Cross-Linked "Matrix-Free" Nanocomposites from Reactive Polymer−Silica Hybrid Nanoparticles

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Nanoparticles have been used to reinforce polymers for at least 150 years, beginning perhaps with the development of carbon black filled elastomers for the tire industry.[1] The incorporation of nanoparticles generally brings about significant improvements in a number of important polymer properties.[2,3] Silica nanoparticles dispersed homogeneously within polymer matrices, for example, have been reported to enhance mechanical properties[4,5] including modulus, flexural, tensile, and impact strength up to a silica content of about 2.5%.[6] As a result, fracture toughness[7] and thermal stability[8,9] were also improved.

More recently, the advent of strategies for the synthesis of nanoparticles[10] with unique photonic, magnetic, electrical, and catalytic properties[11] has brought excitement and promise for new nanoparticle applications in a broad range of emergent areas including sensors, optics, membranes, biology, medicine, and microelectronics. While these new properties and applications have garnered great interest, it has not been widely appreciated that these nanoparticles must generally be combined with some organic material, usually polymeric in nature, in order to realize macroscopic materials with useful properties.

The direct dispersion of nanoparticles within a polymer matrix, however, is a process prone to aggregation,[2,3] a phenomenon that cannot be readily overcome by more intensive mixing[12] and that negates many desired property enhancements. Much effort has therefore focused on the modification of nanoparticle−nanoparticle interactions to improve dispersion quality. For example, decorating the nanoparticle surface with a polymer brush screens particle−particle interactions and creates a polymer−inorganic hybrid that disperses more readily into a homopolymer matrix. Unfortunately, nanoparticle aggregation, a deleterious effect that negates many of the desirable nanocomposite properties, is only avoided when the brush molecular weight exceeds that of the polymer matrix, a condition that does not lead to optimal physical properties.[13−15]

We report herein a supramolecular building block approach for the preparation of a new family of nanocomposites that comprise nanoparticles cross-linked by polymer bridges but that do not require a polymer matrix. These "matrix-free" nanocomposites (MFNs) are not prone to the nanoparticle aggregation effects that plague conventional nanocomposites and hold promise to provide exceptionally high strength and toughness owing to the formation of covalent polymer bridges linking nanoparticles. Our novel modular approach is based upon the construction of complementary reactive supramolecular building blocks: nanoparticles decorated with heterobifunctional polymer brushes that provide reactive functionality at their periphery as depicted in

Figure 1. These hybrid building blocks are somewhat analogous to block copolymers, specifically star block copolymers, wherein covalent bonding between different polymer sequences of the block copolymer prevents the aggregation or phase separation that usually occurs in the physical blend of the corresponding two homopolymers. In a similar fashion, covalent bonding between the polymer and a nanoparticle can prevent nanoparticle aggregation in a MFN. In the present case, nanoparticles with covalently bound azide-terminated polymer brushes and nanoparticles with covalently bound alkyne-terminated polymer brushes constitute hybrid building blocks that are simply "clicked" together like molecular Legos or Tinker Toys to form cross-linked nanoparticle assemblies as shown in Figure 1. Reinforcement is provided by polymer bridges joining adjacent nanoparticles, yet aggregation is avoided because a polymer matrix is not employed. "Click" chemistry, specifically the 1,3-dipolar cycloaddition of alkyne and azide end groups to produce triazole cross-links,[16] is chosen as the curing chemistry because its quantitative and chemoselective nature allows nanoparticles to be decorated with virtually any polymer. Polymer brushes on the azide- and alkyne-functional supramolecular building blocks need not be the same polymer species (two different polymers are illustrated in Figure 1), and the nanoparticles may also differ in chemical nature (identical nanoparticles are shown).

MFNs offer unique gelation behavior because the supramolecular building blocks from which they are formed provide exceptionally high reactive functionality. Conventional gels, typically based on cross-linkers with a functionality of 3−4, require a reaction conversion in the range of 50−75% to reach the gel point.[17,18] The cross-linkers in MFNs, in contrast, are hybrid nanoparticles decorated with hundreds of end-functional polymer brushes, potentially lowering the conversion required for gelation to 1% or less and minimizing the formation of any sol fraction. While cross-linked nanoparticle assemblies have been prepared previously, e.g., by adding bifunctional cross-linkers
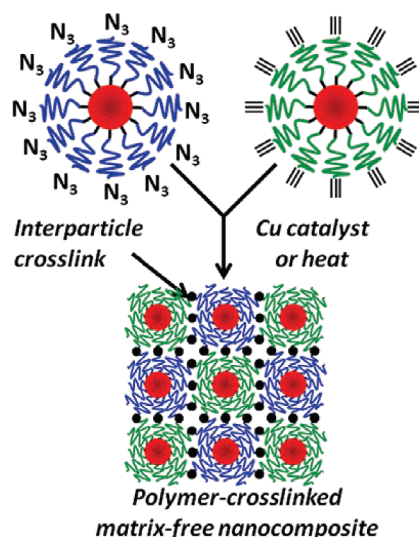

Figure 1. Schematic diagram showing the formation of a matrix-free nanocomposite from azide-functional and alkyne-functional polymer−hybrid nanoparticle building blocks. The red circles represent nanoparticles, and the black dots are triazole cross-links. The schematic illustrates the case where different polymers (a blue polymer and a green polymer) are used to prepare the two complementary building blocks.

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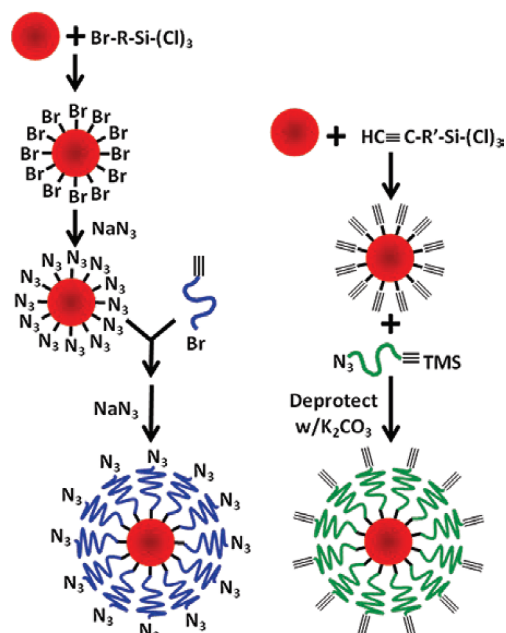
Figure 2. Synthetic route toward polymer−silica nanoparticle hybrids.

Figure 3. DRIFTS spectra of (a) bare silica, (b) azido−poly(styrene)−silica, (c) alkyne−poly(*tert*-butyl acrylate)−silica, and (d) nanocomposite.

and free radical initiators to graft organic−nanoparticle hybrids,[19−26] we are not aware of any previous investigation that has used reactive polymer−nanoparticle hybrids as cross-linkers as we do herein. This Communication focuses on the chemical aspects of MFN preparation; reports on their mechanical and physical properties will follow.

The detailed preparation procedure used to construct the required complementary supramolecular building blocks is given in Figure 2. Details of the synthetic methods employed are given in the Supporting Information. The first step is functionalizing silica nanoparticles with azide and alkyne groups by treatment with *o*-propargyloxy-*N*-triethoxysilylpropylurethane or 1-bromoundecyltrichlorosilane (followed by conversion to azide by reaction with NaN₃), respectively. Heterobifunctional polymers[27] are then covalently bound to the nanoparticles by the appropriate click reactions. Because heterobifunctional polymers are employed, there is no possibility of loop formation in the functional polymer brushes. As a proof of concept, we use different polymers to prepare two complementary azide and alkyne functional supramolecular building blocks: an azido−poly(styrene)−silica nanoparticle hybrid and an alkyne−poly(*tert*-butyl acrylate)−silica nanoparticle hybrid. Homopolymers of polystyrene and poly(*tert*-butyl acrylate) would normally be immiscible.

Matrix-free nanocomposites for infrared spectroscopy studies were prepared according to the following recipe: 50 mg of azido−poly(styrene)−silica nanoparticles, 50 mg of alkyne−(*tert*-butyl acrylate)−silica nanoparticles, and a stir bar were added to a 100 mL round-bottom flask under an inert atmosphere. 10 mL of dimethylformamide (DMF), 12 mg of Cu(I)Br, 5 mg of Na−L-ascorbate, 5 mg of tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA), and 50 μL of pentamethyldiethylenetriamine (PMDETA) were then added to the round-bottom flask, and the solution was stirred under an inert atmosphere at 80 °C for 24 h. After 24 h, the stirring was stopped, and the materials were heated in the round-bottom flask at 80 °C for an additional 24 h. At the end of the 48 h period a hybrid gel with a soft gel-like consistency had formed in the flask. *Because "click" reactions are chemoselective, the polymer grafting reaction and the MFN curing reaction are both insensitive to the chemical nature of the polymer, allowing any click functional polymers to be employed.*
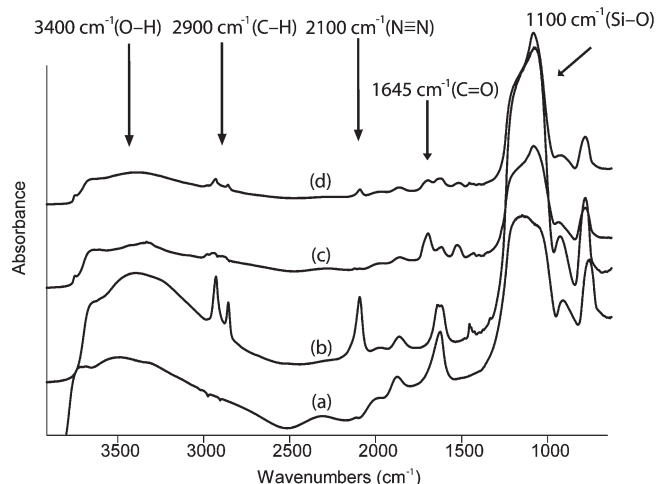
A polymer matrix is not required because all polymeric constituents are covalently bound to the nanoparticle surface before curing. The nanocomposites therefore can, strictly speaking, be considered "matrix-free".

The nanoparticle building blocks and their nanocomposites were characterized by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).[28] Their thermal and mechanical properties were investigated by thermogravimetric (TGA) and rheological analyses, respectively.

Figure 3 shows the results of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis of bare and modified silica nanoparticles. All spectra show a strong and broad absorbance band near 1100 cm^{-1} (Si−O) due to the silica nanoparticles. The azido−poly(styrene)−silica nanoparticle hybrids show an additional azide absorbance band at 2100 cm^{-1} (−N≡N), a signature that confirms successful transformation of the terminal bromine to azide pictured in Figure 2 (left).[29] The spectra for azido−poly(styrene)−silica and alkyne−poly(*tert*-butyl acrylate)−silica exhibit a band at 2900 cm^{-1} associated with the C−H stretching vibrations from organic portions of the surface-bound molecules. A doublet at 1485 cm^{-1} can be seen in the spectrum for azido−poly-(styrene)−silica due to the C=C aromatic bonds in polystyrene. A band at 1650 cm^{-1} is observed in the spectrum for alkyne−poly(*tert*-butyl acrylate)−silica which can be attributed to the C=O bond in the acrylate group. Curve d offers proof that azido−poly(styrene)−silica and alkyne−poly(*tert*-butyl acrylate)−silica nanoparticle building blocks have "clicked" together (i.e., cross-linked) to form the MFN as evidenced by the decrease in the azide peak intensity upon 1,2,3-triazole formation.

The amounts of polymer grafted to the silica nanoparticles were determined by TGA[30] analysis (TA Q50; scan rate of 10 °C/min; nitrogen atmosphere). Figure 4 shows TGA thermograms for several of the silica-based nanoparticles heated to 800 °C. For bare silica the observed weight loss of 5.33% can be attributed to the loss of water and to silanol group dehydroxylation.[31] The alkyne−silica, azide−silica, azido−poly(styrene)−silica, and alkyne−poly(*tert*-butyl acrylate)−silica nanoparticles lost 8.95%, 12.48%, 22.58%, and 23.23% of their weights, respectively. These results indicate that both the ligand modification and subsequent polymer modification steps proceeded as expected from Figure 2. Analysis of the weight loss for the polymer-modified nanoparticles indicates that their polymer grafting density is ∼0.1 polymer chains/nm².
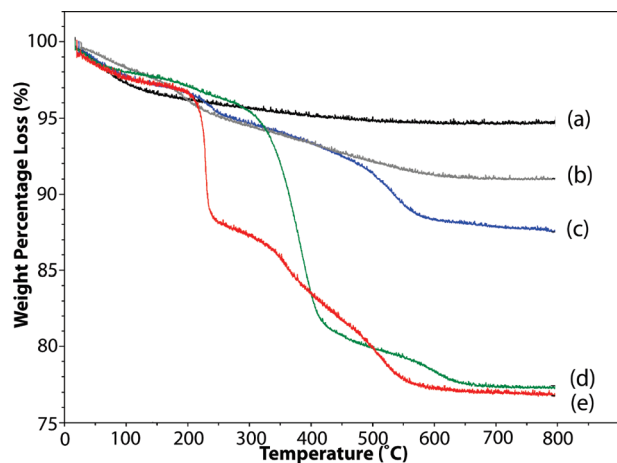
Figure 4. TGA degradation curves for (a) bare silica (black), (b) alkyne−silica (gray), (c) azide−silica (blue), (d) azido−poly(styrene)−silica (green), and (e) alkyne−poly(*tert*-butyl acrylate)−silica nanoparticles (red).

Figure 5. Curing of silica matrix-free nanocomposites: rheological determination of the gel time.

Silica nanoparticles modified with azide-terminated polystyrene brushes and silica nanoparticles modified with alkyne-terminated poly(*tert*-butyl acrylate) brushes were prepared according to the procedures described in Figure 2. 50 mg of each type of nanoparticle, 12 mg of Cu(I)Br, 5 mg of Na−L-ascorbate, 5 mg of TBTA, and 50 μL of PMDETA were codissolved in 1 mL of dimethylformamide solvent and subsequently loaded into a TA Instruments AR2000 rheometer with a 60 mm diameter steel parallel-plate geometry and a 25 μm gap. The results in Figure 5 were obtained by applying a 5% oscillatory strain at rate of 1 Hz to the material at a temperature of 80 °C to follow the curing reaction. In Figure 5, nonfunctional nanoparticles are the control group of nanoparticles without "click" functional groups on their surfaces or bare silica nanoparticles. The same amount of solvent and catalyst was used for the rheology of nonfunctional and functional nanoparticles. The crossover of G', storage modulus, and G'', loss modulus, at about 40 min indicates the gel point of the "click" functional nanoparticles.[32] The progress of the curing reaction was also monitored by DRIFTS as shown in Figure 3d. The absorbance of the azide stretch vibration at 2100 cm^{-1} decreases upon curing as a consequence of azide−alkyne click reactions that form triazole-linked polymer bridges between nanoparticles.

A distinct advantage of MFN's is that they can incorporate large amounts of nanoparticle that approach the close-packed limit. The silica MFNs described herein contain about 75 wt % silica, based upon the TGA analysis; however, the amount of polymer required can be vanishingly small. In principle, only three polymer brushes are required on each nanoparticle to produce a gel.

The MFNs prepared in this initial study have a shear modulus on the order of 0.1 MPa, about 1000 times that of the uncured hybrid nanoparticles. The modulus is quite low compared to reported values of Young's modulus for other silica nanocomposites (ca. 1 GPa for polypropylene−silica[33] and ca. 3 GPa for epoxy−silica[34]), suggesting that the click reaction conversion is low and that the network formed is far from complete. This result is not surprising considering that the complementary nanoparticles used were decorated with different, immiscible polymers and thus were not expected to be well mixed. In fact, we have shown herein that cross-linked nanocomposites can be obtained even in the worst case scenario, when complementary nanoparticles are decorated with immiscible polymer brushes. We expect the moduli to be much higher for complementary nanoparticles decorated with brushes comprising the same polymer; however,
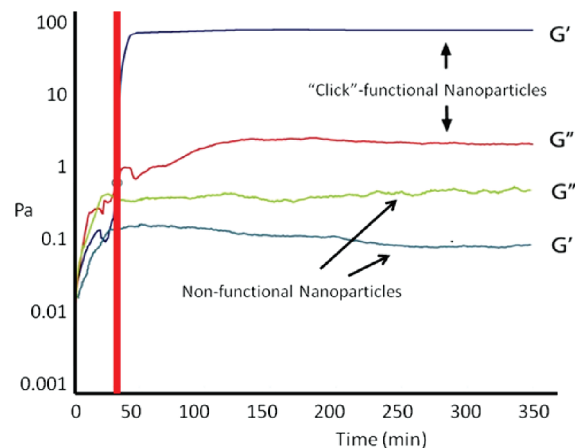
it is not obvious how high the attainable reaction conversion is for these systems or how it might depend on system parameters such as brush molecular weight, aerial density, or nanoparticle size. While sol fraction is essentially absent in these systems, an attractive bonus feature of MFNs, many of the functional groups will remain unreacted after gelation. This attribute, however, may be desirable as these functional groups could be used subsequently to decorate the gels with a variety of interesting side chain constituents such as peptides or sugars to expand the applicability of the gels, particularly in the biological and sensor arenas when water-soluble brushes are used to prepared nanoparticle cross-linked hydrogels. Finally, it is interesting to speculate how MFNs might be processed. While we use a small amount of solvent herein to prepare copper-catalyzed MFNs, it is possible to simply deposit mixtures of nanoparticles into a mold and affect a thermal cure at temperatures as low as 60 °C without copper catalyst, in a sense mimicking powder metallurgy methods of processing. Reports to follow will examine in detail how various molecular parameters affect the reaction conversion and how the mechanical and physical properties correlate with the associated network structure for this new family of nanocomposites.

In summary, we have successfully modified silica nanoparticles with reactive polymer brushes to present both azide and alkyne "click" functional groups at their peripheries. Infrared and rheological analyses document that a cross-linked matrix-free nanocomposite is formed when a mixture of the two complementary nanoparticles is cured by a copper-catalyzed alkyne−azide click reaction.

Supporting Information Available: Experimental details and additional TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Goodyear, C. *Dinglers Polytech. J.* **1856**, *139*, 376.
(2) Jordan, J.; Jacob, K.; Tannenbaum, R.; Sharaf, M.; Jasiuk, I. *Mater. Sci. Eng.* **2005**, *A393*, 1.
(3) Schmidt, G.; Malwitz, M. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 103.
(4) Zheng, Y. P.; Ning, R. C.; Zheng, Y. *J. Reinforced Plast. Compos.* **2005**, *24*, 223.

(5) Liang, K. W.; Li, G. Z.; Toghiani, H.; Koo, J. H.; Pittman, C. U. *Chem. Mater.* **2006**, *18*, 301.

(6) Singh, P.; Kaushik, A.; Kirandeep, A. *J. Reinforced Plast. Compos.* **2006**, *25*, 119.

(7) Ragosta, G.; Abbate, M.; Musto, P.; Scarinzi, G.; Mascia, L. *Polymer* **2005**, *46*, 10506.

(8) Chen, Q.; Xu, R. W.; Zhang, J.; Yu, D. S. *Macromol. Rapid Commun.* **2005**, *26*, 1878.

(9) Lee, T. M.; Ma, C. C. M. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 757.

(10) Murray, C.; Kagan, C.; Bawendi, M. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.

(11) Shipway, A.; Katz, E.; Willner, I. *ChemPhysChem* **2000**, *1*, 18.

(12) Dennis, H.; Hunter, D.; Chang, D.; Kim, S.; White, J.; Cho, J.; Paul, D. *Plast. Eng.* (*Boca Raton, FL, U. S.*) **2001**, *1*, 56.

(13) Lan, Q.; Francis, L.; Bates, F. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2284.

(14) Harton, S.; Kumar, S. *J. Polym. Sci., Polym. Phys.* **2008**, *46*, 351.

(15) Wu, C.-W. Ph.D. Dissertation, Columbia University, 2006.

(16) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004.

(17) Flory, P. J.; Rehner, J. *J. Chem. Phys.* **1943**, *11*, 521.

(18) Miller, D.; Macosko, C. *Macromolecules* **1976**, *9*, 206.

(19) Sun, T.; Feng., L.; Gao, X.; Jiang, L. *Acc. Chem. Res.* **2005**, *38*, 644.

(20) Joseph, Y.; Krasteva, N.; Besnard, I.; Guse, B.; Rosenberger, M.; Wild, U.; Knop-Gericke, A.; Schloegl, R.; Krustev, R.; Yasuda, A.; Vossmeyer, T. *Faraday Discuss.* **2004**, *125*, 77.

(21) Russell, J.; Lin, Y.; Boker, A.; Su, L.; Carl, P.; Zettl, H.; He, J.; Sill, K.; Tangirala, R.; Emrick, T.; Littrell, K.; Thiyagarajan, P.; Cookson, D.; Fery, A.; Wang, Q.; Russell, T. P. *Angew. Chem., Int. Ed.* **2005**, *44*, 2420.

(22) Song, H. M.; Kim, Y. J.; Park, J. H. *J. Phys. Chem. C* **2008**, *112*, 5397.

(23) Lin, Y.; Skaff, H.; Boker, A.; Dinsmore, A.; Emrick, T.; Russell, T. P. *J. Am. Chem. Soc.* **2003**, *125*, 12690.

(24) Skaff, H.; Lin, Y.; Tangilara, R.; Breitenkamp, K.; Boker, A.; Russell, T. P.; Emrick, T. *Adv. Mater.* **2005**, *17*, 2082.

(25) Liu, X.; Basu, A. *Langmuir* **2008**, *24*, 11169.

(26) Zhou, Y.; Wang, S.; Zhang, K.; Jiang, X. *Angew. Chem., Int. Ed.* **2008**, *47*, 7454.

(27) Prepared by atom transfer radical polymerization. See: Matyjaszewski, K.; Xia, J. Fundamentals of Atom Transfer Radical Polymerization. In *Handbook of Radical Polymerization*; Matyjaszewski, K., Davis, T. P., Eds.; Wiley-Interscience: New York, 2002; pp 523−628.

(28) White, M.; Johnson, J. J.; Koberstein, J. T.; Turro, N. J. *J. Am. Chem. Soc.* **2006**, *128*, 11356.

(29) Wu, C.-K.; Hultman, K. L.; O'Brien, D.; Koberstein, J. T. *J. Am. Chem. Soc.* **2008**, *130*, 3516–3520.

(30) Willis, A.; Turro, N. J.; O'Brien, S. *Chem. Mater.* **2005**, *17*, 5970–5975.

(31) Shin, Y.; Lee, D.; Lee, K.; Ahn, K. H.; Kim, B. *J. Ind. Eng. Chem.* **2008**, *14*, 515–519.

(32) Macosko, C. W. *Rheology: Principles, Measurements and Applications*; VCH: New York, 1994.

(33) Rong, M. Z.; Zhang, M. Q.; Zheng, Y. X.; Zeng, H. M.; Walter, R.; Friedrich, K. *Polymer* **2001**, *42*, 167–183.

(34) Johnsen, B. B.; Kinloch, A. J.; Mohammed, R. D.; Taylor, A. C.; Sprenger, S. *Polymer* **2007**, *48*, 530–541.