate sets of gumstock samples, which were cured in standard dogbone molds at 55°C for 72 h. The cured polymers were tested using the Instron tensile testing machine.

TABLE V
Effect of Filler Loading (NaCl: 83–105 μm) on Strain and Modulus of Crosslinked Triazole Polymers

Entry	Crosslinker concentration (mol %)	Filler wt % (NaCl: 83–105 μm)	Strain (%)	Modulus (MPa)
1	8	34.2	180.3	0.27
2	8	43.0	128.8	0.33
3	8	58.0	95.8	1.09
4	8	67.5	56.0	1.48

TABLE VI
Effect of Mixed Filler Loading (Mixture of Two Different Particle Sized Aluminum)
on Strain and Modulus of Crosslinked Triazole Polymers

Entry	Crosslinker concentration (mol %)	Filler wt % (Al: < 75 μm + Al: 10–14 μm) (1:1)	Strain (%)	Modulus (MPa)
1	8	34.2	100.8	0.78
2	8	43.0	91.2	1.47
3	8	58.0	63.6	3.51
4	8	67.5	36.2	4.70
5	8	71.7	21.3	7.21
6	8	74.2	19.4	9.37

Figures 1 and 2 show the variation of the modulus and strain values of these two separate sets of filled gumstock samples with the increase in filler loading.

In general, it was concluded that the modulus of the aluminum-filled crosslinked triazole polymers increases with the increase in the filler content while using either of the two particle sizes of aluminum powder. The value of the modulus was increased from 0.64 to 13.68 MPa as aluminum of particle size 10–14 μm was increased from 34.2 to 74.2 wt % of the binder; 74.2 wt % being maximum percentage of filler that resulted in polymers which were processable. Beyond this point the binder does not completely wet all the filler particles resulting in highly viscous, nonuniform material difficult to cast into molds before curing. The same result was inferred from the mechanical data generated by using <75 μm aluminum powder. The addition of rigid particles to a polymeric matrix improves the modulus since the rigidity of the inorganic fillers is generally higher than that of organic polymers.¹² Anuar et al. observed similar trends with the use of aluminum on NR and ethylene-propylene-diene-terpolymer (EPDM) composites.²⁸

However, there is an increase in the value of the modulus while shifting from 10–14 μm to <75 μm particle size for the same filler content (for example 0.64 to 0.88 MPa; 0.90 to 1.68 MPa). For lower weight percentages of filler used, the modulus is almost independent of the particle size,¹² but the difference in

their modulus values increases with the increase in filler loading.

Similar observations may be inferred from the strain data obtained by the mechanical testing of these two sets of filled crosslinked triazole polymers. (Tables I and II, Fig. 2). The strain of the filled crosslinked triazole polymers decreases with the increase in the filler content as expected. However, the strain values are reduced by almost half by switching from 10 – 14 μm to <75 μm aluminum powder (for example 205.4 to 108.1%; 18.7 to 9.2; for 34.2 and 74.2 wt % of the filler used respectively). Given that the modulus values of both filled systems are similar, it is likely that the strain differences are mainly due to the larger filler particles providing more nucleation sites for failure. Perhaps, the smaller particles resist dewetting of the binder better than the larger particles until a concentration of solids is reached where the binder is unable to fully cover either size of particle.

We also explored the use of two different particle sizes of NaCl powder as fillers. Tables IV and V shows the variation of the modulus and strain of the filled crosslinked triazole polymers synthesized using NaCl as the main filler with the increase in the content and particle size of NaCl (Scheme 1). The samples were somewhat sticky and nonuniform, and the mechanical testing was thus difficult. However, the trend for the modulus and the strain with increase in the filler content was similar to that obtained in the case of aluminum, although the values of the modulus are quite low. Thus it made

TABLE VII
Effect of Mixed Filler Loading (Mixture of Aluminum and NaCl) on Strain and
Modulus of Crosslinked Triazole Polymers

Entry	Crosslinker concentration (mol %)	Filler wt % (Al: 10–14 μm + NaCl: 45–50 μm) (1:1)	Strain (%)	Modulus (MPa)
1	8	34.2	79.8	0.73
2	8	43.0	57.7	0.91
3	8	58.0	40.9	1.90
4	8	67.5	34.8	3.52
5	8	71.7	26.7	4.68

TABLE VIII
Effect of Mixed Filler Loading (Mixture of Aluminum and NaCl) on Strain and Modulus of Crosslinked Triazole Polymers

Entry	Crosslinker concentration (mol %)	Filler wt % (Al: 10–14 μm + NaCl: 83–105 μm) (1 : 1)	Strain (%)	Modulus (MPa)
1	8	34.2	68.6	0.71
2	8	43.0	55.4	0.95
3	8	58.0	44.9	1.32
4	8	67.5	35.7	3.59
5	8	71.7	24.8	4.45

sense to study the effect of NaCl as a secondary/additional filler keeping aluminum as the main filler.

It appears that addition of NaCl increases strain capability but only at the expense of lower modulus values, which in turn may be due to poorer adhesion between the binder and filler.

Further, the effect of the use of the additional or secondary fillers such as NaCl of particle size 45–50 μm and 83–105 μm and aluminium of particle size <75 μm along of aluminium of particle size 10–14 μm as the main filler was compared against the increase in the total filler content. The mixture of fillers was systematically increased separately (Scheme 1) from 34.2 to 74.2 wt % (Tables II and III) resulting in three separate sets of gumstock samples (Tables VI–VIII), which were cured and mechanically tested as previously described.

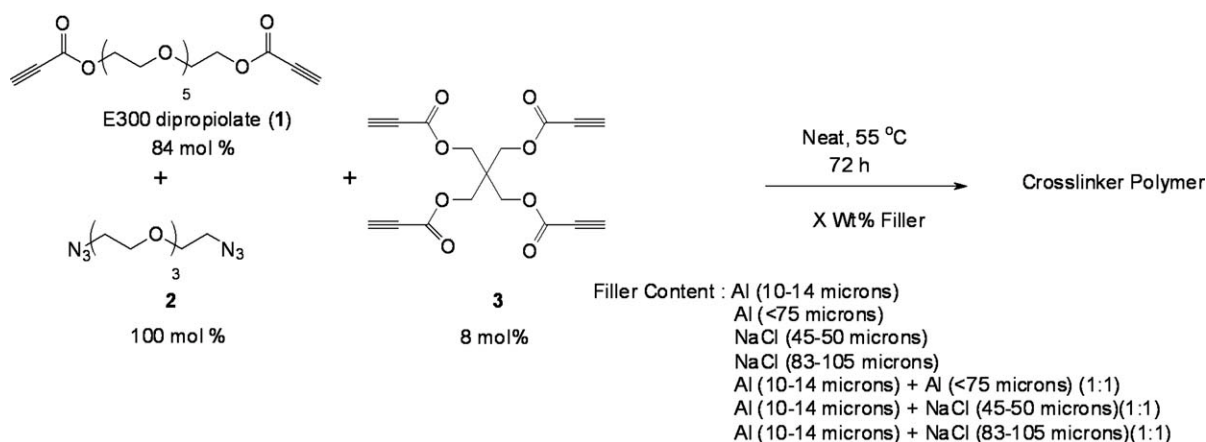
Figures 3 and 4 compare the results on the use of additional fillers together with the main filler in the ratio 1 : 1 on the mechanical properties of cross-linked triazole polymers. These data sets include equal weights of mixed fillers of two different particle sized aluminum powders and aluminum with two different particle sized NaCl powders. In general, the use of Al (particle size <75 μm) and NaCl (particle size 45–50 μm and 83–105 μm) as secondary or additional fillers while using aluminum (10–14

μm) as the main filler, has a diminishing effect on both the modulus and strain of the crosslinked triazole polymers. Perhaps the effect of the larger aluminum particles in reducing strain capability is overriding the effect of the smaller aluminum.

Also, 74.2 wt % was not achievable while using mixed fillers of aluminum and NaCl due to non uniformity and brittleness of the resultant filled triazole polymers. On comparing the strain and the modulus values of the triazole polymers obtained by using mixtures of aluminum and two different particle sized NaCl fillers, little difference in their values was observed. These data suggest that the mixed systems show lower stain values regardless of particle size or type.

CONCLUSION

Overall, this study suggests that, as expected, the aluminum fillers give rise to better mechanical properties than the inorganic materials (sodium chloride). The data suggest that the smaller metal particles act to produce enhanced mechanical properties whereas the mixed metal/inorganic filler simply produced samples of intermediate mechanical properties over the compositions tested. Triazole polymers described here have the ability to wet and adhere to large quantities of these inorganic salts and thus maintain



Scheme 1 Preparation of the crosslinked triazole polymers with different filler loading.

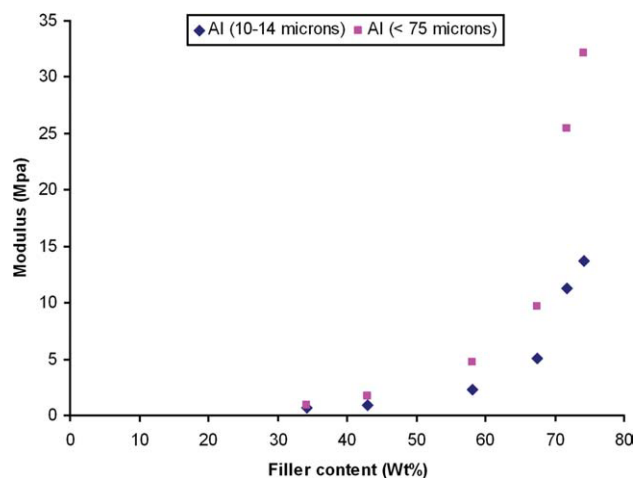


Figure 1 Effect of filler loading on modulus of crosslinked triazole polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the tensile strength of the composite, regardless of the chemistry of the oxidizer, which imparts them an important and necessary binder characteristic for energetic composites.

SYNOPSIS

1,2,3-Triazole-polymers prepared by the utilization of “Click Chemistry” are novel binders for high-energy explosive and propellant materials. The mechanical properties of a composite material depend strongly on particle-matrix interface adhesion, particle size and particle loading. The effects of using different weight percentages of fillers such as carbon black, silica, aluminum oxide, zirconium oxide, metal or metal clad fillers, carbon nanotubes, glass-

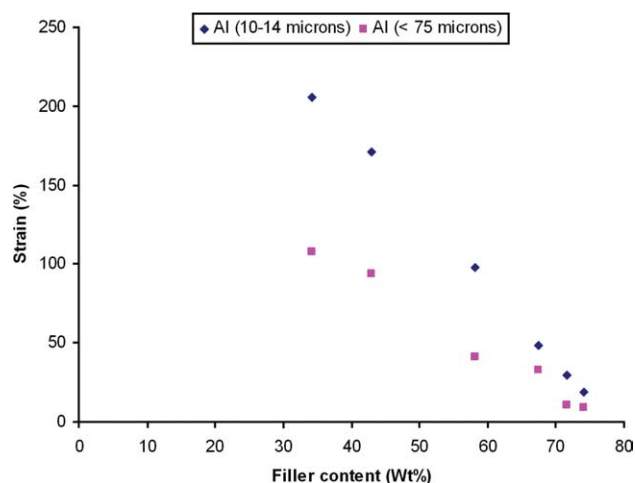


Figure 2 Effect of filler loading on strain of crosslinked triazole polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

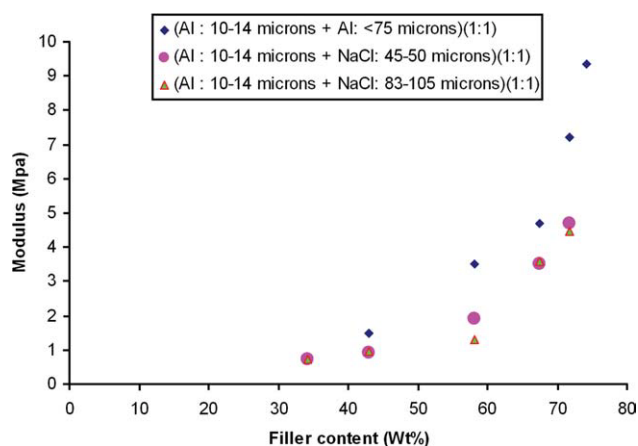


Figure 3 Effect of mixed filler loading on modulus of crosslinked triazole polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ceramic, soda lime glass particles, and sodium sulfate on the thermal and mechanical properties of elastomers have been reported in detail by several groups. Aluminum powder is a commonly used filler that improves mechanical, electrical and thermal properties of polythiourethane-modified epoxy adhesives, LDPE and HDPE composites, NR composites, PMMA and EPDM composites. Our earlier studies on triazole polymers emphasised that with the use of 43 wt % aluminum filler in a crosslinked triazole polymerization process, the polymer has good processability and better modulus as compared to unfilled triazole polymers. The effect of fillers loading on the mechanical properties of triazole polymers has not been studied yet. Ozkar systematically studied the effect of the use of auxiliary fillers in addition to the main filler, for improving the thermal, rheological and tensile properties of polyurethane elastomers. However, no such studies on the

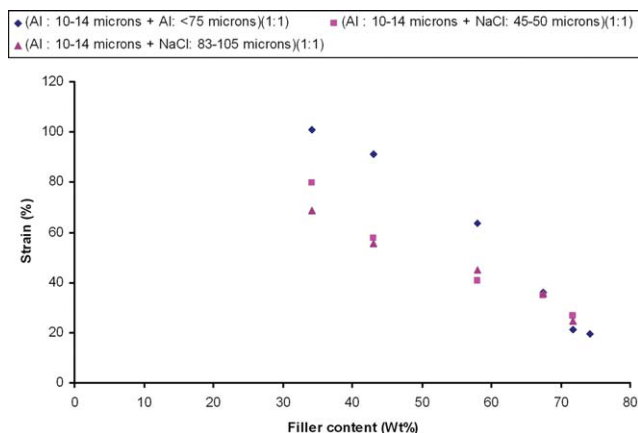


Figure 4 Effect of mixed filler loading on strain of crosslinked triazole polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

use of mixed fillers on the mechanical properties of triazole polymers have been conducted to date. Herein, we report the results of our studies on the effect of use of two different particle sized aluminum fillers and mixtures of different particle sized aluminum and sodium chloride fillers, on the mechanical properties of crosslinked triazole polymers.

The modulus of the aluminum-filled crosslinked triazole polymers increases with the increase in the filler content while using either particle sized aluminum powder. The use of Al (particle size <75 μm) and NaCl (particle size 45–50 μm and 83–105 μm) as secondary or additional fillers while using aluminum (10–14 μm) as the main filler, has a diminishing effect on the modulus and strain of the crosslinked triazole polymers. Triazole polymers described herein have the ability to wet and adhere to large quantities of these inorganic salts and thus maintain mechanical properties of the composite comparable to typical polyurethane elastomeric matrices, regardless of the chemistry of the oxidizer, which imparts an important and necessary binder characteristic for energetic composites.

References

1. Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew Chem Int Ed* 2001, 40, 2004.
2. Binder, W. H.; Sachsenhofer, R. *Macromol Rapid Commun* 2007, 28, 15.
3. Lutz, J.-F. *Angew Chem Int Ed* 2007, 46, 1018.
4. Katritzky, A. R.; Meher, N. K.; Hanci, S.; Gyanda, R.; Tala, S. R.; Mathai, S.; Duran, R. S.; Bernard, S.; Sabri, F.; Singh, S. K.; Doskocz, J.; Ciaramitaro, D. A. *J Polym Sci Part A: Polym Chem* 2008, 46, 238.
5. Thompson, C. M.; Hergenrother, P. M. *High Perform Polym* 2001, 13, 313.
6. Reed, R. U.S. Pat. 6,103,029, 2000.
7. Fan, R.; Zhang, Y.; Huang, C.; Zhang, Y.; Fan, Y.; Sun, K. *J Appl Polym Sci* 2001, 81, 710.
8. Wang, L.; Song, Y.; Gyanda, R.; Sakhuja, R.; Meher, N. K.; Hanci, S.; Gyanda, K.; Mathai, S.; Sabri, F.; Ciaramitaro, D. A.; Bedford, C. D.; Katritzky, A. R.; Duran, R. S. *J Appl Polym Sci* 2010, to appear.
9. Song, Y.; Wang, L.; Gyanda, R.; Sakhuja, R.; Cavallaro, M.; Jackson, D. C.; Meher, N. K.; Ciaramitaro, D. A.; Bedford, C. D.; Katritzky, A. R.; Duran, R. S. *J Appl Polym Sci* 2010, to appear.
10. Landon, G.; Lewis, G.; Boden, G. F. *J Mater Sci* 1977, 12, 1605.
11. Tavman, I. H. *J Appl Polym Sci* 1996, 62, 2161.
12. Fu, S. Y.; Feng, X. Q.; Lauke, B.; Mai, Y. W. *Compos Part B* 2008, 39, 933.
13. Adams, J. M. *Clay Miner* 1993, 28, 509.
14. Bhattacharyya, S. K.; Basu, S.; De, S. K. *J Mater Sci* 1978, 13, 2109.
15. Kim, M. H.; Park, C. I.; Choi, W. M.; Lee, J. W.; Lim, J. G.; Park, O. O.; Kim, J. M. *J Appl Polym Sci* 2004, 92, 2144.
16. Liu, L.; Qi, Z.; Zhu, X. *J Appl Polym Sci* 1999, 71, 1133.
17. Zhang, Y. H.; Wu, J. T.; Fu, S. Y.; Yang, S. Y.; Li, Y.; Fan, L.; Li, R. K. Y.; Li, L. F.; Yan, Q. *Polymer* 2004, 45, 7579.
18. Benli, S.; Yilmazer, Ü.; Pekel, F.; Özkaz, S. *J Appl Polym Sci* 1998, 68, 1057.
19. Hajmrlle, K.; Callen, B. W.; Mah, J. K. U.S. Pat. 0,113,531, 2003.
20. Liang, G. D.; Tjong, S. C. *Mater Chem Phys* 2006, 100, 132.
21. Juhasz, J. A.; Best, S. M.; Brooks, R.; Kawashita, M.; Miyata, N.; Kokubo, T.; Nakamura, T.; Bonfield, W. *Biomaterials* 2004, 25, 949.
22. Sumita, M.; Ookuma, T.; Miyasaka, K.; Ishikawa, K. *J Mater Sci* 1982, 17, 2869.
23. Vargo, R. D.; Kelley, F. N. *Rubber Chem Technol* 1991, 64, 181.
24. Strzelec, K.; Pospiech, P. *Prog Org Coat* 2008, 63, 133.
25. Dasture, M. D.; Kelkar, D. S. *J Appl Polym Sci* 2007, 106, 2436.
26. Anuar, J.; Mariatti, M.; Ismail, H. *Polym Plast Technol Eng* 2007, 46, 667.
27. Goyanes, S. N.; Marconi, J. D.; König, P. G.; Rubiolo, G. H.; Matteo, C. L.; Marzocca, A. J. *Polymer* 2001, 42, 5267.
28. Anuar, J.; Mariatti, M.; Ismail, H. *Polym Plast Technol Eng* 2007, 46, 1201.
29. Riser, D.; Hunter, J.; Rast, R. AIAA/SAE/ASME/ASEE 28th Joint Propulsion Conference and Exhibit; Nashville, TN, 1992, July 6–8.