

Effect of Colloidal Silica Dispersions on the Properties of PDMS-Colloidal Silica Composites

Dinkar Sumi,¹ A. Dhanabalan,¹ B. H. S. Thimmappa,² Sriram Krishnamurthy³

¹Momentive Performance Materials Inc. Program, Global Research GEITC, 122, EPIP, Bangalore, India

²Department of Chemistry, Manipal University, Manipal, India

³Global Research GEITC, 122, EPIP, Bangalore, India

Received 14 July 2011; accepted 29 September 2011

DOI 10.1002/app.36226

Published online 1 February 2012 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Polydimethylsiloxane (PDMS) colloidal silica composites prepared with the use of the dispersion of colloidal silica (CS) of similar particle size and distribution in different mediums/solvents are investigated for their rheological, thermal, and mechanical properties. Regardless of the dispersion medium of CS, thermal analysis showed the increased thermal stability of PDMS with the addition of CS. The rheological analysis showed that the composites prepared from CS dispersed in isopropanol (IPA) and CS dispersed in methylethylketone (MEK) showed significant enhancement in viscosity at higher loadings as compare with the composite prepared from the CS dispersed in water and methanol indicating more

Filler–polymer interactions. Similarly, the tensile stress–strain curves, hardness, and tear strength displayed significant improvement with PDMS-CS-MEK and PDMS-CS-IPA composites. The results of this study not only provide the insights of solid–liquid–liquid interface leading to different extent of polymer–filler interaction, there by the bulk properties, it also helps to minimize the surface treatment steps while preparing the composites. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: E515–E522, 2012

Key words: colloidal silica; composites; poly (dimethylsiloxane); mechanical properties; thermal properties

INTRODUCTION

Polydimethylsiloxane (PDMS) has unique properties, such as low T_g resulting in low temperature ductility, high thermal and oxidative stability, outstanding dielectric properties, and physiological inertness.^{1–4} However, pure siloxane polymers are rarely used without modification for technological applications; typically, they are modified with fillers, pigments, copolymerization, and curing agents to convert them to useful products, including rubbers and resins. Apart from their known applications, PDMS composites with selected fillers find applications in the field of biomaterials as drug delivery systems,⁵ dental liners and biomedical balloons,⁶ and in reconstructive plastic surgery and as encapsulants in electronics, lithographic molds for manufacturing microchemical devices.^{7,8}

Fumed silica, which consists of agglomerated aggregates of amorphous silica nanoparticles has been one of the most favored reinforcing (nano) fillers studied and used for decades.^{9–11} However, the key issue with usage of fumed silica being the poor dispersity in PDMS matrix, because of its physical

state (fluffy powder) and hydrophilic surface. Hence often fumed silica requires an additional step of modification before incorporating into the PDMS matrix. These surface treatments and blending process are time-consuming, energy-intensive process. Also, it is difficult to control the morphological structure of the resulting materials, especially the degree of particle dispersion. As a result, particles tend to agglomerate and inhomogeneous systems are usually obtained. In this study, commercially available spherical colloidal silica dispersions are used to replace the fumed silica systems.

The colloidal silica sols have several advantageous properties, they are nearly spherical in shape and have a narrow size distribution and easy to handle as they are available in different dispersions. This factor makes them attractive to replace the fumed silica systems, as they can provide better wettability assisted by the solvent dispersion and less intensive possessing. Moreover, CS is commercially available in various different sizes, shapes, dispersions (aqueous and organic), which helps to tailor the surface interactions which is key for the reinforcement.

Even though colloidal silica has been extensively used over many years in a wide range of industrial applications such as ceramics, glass, optics, health, chromatography, pulp and paper, electronics, foods, gels, colloids and composite materials,^{12–16} there are very limited literatures available with their usage as

Correspondence to: D. Sumi (sumi.suvarna@ge.com).

reinforcing filler in PDMS matrix. Hence, a key question arises whether good reinforcement can be achieved with unstructured particles such as CS. The earlier work by Castaing¹⁷ reports the formation of reinforced PDMS elastomer with exceptional good properties when CS adsorbed onto PDMS. And most recently Kwan et al. further studied the modification of aqueous CS and their reinforcing capability in PDMS using two-step process. The first step was formation of functionalized colloidal silica (FCS) and the second step was preparation of composites by addition of FCS suspension in toluene and showed that FCS can provide fumed silica like reinforcing properties with significantly better rheological properties.¹⁸ This study is aimed to eliminate the two-step process into one by direct incorporation of the commercially available CS dispersions and study their influence on the thermal, rheological, and mechanical properties. The four different commercial CS dispersions of similar particle size were primarily characterized to understand the surface properties using FTIR, TEM, and elemental analysis. Further PDMS-CS composites prepared and the interfacial interaction involving the nature of dispersion medium, solubility of solvent and organophilic character of corresponding CS were investigated as a function of filler loadings. The viscoelastic, tensile properties, and morphology of fractured tensile samples of resultant composites are studied and compared with the pure PDMS elastomer. The results of this study not only provide the insights of solid-liquid-liquid interface leading to different extent of polymer-filler interaction, there by the bulk properties, it also helps to minimize the surface treatment steps while preparing the composites.

MATERIALS AND TEST METHODS

Materials

The dispersions of CS (SNOWTEX[®] and ORGANOSILICASOL[™]) with average particle size of ~ 15 nm in aqueous/organic [methanol, isopropanol and methylethylketone (MEK)] media were received from Nissan Chemicals, USA. Vinyl end capped PDMS ($M_w \sim 65,000$), hydride functionalized PDMS cross-linker ($M_w \sim 2800$), chloroplatinic acid and ethynylcyclohexanol (ECH) were received from Momentive Performance Materials, Inc. Leverkusen, Germany.

Procedure for making PDMS composites

Cured PDMS-FCS composites were prepared using a two-step process. The first step comprised of the preparation of the composite base, while the second step involved curing of the composite base with the

TABLE I
PDMS and CS Compositions (wt %) For Preparing the PDMS-CS Composites

Sample ID	PDMS loading (wt %)	CS loading (SiO ₂ wt %)
CS 0	100	0
CS-Water 10	90	10
CS-Water 20	80	20
CS-Water 30	70	30
CS-Water 40	60	40
CS-MeOH 10	90	10
CS-MeOH 20	80	20
CS-MeOH 30	70	30
CS-MeOH 40	60	40
CS-IPA 10	90	10
CS-IPA 20	80	20
CS-IPA 30	70	30
CS-IPA 40	60	40
CS-MEK 10	90	10
CS-MEK 20	80	20
CS-MEK 30	70	30
CS-MEK 40	60	40

addition of a cross linker, an inhibitor, and a catalyst.

The composite base was prepared by mixing PDMS fluid (60 wt % PDMS) taken in a double planetary mixer kettle (Ross-DPM) with the CS (40 wt % CS dispersed in 60 wt % of methanol solvent) at the room temperature, for a period of 45 min. The CS dispersion was added in portions (100 mL per 10 min) to ensure a homogeneous mixing. Subsequently, the contents were heated to a temperature of 80°C with concomitant application of vacuum for an hour to remove the volatile dispersion medium. The temperature of the kettle was further raised to 110°C and maintained for 60 min under vacuum (10 mbar), to remove traces of volatiles, if any.

In the second step, the composite base was mixed with the required amounts of hydride functionalized PDMS (cross-linker), ethynylcyclohexanol (inhibitor) and platinum catalyst, in a kitchen blender. It is essential to remove air bubbles from the mass with the application of vacuum prior to curing. The curing of the composite into the sheets in the compression-molding machine was carried out at 170°C using 90 KN pressure, for a period of 10 min. PDMS composites consisting of various loadings (30, 20, and 10 wt %) of CS were prepared by similar procedure (Table I).

Characterization of PDMS composites

Thermal

The thermal characteristics of uncured PDMS composite base was inferred by thermo gravimetric analysis (TGA) using TGA 2950 from TA instruments. TGA measurements were done by the heating the

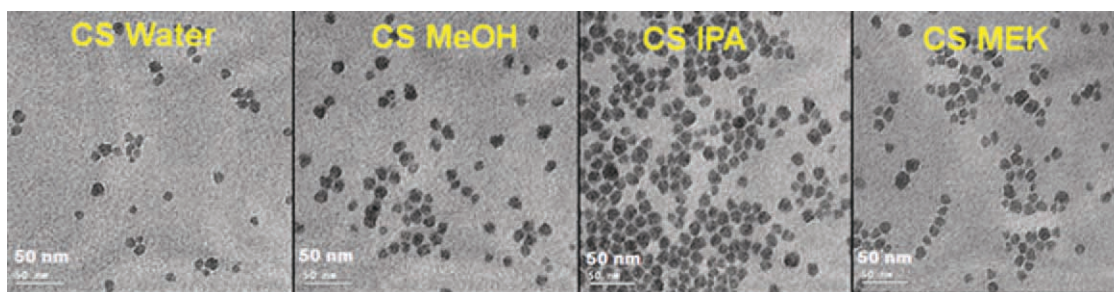


Figure 1 TEM micrographs of CS in different dispersion mediums. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sample kept in a platinum pan, from 25 to 700°C at a heating rate of 10°C min⁻¹, under nitrogen atmosphere.

Fourier transform infrared analysis

Fourier transform infrared (FTIR) analysis of dried CS powder was carried out in the range of 400–4000 cm⁻¹ with attenuated total reflection (ATR)-FTIR spectrophotometer using Perkin Elmer FTIR instrument.

Elemental analysis

Elemental Analyzer was used to quantify the elemental composition (C, H, N, and S) of CS powder. Elements C, H, N, and S were converted to respective oxides by combustion of the organic material in oxygen atmosphere. The released gases were separated in a gas chromatographic column (PorapakQ) and detected by Thermal Conductivity Detector (TCD). Oxygen content is determined by the reduction of the oxygen to water and passed through different column and TCD.

Rheology

Rheological properties of uncured PDMS base composites were inferred using an ARES II strain controlled Rheometer from Rheometric Scientific, in dynamic frequency mode. In a typical rheological measurement, the uncured sample was loaded between two disks (diameter = 25 mm) separated by a distance of 1.5 mm and the experiments were conducted from an initial frequency of 0.1 rad/s to a final frequency of 100 rad/s with dynamic strain of 2%, at a fixed temperature of 24°C.

Mechanical

The mechanical properties such as the tensile properties (at a crosshead speed of 100 mm/min) and the tear strength were measured using Instron UTM, adapting protocols specified in ASTM D53504 S2 and ASTM D624 S1, respectively. The transmission electron micro-

scope (TEM) and scanning electron microscope (SEM) were used to analyze the morphology and fracture behavior of PDMS composites. The hardness of the cured PDMS composites was measured by using a Shore-A Durometer, following DIN 53505 method.

RESULTS AND DISCUSSION

Characterization of commercial colloidal silica dispersions

Prior to the preparation of PDMS-CS composites, the colloidal silica dispersions were analyzed to understand the particle size distribution using Transmission Electron Microscopy (TEM) with 1% diluted CS dispersions (Fig. 1). From TEM analyses it was observed that all the commercially available CS dispersions show particle size of 15 ± 5 nm. FTIR analysis was also performed on dried samples (at 110°C for 8 h) of all the CS dispersions (see Fig. 2). All the samples showed the absorption between 950 and 1100 cm⁻¹ and ~ 785 cm⁻¹, are assigned to the Si–O–Si stretching (both symmetric and asymmetric) and bending vibrations, respectively. The broad peak at 3000–3800 cm⁻¹ is assigned to –OH stretching vibrations of Si–OH and H₂O. The peak at 950 cm⁻¹ is assigned for residual Si–OH. Of all the CS-dispersions only CS dispersed in MEK sample showed an additional peak at ~ 2900 cm⁻¹, which is typically observed for C–H stretching. To understand the difference, the % CH analyses were performed (Table II). The CH analysis results indicate that CS-MEK has high % carbon and hydrogen followed by CS-IPA and CS-MeOH. The CS-water showed least % of carbon and hydrogen content. The observed carbon content in the dried samples indicates the possible surface functionalization of CS in CS-MEK and possible esterification or van der Waals interactions of CS with the alcoholic solvents in CS-IPA and CS-MeOH.¹⁹

Thermal characteristics

Figure 3 presents the TGA data of the uncured neat PDMS and CS-PDMS composites obtained with the

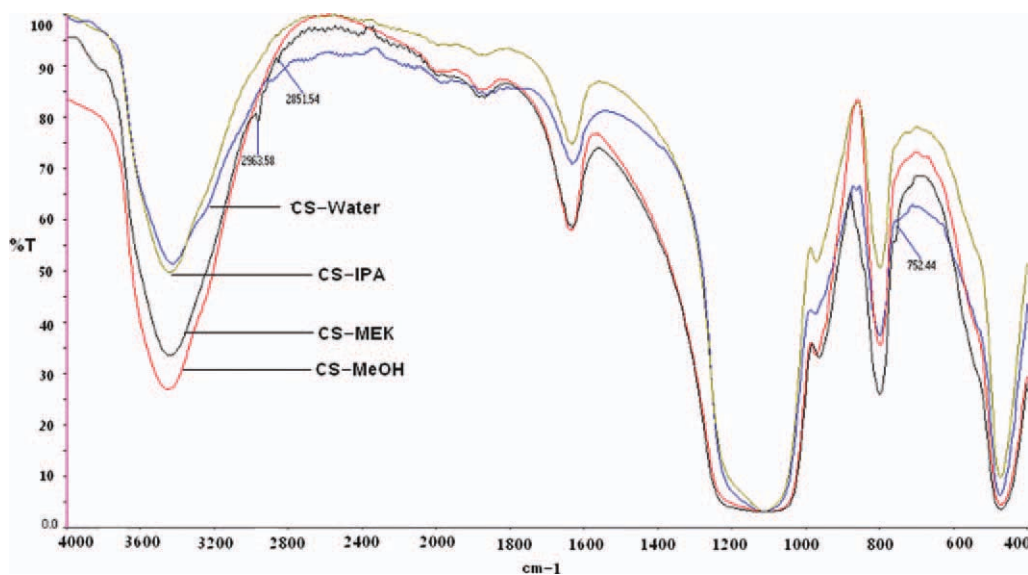


Figure 2 FTIR spectra of dried samples of CS-Water, CS-IPA, CS-MeOH, CS-MEK. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

use of different CS dispersions (CS-water, CS-MeOH, CS-IPA, and CS-MEK) at a fixed loading of 40 wt % of CS in nitrogen atmosphere. Both the on-set degradation temperature (T_d) and the char residue at elevated temperatures ($>650^\circ\text{C}$) are found to be higher for CS containing PDMS composites and such trend is similar to that reported in the literature for poly (methylmethacrylate) based hybrid material containing CS.²⁰ The PDMS composites containing CS-MeOH and CS-water are found to have higher T_d (by 20°C), as compared with that observed for PDMS composites with CS-MEK and CS-IPA and such trend can be potentially be attributed to the alteration of pyrolysis characteristics of PDMS by relatively more hydrophilic CS (through surface OH functionalities) dispersed with the aid of polar dispersion medium such as water and methanol. A relatively higher wt % loss observed in the case of the PDMS composites with CS-IPA and CS-MEK at 490°C indicates possible partial surface modification. The same observation further supports the CH analysis (Table II). The char residue for different PDMS composites are in the range of 38–43% and the observed slight variations in the dispersion of CS in the chosen samples. The lower thermal degradation and lesser char yield observed for pure PDMS in an inert atmosphere is usually attributed to the depolymerization PDMS and formation of volatile cyclic oligomers.²¹

Rheological characteristics

Figure 4 represents the change in the viscosities of uncured PDMS-CS composites with varying loading of CS dispersed with the aid of different media. The

viscosity of PDMS-CS composite is found to increase with increasing loading. Increment of viscosity is in the order of CS-MEK > CS-IPA > CS-MEOH > CS-water. CS-MEK shows higher viscosity at all loadings as compare to other composites. An abrupt increase in viscosity found at 40 wt % loadings of CS-IPA and CS-MEK composites. The higher viscosities for the same CS loading observed for both CS-MEK and CS-IPA could be attributed to good dispersion derived from the partial modification (as evidenced from the FTIR (Fig. 2) and the elemental analysis (Table II)) and space filling particle network of percolating aggregates. The CS-MeOH and CS-Water though shows linear increment, the increase is higher for CS-MEOH as compared with CS-Water. As water is more polar and less soluble in PDMS, filler-filler interaction dominates by hydrogen bonding leading to low viscose composites. On the other hand, methanol dispersions known to wet the surface via adsorption¹⁹ (Table II) and have higher solvation capability with PDMS resulting in relatively thicker composites. Even though, it had generally been observed that with the addition of CS fillers into an elastomer matrix enhances the viscosity,²² the raise in the viscosity is, in general, related to structuring of the filler within the matrix. Hence, the

TABLE II
% Carbon and Hydrogen Analysis of Dried Powders of CS

Sample ID	Carbon (%)	Hydrogen (%)
CS-Water	0.03	0.27
CS-MeOH	0.32	0.41
CS-IPA	0.78	0.53
CS-MEK	1.86	0.67

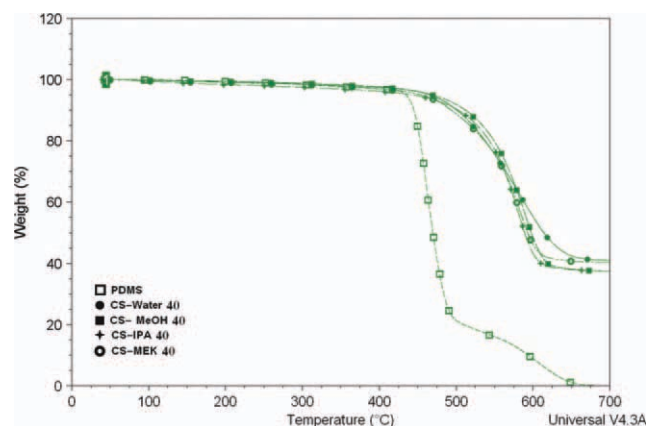


Figure 3 TGA curves of neat PDMS and PDMS-CS composites containing CS-Water 40, CS-IPA 40, CS-MeOH 40, and CS-MEK 40. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

observed trend in the variation of the viscosities of uncured PDMS-CS composites with different loadings of CS dispersed with the aid of different media can be attributed to the variation of the filler–filler and the filler-PDMS interactions, as dictated by miscibility of the dispersion media with PDMS and the surface functionality of CS and their hydrogen bonding capability.

Microscopic analysis of PDMS composites

The TEM images of all cured PDMS-CS composites were studied to understand the effect of dispersion medium on the CS dispersion in PDMS matrix. Figure 5 shows the TEM images of PDMS-CS composites with 40 wt % CS loading. Relatively larger aggregates of CS in PDMS matrix are evident for the composites in which the CS is dispersed with polar solvents such as water and methanol and such observation can be related to the poor miscibility of polar dispersion media with the nonpolar PDMS and their sorption efficiency on the CS during their removal. On the other hand, a relatively good dispersion of CS in PDMS was observed with the use of IPA and MEK as dispersing mediums. CS-IPA shows relatively better dispersion than CS-MEK

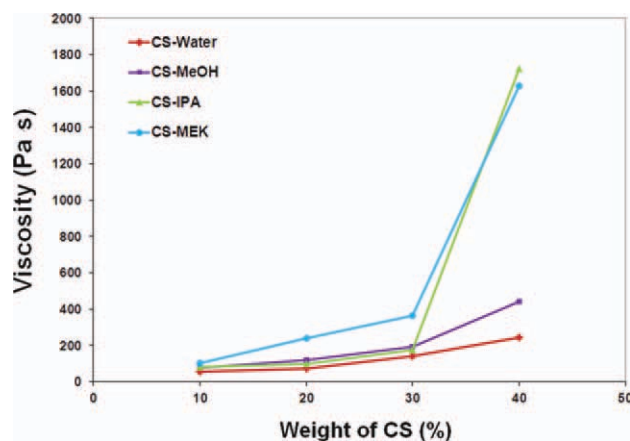


Figure 4 Rheology of uncured PDMS-CS composites containing various loadings of CS-Water, CS-IPA, CS-MeOH, and CS-MEK. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composites, the observed improvement and difference in dispersion of CS-IPA and CS-MEK composites can be attributed to the relatively nonpolar nature of dispersion medium (IPA and MEK as compared with water and MeOH) and their compatibility with PDMS leading to different degree of polymer–filler interaction. Also it can arise from the possible different type and extent of surface functionalization of CS-IPA and CS-MEK as evidenced from the above studies (FTIR, CH analysis, TGA, and TEM).

Mechanical properties

Tensile properties

The Figures 6, 7, and 8 represents the modulus, tensile strength, and elongation at break of PDMS-CS composites, respectively. Figure 6 presents normalized modulus of PDMS-CS composites with neat PDMS. As evidenced, irrespective of the dispersion medium with which CS is dispersed into the PDMS matrix, the modulus of composites increased with CS loadings. The modulus is found to vary with varying dispersion mediums of CS. The highest elastic modulus is found with CS-MEK composites with

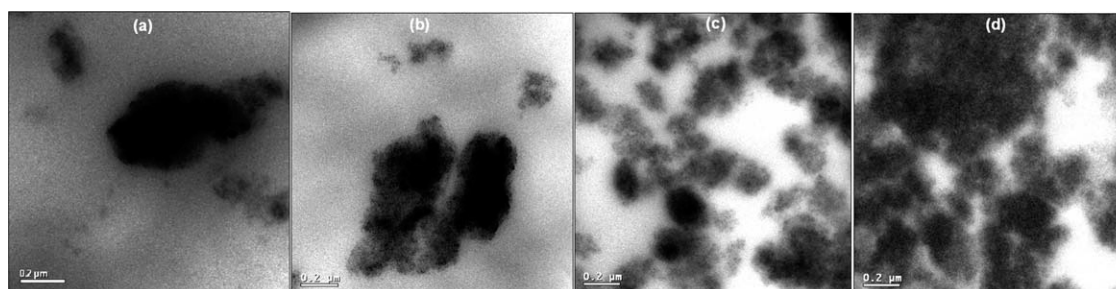


Figure 5 Transmission electron micrographs of cured PDMS-CS composites: (a) CS-Water 40 (b) CS-MeOH 40 (c) CS-IPA 40, and (d) CS-MEK 40.

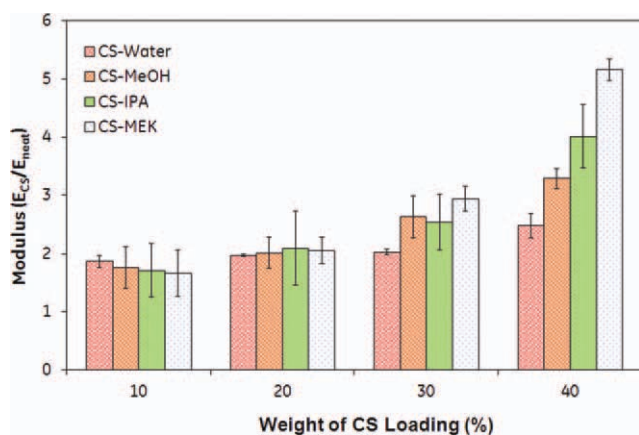


Figure 6 Normalized modulus of PDMS-CS composites at different CS loading. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

40 wt % loading. Higher modulus for CS-MEK as compare to the CS-IPA may be due to percolation of particles leading to secondary filler–filler aggregation as evidenced by TEM results. The Figure 7 compares the tensile strength of all PDMS-CS composites normalized to neat PDMS. Irrespective of the type of dispersions of CS, PDMS-CS composites showed increased tensile strength with increased CS loadings. The extent of increment found to vary with dispersion mediums. In particular, the CS-MEK and CS-IPA systems shows significantly enhanced improvement in tensile properties compared to CS-Water and CS-MeOH. This observation is in line with earlier observations. The Figure 8 presents the normalized elongation at break (%E) of the PDMS-CS composites. As evidenced from Figure 8, the %E increases with the incorporation of CS loadings. The extent of increment seems to vary with dispersion medium and the loading of CS. In case of CS-Water composites a linear trend is found, whereas the composites with CS-IPA showed increased % elongation

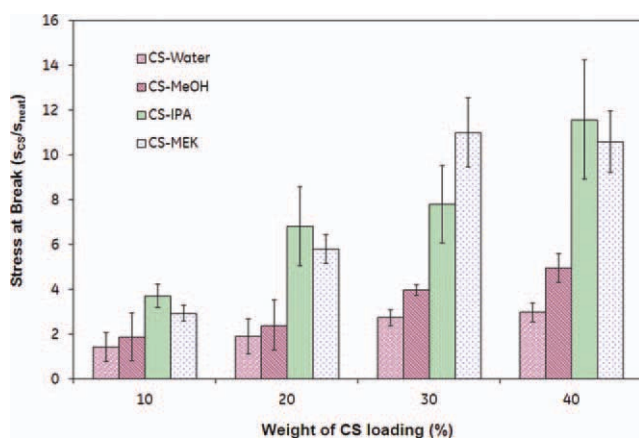


Figure 7 Normalized tensile strength of PDMS-CS composites at different CS loading. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

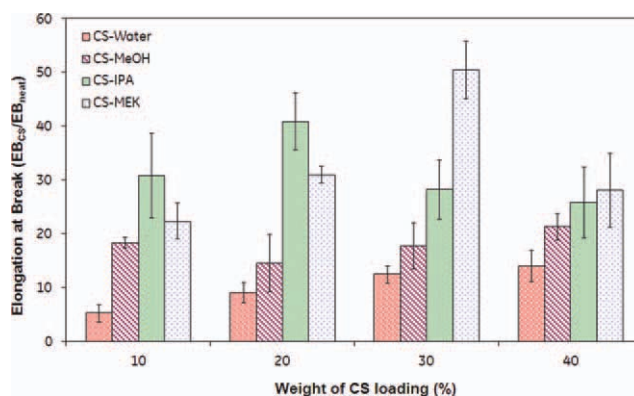


Figure 8 Normalized plot of elongation at break of PDMS-CS composite at different CS loadings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

values up to 20 wt % loading of CS, further increment in CS loading resulted in lower %E values. The CS-MEK composite showed increased elongation up to 30 wt % CS loading beyond which the %E drops. In general the larger concentration of filler incorporated into the matrix, greater amounts of network chain inhomogeneities exist, as a result network strains and filler particle move away from each other this results in different levels of elongation at break values. The increased modulus, tensile strength and %E in case of CS-IPA and CS-MEK composites may be due to the better dispersion of CS-IPA, CS-MEK in PDMS facilitated by the better polymer–filler interaction derived from the partial surface modification of CS-MEK and CS-IPA [as evidenced from above studies]. The above results indicate that there seems to be optimal loading of CS for the selected dispersion medium which is crucial for optimal reinforcement.

Further the stress–strain behaviors at 30 wt % loading were plotted to understand their reinforcement effect (Fig. 9). The stress–strain curves show pronounced increase of stress followed by nearly linear region. All the CS-loaded composites provide

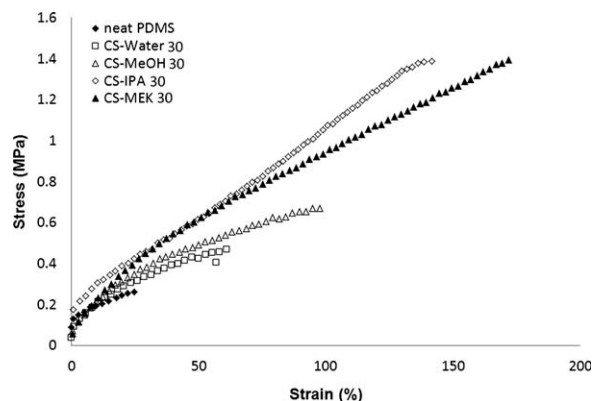


Figure 9 Tensile stress–strain behavior of 30 wt % CS-loaded composites.

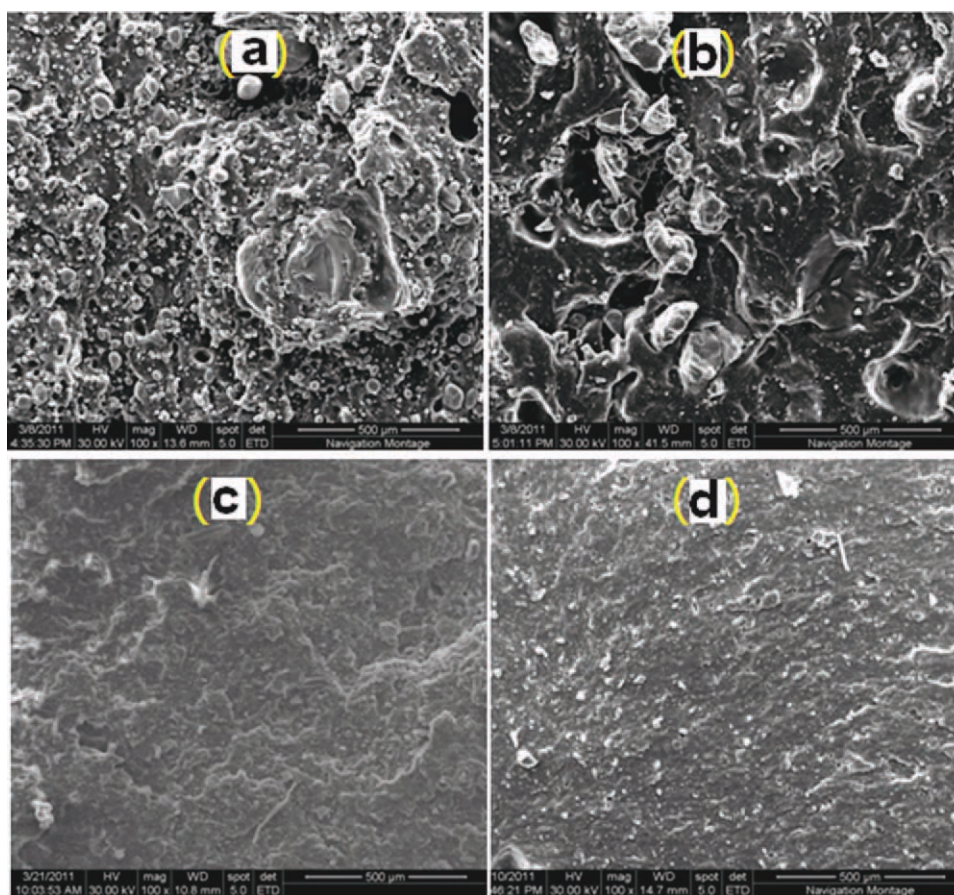


Figure 10 SEM micrographs of tensile fracture surface of composites: (a) PDMS-CS-water composite (b) PDMS-CS-MeOH composite (c) PDMS-CS-IPA composite (d) PDMS-CS-MEK composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mechanical reinforcement for PDMS as shown by higher stress relative to the values of neat PDMS. The stress-strain curves for CS-IPA and CS-MEK composites are significantly above the neat PDMS, indicating better reinforcing ability of CS. To get more insights on interfacial interaction the tensile fractured PDMS-composites with 30 wt % loaded CS in PDMS were examined under the Scanning Electron Microscope (SEM). From the SEM analysis [Fig. 10(a,b)] it can be seen that the CS-Water and CS-MeOH reinforced composites show more of push out fractures with many agglomerations indicating poor filler-PDMS interactions. Whereas both CS-MEK and CS-IPA composite [Fig. 10(c,d)] systems show wavy shear banding of the matrix indicating considerable energy is absorbed in these specimens during tensile test. The fractographs also shows good interactions between the filler and PDMS indicated by uniform distribution of CS MEK and CS IPA in the PDMS matrix.

Tear resistance and durometer hardness tests

Figures 11 and 12 presents normalized tear and hardness data of PDMS-CS composites with neat PDMS respectively. As shown in Figures 11 and 12,

an increased tear and hardness was evidenced with increased loading of CS, which is due to the increased ability of elastomer to dissipate the strain energy near the tip of growing cracks facilitated by the filler dispersions. The extent of increment is

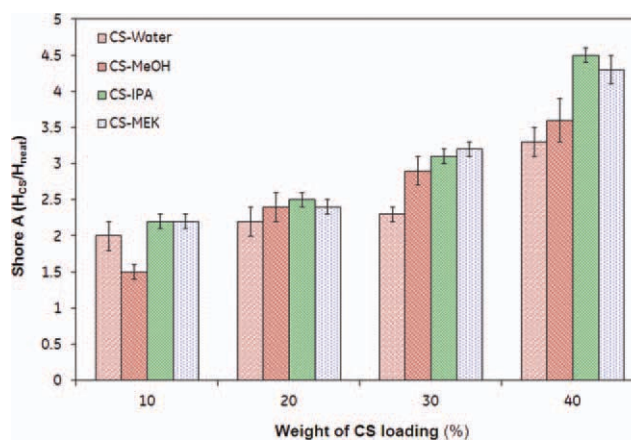


Figure 11 Normalized shore A hardness values for the different PDMS-CS composites at different CS loadings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

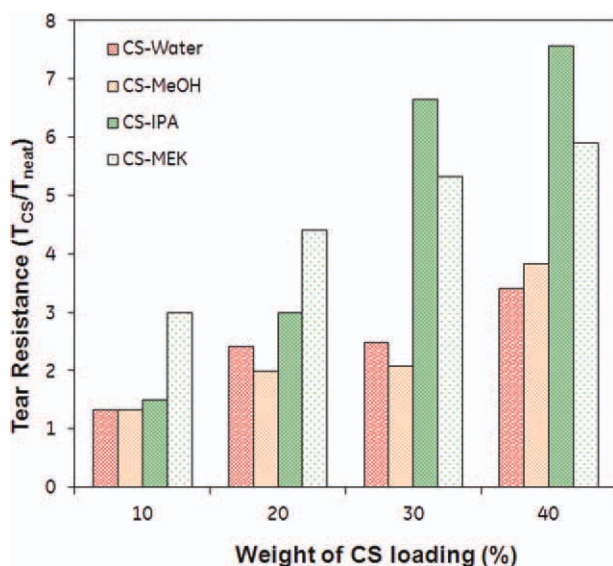


Figure 12 Normalized tear strength of PDMS-CS composites at different CS loadings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

significant in case of the composites prepared from the CS dispersions in IPA and MEK emphasizing the better interfacial interaction of filler with polymer, resulting from the dispersion medium of CS (IPA and MEK) and the possible functionality on the surface. Further the increase in filler-particles also enhances its ability to deflect or arrest crack growth there by increasing the tear strength. The extent of enhancement and their difference could be due to the type of functionality on the surface and dispersion medium. Also the difference further can be attributed to the different extent of interfacial interactions arising from the different degree of filler-filler and filler-polymer interactions. The lower values for the CS-water and CS-MeOH dispersions can be attributed to their higher surface energies resulting in higher filler-filler interaction as evidenced by morphology and rheology studies (Figs 4 and 5).

CONCLUSIONS

In this study, polydimethylsiloxane composites containing varying loading of colloidal silica are prepared with the use of different colloidal silica dispersions and studied for their thermal, rheological and mechanical properties. Both the filler-filler and the filler-polymer interactions are evident in these composites and the extent of these interactions is found to vary with the surface modification and the dispersion medium with which CS is dispersed into the PDMS matrix. The composites prepared from the CS-water and CS-methanol led to an enhanced filler-filler interaction thereby resulting in the PDMS composites with lower mechanical properties. The composites prepared with the use of CS-IPA and

CS-MEK, resulted in a better dispersion of CS in PDMS, leading to the PDMS composites with improved mechanical properties. The results of this study not only provide the insights of solid-liquid-liquid interface leading to different extent of interfacial interactions, but also help to minimize the surface treatment and intensive processing steps while preparing the composites. Although this study is pertained to CS containing PDMS composites, the knowledge derived from this study can potentially be extended to other composites with various functional fillers.

The authors would like to acknowledge Dr. Chandra Bajgur, Dr. Indumathi Ramakrishna, Dr. Mihirkumar Patel, Dr. Vikram Kumar, Mr. Swayagith.S.S, Mrs. Pallavi.M.B, Dr. Avdhut Maldikar, and Dr. Helmut Steinberger for helpful discussions. The authors would also like to thank the Nissan chemicals for providing the samples of CS dispersions and GEITC, India for its support.

References

- Bokobza, L.; Rapoport, O. *J Appl Polym Sci* 2002, 85, 2301.
- Clarson, S. J.; Semlyen, J. A.; *Siloxane Polymers*; Englewood Cliffs: N.J. Prentice-Hall, 1993.
- Noll, W. *Chemistry and Technology of Silicones*; New York: Academic Press, 1968.
- Shimamoto, A.; Kanemitsu, S.; Fuginaga, K.; Takao, M.; Onoda, K.; Shimono, T.; Tanaka, K.; Shimpo, H.; Yada, I. *Ann Thorac Surg* 2000, 69, 115.
- Gao, Z.; Nahrup, J. S.; Mark, J. E. *J Appl Polym Sci* 2003, 90, 658.
- El-Zaim, H. S.; Hegggers, J. P. *Polymeric Biomaterials*. In: Dumitriu, S., ed.; Marcel Dekker: New York, 2000; Chapter 3.
- McDonald, J. C.; Duffy, D. C.; Anderson, J. R.; Chiu, D. T.; Wu, H.; Schueller, O. J. A.; Whitesides, G. M. *Electrophoresis* 2000, 21, 27.
- Ng, J. M. K.; Gitlin, I.; Stroock, A. D.; Whitesides, G. M. *Electrophoresis* 2002, 23, 3461.
- Konkle, G. M.; McHard, J. A.; Polmanteer, K. E. U.S. Pat. 2,890,188 (1959).
- Kay, E.; Thamos, D. K. *J Inst Rubber Ind* 1971, 5, 148.
- Edwards, D. C. *J Mater Sci* 1990, 25, 4175.
- Hunter, R. J. *Introduction to Modern Colloid Science*; Oxford University Press: New York, 1993.
- Corrie, S. R.; Lawrie, G. A.; Trau, M. *Langmuir* 2006, 22, 2731.
- Kneuer, C.; Sameti, M.; Haltner, E. G.; Schiestel, T.; Schirra, H.; Schmidt, H.; Lehr, C. M. *J Pharm* 2000, 196, 257.
- Bourgeat-Lami, E.; Lang, J. *J Colloid Interface Sci* 1998, 210, 281.
- Kim, J. W.; Kim, L. U.; Kim, C. K. *Biomacromolecules* 2007, 8, 215.
- Castaing, J. C.; Allain, C.; Auroy, P.; Auvray, L.; Pouchelon, A. *Europhys Lett* 1996, 36, 153.
- Kwan, K. S.; Harrington, D. A.; Moore, P. A.; Hahn, J. R.; Degroot, J. V., Jr.; Burns, G. T. *Rubber Chem Technol* 2001, 74, 630.
- Renee Siler, A.; Robert, A. W. *J Phys Chem C* 2011, 115, 9637.
- Sugimoto, H.; Daimatsu, K.; Nakanishi, E.; Ogasawara, Y.; Yasumura, T.; Inomata, K. *Polymer* 2006, 47, 3754.
- Camino, G.; Lomakin, S. M.; Lazzari, M. *Polymer* 2001, 42, 2395.
- Kosinski, L. E.; Caruthers, J. M. *J Appl Polym Sci* 1986, 32, 3393.