CHAPTER 5
CHARACTERISTICS OF PDMS-FCS COMPOSITES PREPARED WITH DIFFERENT CS DISPERSIONS

5.1 INTRODUCTION

The characterization of different polydimethylsiloxane (PDMS)-colloidal silica (CS) composites obtained with the use of CS of varying particle size, dispersion medium and surface functionalization revealed that the proper choice of these parameters is critical to obtain PDMS-CS composites with desired optical and mechanical properties. The type of surface functionalization and the type of dispersing aid are found to have a significant influence on the properties of resultant PDMS-CS composites. Hence, it is important to understand the effect of using different dispersing aids while dispersing differently surface functionalized CS particles within PDMS matrix. The use of methylethylketone (MEK) as a dispersing aid and the use of methyl functionalized CS had led to PDMS-FCS composites with optimal optical and mechanical properties, as discussed in the earlier chapters. It is important to note that though the CS particles which are commercially available as MEK and isopropanol (IPA) dispersions are most probably surface functionalized. The use of such already surface functionalized CS did not lead to PDMS-CS composites with satisfactory optical and mechanical properties. Further, the surface modification of CS in MEK and IPA dispersion is necessary to obtain PDMS-CS composites with optimal performance.

The use of mixture of solvents, rather than the use of a single solvent had beneficial effect on the performance of the resultant PDMS-CS composites (Chapter -2), owing to an improved dispersion of CS within the PDMS matrix. Typically, the surface of the CS particles becomes more hydrophobic after their surface functionalization and hence it is inevitable to have them in non-polar solvents such as xylene to ensure a stable dispersion. The use of xylene as a dispersion medium also ensures a uniform dispersion of FCS when they are dispersed within the PDMS matrix, due to the close proximity of its solubility parameter with that of PDMS.
As described in Chapter-4, the PDMS-FCS composites prepared with the use of functionalized CS which are obtained by modifying aqueous dispersions of CS with different mono-functional silanes are found to have varying thermal, rheological, optical and mechanical properties, depending on the type of surface functionalized CS particles used. Among the various mono-functional silanes screened, the methyl surface functionalized CS based PDMS-FCS composites possess improved optical & mechanical properties. However, it is not straightforward to draw parallel to the surface functionalization of CS which are originally obtained as methanol (CS-MeOH), isopropanol (CS-IPA) and methyl ethyl ketone (CS-MEK) dispersions versus aqueous dispersion. Hence, a detailed investigation which comprises of the preparation of methyl functionalized FCS via surface functionalization of CS available in different dispersions (using similar procedure as described in Chapter-4) is undertaken. The resultant different types of FCS are used to prepare PDMS-FCS composites. The PDMS-FCS composites prepared with varying loadings of FCS are investigated for their thermal, rheological, optical and mechanical properties. The effect of using tri-functional coupling agent derived from HMDZ without the use of a mono-functional coupling agent, to treat the surface CS particles, has also been probed, with an aim of obtaining PDMS-FCS composites with optimal performance characteristics.

5.2 EXPERIMENTAL

5.2.1 Preparation of FCS

A three necked round bottom flask fitted with a reflux condenser and an overhead stirrer was charged with CS dispersion (396 g, 31.14 % solid dispersed in MeOH / MEK / IPA / water), 1-methoxy-2-propanol (200 g), methyltrimethoxysilane (MTMS) (75 g), water 0.5 g and the reaction mixture was stirred at 80 °C for 1 h. Triethylamine (TEA) (0.5 g) was added to the above mixture and the stirring was continued for another 1 h. Subsequently, the low boiling solvents were exchanged with 1-methoxy-2-propanol by distillation. The resulting suspension was heated to 60 °C and hexamethyldisilazane (HMDZ) (10 g) was added dropwise to it. At the completion of the addition, the reaction mixture was kept at the same temperature for 2 h. To this reaction mixture, xylene (250 g) was added slowly while stirring and 1-methoxy 2-propanol (200 g) was distilled-off to
get FCS dispersion in xylene. In separate set of experiments, CS particles in MeOH / water dispersions were subjected to HMDZ treatment with monofunctional silane only. Subsequently, the FCS particles were characterized using the FTIR, TGA and TEM, using similar procedures as described in the section 2.2.2 of Chapter 2.

5.2.2 Preparation of PDMS-FCS composites

Various PDMS-FCS composites with different loadings (40 wt %, 30 wt %, 20 wt % and 10 wt %) of FCS were prepared, using the similar procedure as described in section 2.2.3 of Chapter 2. The loading levels along with sample code of various PDMS-FCS composites prepared in the present study are provided in Table 5.1.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>PDM S (wt %)</th>
<th>FCS (Solid wt %)</th>
<th>Sample Name</th>
<th>PDM S (wt %)</th>
<th>FCS (Solid wt %)</th>
</tr>
</thead>
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<td>FCS-MEK 10</td>
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<td>10</td>
</tr>
<tr>
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<td>10</td>
<td>FCS-MEK 20</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
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<td>80</td>
<td>20</td>
<td>FCS-MEK 30</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>FCS-MeOH 30</td>
<td>70</td>
<td>30</td>
<td>FCS-MeOH-HMDZ 25</td>
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<td>25</td>
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<tr>
<td>FCS-MeOH 40</td>
<td>60</td>
<td>40</td>
<td>FCS-MeOH-HMDZ 40</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>FCS-IPA 10</td>
<td>90</td>
<td>10</td>
<td>FCS-MeOH-HMDZ 55</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>FCS-IPA 20</td>
<td>80</td>
<td>20</td>
<td>FCS-H\textsubscript{2}O-HMDZ 25</td>
<td>75</td>
<td>25</td>
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<tr>
<td>FCS-IPA 30</td>
<td>70</td>
<td>30</td>
<td>FCS-H\textsubscript{2}O-HMDZ 40</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>FCS-IPA 40</td>
<td>60</td>
<td>40</td>
<td>FCS-H\textsubscript{2}O-HMDZ 55</td>
<td>45</td>
<td>55</td>
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</tbody>
</table>

Table 5.1 Sample code and loading levels (in wt %) of PDMS-FCS composites.

5.3 RESULTS AND DISCUSSION

5.3.1 Characterization of FCS

5.3.1.1 Reaction of coupling agents

As described in Chapter 4, the reaction of coupling agents with silanol group on CS surface takes place in two steps. The first step involves the hydrolysis of coupling agents and the second step consists of the condensation of silanol groups with those present at the surface of CS. Three types of anchoring of coupling agent on to the surface of CS are prevalent with the use of a tri-functional silane (trialkoxy silane) (refer Figure 4.1 of chapter four). It is important to note that the surface functionalization was carried out for CS particles in aqueous dispersion in the earlier case (Chapter-four). However, in
comparison, a noticeably different behavior is evident while functionalizing the CS particles with methyltrimethoxysilane in non-aqueous dispersions. For instance, a clear dispersion as indicated by water like appearance of FCS without any gelation up to 30 wt % CS is evident with the use of CS-MeOH dispersion. The use of CS-IPA, however, led to a relatively thick and turbid dispersion even at 20 wt %, upon the surface functionalization. The surface functionalization of CS in MEK dispersion, on the other hand, results in a thick and slightly orange colored dispersion even with 15 wt % of CS. The observed physical appearance and coloration of CS-IPA and CS-MEK functionalized CS indicate the possible hindrance of already existing functionality with methyltrimethoxysilane. The enhancement of viscosity (gelation) may indicate the coagulation of FCS particles, owing to their incompatibility with the dispersion medium (xylene). The observed difference in the appearance of the FCS dispersions, prepared starting from different precursor CS dispersions, may be attributed to the partial pre-functionalization of CS to make it dispersible in a given dispersion media. The compositional analysis of different dispersions of CS is indeed indicative of possible partial organic modification of CS dispersed in isopropanol and methylethylketone (refer Chapter 3 section 3.3.1).

5.3.1.2 Analysis of FCS

Prior to the preparation of PDMS-FCS composites with the use of FCS prepared in the present study, it is important to understand the characteristics of these FCS. The Figure 5.1 depicts TEM images of FCS. A comparison of these results with those of un-functionalized precursor CS (refer Figure 3.1 of Chapter-3) reveals that though there is no significant difference in particle size and distribution (15 ± 5 nm), the FCS particles prepared from CS-IPA and CS-MEK precursor dispersions appeared to have more tendency for aggregation.

Figure 5.1 TEM micrographs of different dispersions of CS used in the present study.
FTIR analyses of dried samples (at 110°C for 8 h) obtained from different FCS are shown in Figure 5.2. All the samples showed the vibration absorption peaks between 950-1100 cm\(^{-1}\) and ~ 785 cm\(^{-1}\). While the peaks in the range of 950-1100 cm\(^{-1}\) are assigned to Si-O-Si asymmetric stretching modes, the peak at 785 cm\(^{-1}\) can be assigned to both symmetric Si-O-Si stretching and bending vibrations. The broad peak at 3000-3800 cm\(^{-1}\) which is typically assigned for –OH stretching vibrations of Si-OH and residual H\(_2\)O is completely disappeared, as compared to the neat CS (chapter 3 Figure 3.2) of all FCS. Though a complete disappearance of the peak at 950 cm\(^{-1}\) which is assigned for residual Si-OH bending vibrations is evident in case where FCS prepared from CS-MeOH, the peak is only partially disappeared in cases of FCS prepared from CS-IPA and CS-MEK, indicating the presence of some free Si-OH groups, even after the functionalization in these cases. The observed “incomplete” functionalization of CS (via treatment with methyltrimethoxy silane) with the use of CS-IPA and CS-MEK dispersions can be related to the steric hindrance by organic groups already present on the surface of the CS. All three FCS, however exhibit a characteristic peak at ~2900 cm\(^{-1}\), which is typically assigned to C-H stretching vibration absorption.

The CH analyses of dried FCS, as tabulated in Table 5.2, is indicative of a higher % C and H for the FCS prepared from CS-IPA precursor dispersion, as compared to those prepared from CS-MEK and CS-MeOH dispersions. However, the extent of increase of carbon content upon surface functionalization (as compared to that of un-
functionalized CS) is significantly higher for FCS prepared from CS-MeOH dispersion (5.8X), as compared that observed with samples prepared from CS-IPA (3.6X) and CS-MEK (1.2X) dispersions. The observed relatively lesser extent of functionalization of CS in IPA and MEK dispersions is in line with the observation made from FTIR results described above.

<table>
<thead>
<tr>
<th></th>
<th>% Carbon</th>
<th>% Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCS-MeOH</td>
<td>1.86</td>
<td>0.46</td>
</tr>
<tr>
<td>FCS-IPA</td>
<td>2.82</td>
<td>0.83</td>
</tr>
<tr>
<td>FCS-MEK</td>
<td>2.32</td>
<td>0.91</td>
</tr>
</tbody>
</table>

**Table 5.2:** Percentage carbon and hydrogen data of FCS derived from different CS dispersions.

The TGA analyses of pre-dried FCS samples are shown in Figure 5.3. The observed thermal degradation characteristics with different FCS are indicative of different thermal stabilities of FCS, prepared from different CS precursors. For example, a significant weight loss (> 5 wt %) is apparent while heating the sample up to 800 °C for the FCS prepared from CS-MEK precursor. The weight loss patterns involving two step degradation observed for FCS prepared from CS-IPA and CS-MeOH dispersions themselves are different from that observed for the sample prepared from CS-MEK that involves one step degradation. This result could possibly indicating a similar and thermally more stable surface functionalities of FCS, prepared from CS-MeOH and CS-IPA dispersions. Though the thermal degradation patterns observed for FCS, prepared from CS-IPA and CS-MEK dispersions remain unchanged even after the functionalization, a significantly different thermal degradation pattern is evident for FCS, prepared from CS-MeOH dispersion, as compared to that of un-functionalized CS derived from CS-MeOH (*refer the section 3.3.1 of Chapter-3*). From the above results, it is apparent that the extent of functionalization of CS varies with the type of CS precursor dispersions, though the functionalization of CS with MTMS and HMDZ is performed under similar reaction conditions in all these cases and such variations are ascribed to the possible hindrance to in-coming surface treating agent by the preexisting organic functionalities on the surface of the CS.
5.3.2 Thermal and rheological characteristics of uncured PDMS-FCS composites

5.3.2.1 Thermal characteristics

Thermogravimetric analyses (TGA) and differential thermogravimetric analyses (DTGA) curves of PDMS-FCS composites, prepared with the use of different CS dispersions, are shown in Figure 5.4. The thermal stability of PDMS is improved with the incorporation of FCS, similar to the characteristics observed with PDMS-CS / PDMS-FCS composites as described in earlier chapters, irrespective of type of precursor dispersion medium used. Among different PDMS-FCS composites, those prepared with the use of CS-MEK and CS-IPA is found to have a relatively higher on-set Td (40 °C), in comparison to that prepared from FCS-MeOH dispersion.

Figure 5.3 TGA curves of dried samples of FCS derived from CS-MeOH, CS-IPA and CS-MEK.
5.3.2.2 Rheological characteristics

The incorporation of fillers into PDMS matrix typically leads to the enhancement of the viscosity of PDMS due to both the structuring of fillers via filler interactions and...
the interaction of filler with PDMS backbone (filler-polymer interactions). A similar phenomenon is evident for PDMS-FCS composites prepared in the present study as well. The PDMS-FCS composites prepared with the use of CS-MEK dispersion are found to possess a very high viscosity even at 20 wt % loading of FCS and hence these composites are considered not suitable for further investigation. The Figure 5.5 shows the change in the viscosities of uncured PDMS-FCS composites containing varying loadings of FCS, prepared from CS-IPA and CS-MeOH precursor dispersions.

![Figure 5.5 Viscosity of PDMS-FCS-IPA and PDMS-FCS-MeOH composites containing different wt % of FCS.](image)

The viscosity of both uncured composites (PDMS-FCS-MeOH and PDMS-FCS-IPA) is found to increase almost linearly with the increasing loading FCS in the composite. However, the magnitude of increase in the viscosity is found to vary with the type of precursor dispersion medium from which FCS is prepared. For instance, in general, the composites containing FCS-MeOH are found to have lower viscosities, as compared to those with FCS-IPA, irrespective of the loading of FCS in the composite.

The uncured composites with 30 and 40 wt % of FCS, prepared with the use of CS-MeOH are found to have almost similar viscosities and they are similar to the viscosities of uncured composites with 10 and 20 wt % of FCS, prepared with the use of CS-IPA. The observed variation of viscosity of the composites, is indicative of the
different extent of particle-particle and particle-polymer interactions, arising from different extent of functionalization of CS with the use of different precursor CS dispersion is used.

The viscoelastic characteristics of these uncured composites are also investigated, by studying their storage (\(G'\)) and loss modulus (\(G''\)) at varying frequencies. The Figure 5.6 and the Figure 5.7 shows the comparative \(G'\) and \(G''\) behaviors of uncured PDMS-FCS-MeOH and PDMS-FCS-IPA composites. Both the storage and the loss moduli are found to increase with increasing loading of FCS in the uncured PDMS-FCS composites. The storage modulus (\(G'\)) is typically higher than loss modulus (\(G''\)) for FCS-MeOH based composites, especially at lower frequency range, indicating more solid like behavior, irrespective of the loading of FCS. However, a cross-over is evident for 10 and 20 wt % FCS containing composite at higher frequencies.

![Figure 5.6 Storage and loss modulus of PDMS-FCS-MeOH composites versus frequency.](image)

However, in cases of FCS-IPA based uncured composites, a relatively larger enhancement of both \(G'\) and \(G''\) with the increasing loading of FCS in the composite, as compared that observed with FCS-MeOH is apparent. Similar to the observations made with FCS-MeOH based uncured composites, irrespective of the loading of FCS in the composites, the \(G'\) is higher than \(G''\) and a cross over is evident at higher frequencies, especially for the composites with lower loading of FCS.
It is interesting to compare the viscoelastic behavior of the uncured PDMS-FCS-MeOH composites with that of PDMS-FCSA3 (methyltrimethoxy silane treatment of aqueous dispersion of CS - refer Chapter-4 for the details) (Figure 5.7), as they have similar size and are likely to be either un-functionalized in their original dispersions (either methanol or water) or functionalized with same surface treating agent. In comparison, the uncured PDMS-FCS-MeOH composite exhibits a shear thinning behavior irrespective of the loading of FCS in the composite, while the uncured PDMS-FCSA3 composites typically showed Newtonian behavior. The observed shear thinning behavior of PDMS-FCS-MeOH can possibly be related to the breakdown of aggregated particles at higher frequencies as well as the different extent of interactions of FCS-MeOH with PDMS, as compared those prevalent in PDMS-FCSA3 composites.

![Figure 5.7](image_url) The storage and loss modulus of FCS-IPA composites versus frequency.

### 5.3.3 Morphological characteristics of cured PDMS-FCS composites

The TEM images of 10 and 30 wt % of FCS containing cured PDMS-FCS-MeOH, PDMS-FCS-IPA and PDMS-FCS-MEK composites are depicted in Figure 5.8. The dispersion of FCS has greatly enhanced in PDMS-FCS composites, as compared to that observed with the composites containing un-functionalized CS particles, prepared with the use of CS-MEK, CS-IPA and CS-MeOH. The presence of relatively larger aggregates is evident in cases of PDMS-FCS-MEK and PDMS-FCS-IPA composites and
relatively a good dispersion of FCS is observed for PDMS-FCS-MeOH composites. Since CS-IPA, CS-MEK and CS-MeOH are surface functionalized with MTMS and HMDZ under similar conditions, one would expect to have a similar dispersion of FCS in the composites, as the functionalization typically leads to passivation of surface silanol groups and thus results in weaker particle-particle interactions. Hence, the observed improved dispersion of FCS in PDMS-FCS-MeOH composites can be rationalized to a weaker particle-particle interaction due to a relatively better compatibility of FCS-MeOH with PDMS matrix. A relatively inferior dispersion of FCS in both PDMS-FCS-IPA and

![Figure 5.8 TEM micrographs of cured PDMS-FCS composites prepared with the use of different precursor CS dispersions.](image)

PDMS-FCS-MEK composites, can be attributed to lesser extent of particle-polymer interactions. This is due to the type of functionalities already present on the surface of the CS particles prior to the functionalization with MTMS and HDMZ. The observed agglomerated structure of FCS in PDMS-FCS-MEK may possibly indicate that the functionalities, which ensure a stable dispersion of CS in MEK, may not be compatible with PDMS matrix. A relatively better dispersion of FCS in PDMS-FCS-IPA composites, may indicate that CS-IPA is pre-functionalized with different groups other than those on the CS-MEK and these groups are either more compatible with PDMS matrix or offer less steric hindrance to MTMS / HMDZ functionalization.
5.3.4 Optical and mechanical properties of cured PDMS-FCS composites

5.3.4.1 Optical properties

The optical properties of PDMS-FCS-IPA and PDMS-FCS-MeOH composites are inferred through % transmittance (% T) measurements, as shown in the Figure 5.9. As expected, the incorporation of FCS particles is found to lower the % T of PDMS, due to the increased scattering of light by the incorporated particles. Among different PDMS-FCS composites PDMS-FCS-IPA composites have been found to possess a relatively lower transmittance, as compared to PDMS-FCS-MeOH composites. For instance, nearly ~ 15-20 % loss of transmittance is evident with incorporation of 10-40 wt % of FCS in PDMS-FCS-IPA as compared that of neat PDMS. In comparison, only 5-10 % lowering in transmittance is observed in cases of PDMS-FCS-MeOH composites, at similar loading levels.

The % haze values of the composites are also found to vary with the loading of FCS and the type of FCS (FCS-MeOH and FCS-IPA) similar to the trends observed with % T, as shown in Figure 5.10. A relatively high % haze values for PDMS-FCS-IPA composites is in line with the observed lower transmittance of these composites. The observed optical properties of PDMS-FCS-IPA (relatively lower transmittance and higher
haze) can be attributed to the poor dispersion of FCS with in the PDMS as well as the incompatibility of surface functionalities of FCS-IPA with PDMS. Similarly, the better optical properties of PDMS-FCS-MeOH (relatively higher transmittance and lower haze) can be attributed to the homogeneous dispersion of FCS-MeOH within the PDMS and their improved compatibility with PDMS.

![Graph showing percentage haze values of PDMS-FCS composites with different loadings of FCS.](image)

**Figure 5.10** Percentage haze values of PDMS-FCS composites with different loadings of FCS.

5.3.4.2 Mechanical properties of PDMS–FCS composites

The Figures 5.11 and 5.12 represent the modulus, tensile strength and elongation at break values of PDMS-FCS composites, respectively. A relatively large variation of modulus is evident for PDMS-FCS-IPA, in comparison to relatively narrower modulus values observed for PDMS-FCS-MeOH composites. This observation could be related to the inhomogeneous dispersion of FCS, resulting in an un-uniform reinforcement. Among different PDMS-FCS-IPA composites, the samples with 30 wt % loading of FCS are found to have distinctly higher modulus compared to other composites. But the modulus of PDMS-FCS-MeOH composite is found to increase almost linearly with increasing loading of FCS in the composite.
The trends observed with the tensile strength is similar to that observed with tensile modulus of the composites. The tensile strength is found to increase with increasing loading of FCS in the composites and a significantly higher tensile strength is evident for the PDMS-FCS-MeOH composites. The % elongation (% E) is also found to increase with increasing loading of FCS in the composites. The relatively higher % E values observed for PDMS-FCS-IPA composites, as compared to those of FCS-MeOH composites, irrespective of the loading levels, are in line with their lower modulus values.

The observed tensile modulus, tensile strength and % E values for different PDMS-FCS composites clearly indicate the varying reinforcing capabilities of FCS, depending on their loading and the type of their surface functionalization. To understand this phenomena further, the stress at break values observed for these composites are
normalized with respect to those of neat PDMS and those of composites with un-
functionalized CS, as shown in the Figure 5.13 (a) and (b), respectively. The tensile
strength of PDMS-CS composites is found to increase with the increasing loading of CS /
FCS, irrespective of the type of dispersions of CS. The extent of increase of tensile
strength, however, has been found to depend on the precursor dispersion media. In
particular, the PDMS-FCS composites prepared with CS-Water and CS-MeOH are found
to possess higher tensile strength, as compared to PDMS-FCS-IPA composites and such
observation is related to the functionalities already present on the surface of CS-IPA and
their poor interaction with PDMS matrix. Similarly the higher tensile strength of FCS-
MeOH and FCS-Water (FCS-A3) composites can be directly correlated to the methyl
functionalities present on the surface and their better miscibility with PDMS matrix.
However, it appears from the observed tensile strength values that the extent of surface
functionalization on FCS-water is different from that of FCS-MeOH.

![Figure 5.13](image)

Figure 5.13 Normalized tensile strength of PDMS-FCS composites with different loadings of FCS.

The trends observed with tensile strength indicate that even for a given type of
surface functionalization, the particle-particle and the particle-polymer interactions can
vary with the precursor dispersion media, thereby leading to a different degree of
reinforcing capability. The results from Chapter 4 substantiated that the methyl
functionalized FCS prepared from aqueous dispersion of CS possess a better wetting and
space filling structure, which are characteristics of optimal particle-particle and particle-
polymer interactions. In comparison, the methyl functionalized FCS prepared from
methanol dispersion appear to have slightly different surface structure and their
interactions with PDMS matrix and hence improved reinforcing capability.
In most of the present study, the surface functionalization of CS is carried out in two-steps involving the treatment of CS with mono-functional trialkoxy silane in the first step, followed by the treatment with HMDZ in the second step. It is intriguing to understand the characteristics of PDMS-FCS composites which contain the FCS which are treated only with HMDZ. It may be mentioned here that the HMDZ treatment alone does not lead to sufficient reinforcement, due to the umbrella effect, as indicated in relevant prior arts.

5.3.5 Preparation of HMDZ functionalized CS prepared from and CS-MeOH and CS-Water dispersions

5.3.5.1 Reaction of coupling agents

Similar to trifunctional silane coupling agent, the mono-functional silane coupling agents react with silanol groups on the CS surface in two steps. The first step is hydrolysis of coupling agent with the reaction of water. In the second step, the surface silanol groups of CS reacts with the silanol groups of coupling agent via condensation reaction.

5.3.6 Characterization of HMDZ functionalized CS

5.3.6.1 Reaction of coupling agents

In the present case, hexamethyldisilazane (HMDZ) undergoes hydrolysis via the reaction of water in the first step, followed by the condensation reaction of resultant trimethyl silanol with silanol groups present on the surface of CS. The rate of condensation reaction can usually be accelerated with an amine catalyst such as triethylamine (TEA). Unlike the case of tri-alkoxysilanes (refer Figure 4.1 of Chapter 4), the reaction of mono-functional silane with surface silanol groups leads to only one type of anchoring of functional group, as shown in Figure 5.14.
5.3.6.2 Analysis of HMDZ functionalized CS

The surface functionalization of CS with HMDZ does not lead any apparent change in the size of CS particles, as evidenced from TEM images of CS dispersions, before and after the functionalization (Fig. 5.15).

FTIR analyses of dried samples (at 110°C for 8 hour) of different HMDZ treated FCS are depicted in Figure 5.16. All the samples showed the vibration absorption peaks between 950-1100 cm⁻¹ and ~ 785 cm⁻¹. While the peaks in the range of 950-1100 cm⁻¹ are assigned to Si-O-Si asymmetric stretching modes, the peak at 785 cm⁻¹ can be assigned to both symmetric Si-O-Si stretching and bending vibrations.
The broad peak at 3000-3800 cm\(^{-1}\) which is typically assigned for OH stretching vibrations of Si-OH is found to disappear after the HMDZ functionalization. A lowering of intensity of the peak at 950 cm\(^{-1}\) which is typically assigned for residual Si-OH bending vibrations in FCS-H\(_2\)O-HMDZ and FCS-MeOH-HMDZ can also be considered to indicate the surface functionalization. Both FCS-H\(_2\)O-HMDZ and FCS-MeOH-HMDZ exhibit peaks at ~2900 cm\(^{-1}\), which is assigned to C-H stretching vibration absorption.

The surface functionalization is further evidenced from the elemental analyses data, provided in the Table 5.3. Though the commercially available methanol and water dispersions of CS are indistinguishable by FTIR and TEM analyses, the surface OH groups of the colloidal particles are probably esterified with methanol to an extent in the case methanol dispersion, as evidenced from the comparative elemental analyses of CS derived from water and methanol dispersions. A further increase of % carbon content of CS upon the surface functionalization with HMDZ confirms the surface functionalization of both CS-H\(_2\)O and CS-MeOH. The almost similar % C and % H values observed for both FCS-H\(_2\)O-HMDZ and FCS-MeOH-HMDZ possibly indicate a similar surface coverage of CS. Further the pre-dried FCS samples derived from different CS dispersions were analyzed to using TGA analysis as shown in Figure 5.17. The thermal stability and degradation pattern indicates similar degree of decomposition for both FCS powders. Though, FCS-H\(_2\)O- HMDZ shows relatively high % weight loss between 100 °C -200 °C, the decomposition pattern between 200 °C to 500 °C remains almost same for both FCS-H\(_2\)O-HMDZ and FCS-MeOH-HMDZ.
<table>
<thead>
<tr>
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<th>% carbon</th>
<th>% hydrogen</th>
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<tr>
<td>CS-H₂O</td>
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<tr>
<td>CS-MeOH</td>
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<tr>
<td>FCS-H₂O-HMDZ</td>
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<td>FCS-MeOH-HMDZ</td>
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<td>0.82</td>
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</table>

Table 5.3 Percentage carbon and hydrogen data of FCS-MeOH-HMDZ and FCS-H₂O-HMDZ.

5.3.7 Thermal and rheological properties of uncured PDMS-FCS-HMDZ composites

5.3.7.1 Thermogravimetric analysis of uncured composites

Thermogravimetric analyses (TGA) and differential thermogravimetric analyses (DTGA) of uncured PDMS-FCS-H₂O-HMDZ and PDMS-FCS-MeOH-HMDZ composites are shown in Figure 5.18. The thermal stability of PDMS is improved with the incorporation of FCS, similar to the characteristics observed with other PDMS-CS / PDMS-FCS composites described in earlier chapters, irrespective of type of the precursor dispersion medium used. In comparison, PDMS-FCS-H₂O-HMDZ composites are found to have a
relatively higher on-set Td (30 °C), in comparison to that of PDMS-FCS-MeOH-HMDZ, especially at lower loading of FCS in the composites.

Figure 5.18 TGA and DTGA curves of PDMS-FCS-\(\text{H}_2\text{O}\)-HMDZ and PDMS-FCS-MeOH-HMDZ as a function of loading levels of FCS.

5.3.7.2 Rheological characteristics of uncured composites

Similar to our earlier observations with CS and other FCS, the incorporation of FCS-\(\text{H}_2\text{O}\)-HMDZ and FCS-MeOH-HMDZ into PDMS also leads to increase of the viscosity of PDMS\(^6\). Figure 5.19 presents the change in the viscosities of PDMS with the incorporation of different wt % of FCS-MeOH-HMDZ and FCS-\(\text{H}_2\text{O}\)-HMDZ. Though the viscosity of uncured PDMS is found to increase almost linearly with increasing loading of FCS, the magnitude of increase of viscosity is relatively higher with the incorporation of FCS-\(\text{H}_2\text{O}\)-HMDZ at a given loading of FCS in the composite. For instance, the viscosity of uncured PDMS-FCS-\(\text{H}_2\text{O}\)-HMDZ-25 is more than one order higher than that of PDMS-FCS-MeOH-HMDZ-40. Moreover, the uncured PDMS-FCS-\(\text{H}_2\text{O}\)-HMDZ composites exhibit a shear thinning behavior. On the other hand, uncured PDMS-FCS-MeOH-HMDZ composites typically possess a relatively lower viscosity and exhibit Newtonian behavior at all frequencies. The observed trend could possibly indicate a relatively weaker interaction of FCS-MeOH-HMDZ with PDMS.

Further, the uncured PDMS-FCS-\(\text{H}_2\text{O}\)-HMDZ and PDMS-FCS-MeOH-HMDZ composites are investigated for their viscoelastic behavior, by studying their storage and loss modulus, as a function of applied frequencies, as shown in Figure 5.19. Both the
storage and the loss modulus are found to increase with increasing loading of FCS. Though the PDMS-FCS-MeOH-HMDZ-25 exhibits a viscoelastic behavior with $G' > G''$ at all frequencies, $G'$ and $G''$ are found to almost overlap each other in the case of PDMS-FCS-MeOH-HMDZ-40. But, the PDMS-FCS-H$_2$O-HMDZ-25 shows similar $G'$ and $G''$ values at all frequencies and a more solid-like behavior with $G' > G''$ is evident PDMS-FCS-H$_2$O-HMDZ-40. The observed difference in rheological characteristics of uncured PDMS-FCS-H$_2$O-HMDZ and PDMS-FCS-MeOH-HMDZ composites is a clear indication of difference in the interactions of these FCS with PDMS and such difference is attributed to the varying

![Figure 5.19 Viscosity of PDMS-FCS-MeOH-HMDZ and PDMS-FCS-H$_2$O-HMDZ composites.](image)

extent surface functionalization / hydrophobization of CS particles by HMDZ treatment which in turn is reasoned to the use of different precursor CS dispersions (water / methanol). The present results appear to indicate that the surface treatment of CS with HMDZ is not necessarily the same, but can differ based on the precursor medium in which CS particles are originally dispersed when they are prepared. The observed differences can also be attributed to the partial esterification of surface silanol groups of CS with methanol.

5.3.8 Morphological properties of cured PDMS-FCS composites

TEM analyses of cured PDMS-FCS-H$_2$O-HMDZ and PDMS-FCS-MeOH-HMDZ composites is indicative of a relatively improved dispersion of FCS-MeOH–HMDZ, as compared that of FCS-H$_2$O-HMDZ in the composites, irrespective of their loading levels as shown in the Figure 5.20. Such an observation could possibly be
explained by the surface passivation of CS via esterification reaction of surface silanol groups with methanol, in addition to the intended functionalization through HMDZ treatment. Among different composites investigated, those with ~ 40 wt% loading of FCS are found to have optimal dispersion (minimum agglomeration) of FCS and improved dispersion can possibly due to optimal sheer forces while dispersing the CS into the PDMS matrix and the space filling phenomenon, as explained in earlier chapters. At a still higher loading of FCS (55 wt %), the presence of large aggregates as indicated by the darker regions in the micrographs is apparent, possibly due to the forced contact of FCS resulting in more particle-particle interactions, as they are present in an excess amount.

5.3.9 Optical and mechanical properties of cured PDMS-FCS composites

5.3.9.1 Optical characteristics of cured composites

The optical properties of cured PDMS-FCS-H$_2$O-HMDZ and PDMS-FCS-MeOH-HMDZ composites are inferred through % transmittance (% T) and % Haze (% H) data, as shown in the Figure 5.21. In general, the incorporation of FCS particles is found to lower the % T transmittance of PDMS. The PDMS-FCS-MeOH-HMDZ composites are
found to have a relatively higher % T, as compared to that observed for PDMS-FCS-H₂O-HMDZ, irrespective of the loading levels of FCS and such observation is in line with TEM results discussed earlier. Surprisingly, the composites

![Figure 5.21](image)

**Figure 5.21** Percentage transmittance and haze values of PDMS-FCS-H₂O-HMDZ and PDMS-FCS-MeOH-HMDZ composites.

with 40 and 55 wt % of FCS are found have better transmittance, as compared to that observed for the composites with 25 wt% of FCS, irrespective of the type of precursor CS dispersion from which FCS are prepared. Typically, the % T of the PDMS-CS / FCS composites decreases with the increasing loading of CS/FCS in the composites. The observed peculiarly higher % T could possibly be related to the improved dispersion of FCS with PDMS owing to higher hydrophobic characteristic of HMDZ treated FCS and the sheer generated while mixing the composites with higher filler content. Similar to the trends observed with % T, a relatively lower % haze values are evident for PDMS-FCS-MeOH-HMDZ composites as compared those of PDMS-FCS-H₂O-HMDZ composites and in these cases a relatively large variation of haze values is also evident.

**5.3.9.2 Mechanical properties of cured composites**

The trends observed with mechanical properties (tensile strength and % elongation) of the PDMS-FCS composites (Figure 5.22), are in line with the observations made from TEM analyses discussed earlier. In comparison, the PDMS-FCS-MeOH-HMDZ composites are found to possess higher tensile strength and % elongation, as compared to those observed with PDMS-FCS-H₂O-HMDZ composites, irrespective of the loading levels of FCS in the composites.
Figure 5.22 Stress and % E values of PDMS-FCS composites as a function of loading levels.

5.4 CONCLUDING REMARKS

This chapter describes the preparation and the characterization of PDMS-FCS composites obtained with the use of methyl functionalized CS in different dispersions. Prior to the preparation of the composites, methyl functionalized CS particles are characterized by FTIR, TGA and elemental analyses. TGA results indicate the dependence of thermal degradation of FCS on the precursor media in which CS was originally dispersed prior to the functionalization with the use of methyltrimethoxy silane. Among the different FCS investigated, a significant thermal degradation is evident for the FCS-MEK, as compared to that of FCS-IPA and FCS-MeOH. FTIR and elemental analysis indicated a relatively lower extent of functionalization with methyltrimethoxy silane in cases of MEK and IPA dispersions of CS, as compared to that observed with CS dispersed in MeOH, possibly owing to pre-functionalization of CS in cases of MEK and IPA dispersions. Both the loading levels and the type of precursor dispersions are found to have influence on the optical (% T and % haze) and mechanical (tensile strength, % elongation and hardness) properties of the resultant PDMS-FCS composites. While the PDMS composites based on FCS-MeOH possess a relatively higher mechanical and optical properties as compared to those based on FCS-IPA, at a given loading, the composites based on FCS-MEK are not processable under similar experimental conditions. A comparative study on the PDMS-FCS composites prepared with HMDZ treated CS is indicative of improved surface hydrophobicity of HMDZ treated CS, as compared to those treated with methyltrimethoxy silane and subsequently with HMDZ.
Among the two systems studied, HMDZ treatment of CS in methanol led to CS with more hydrophobic surface, in comparison to samples prepared from aqueous dispersion of CS. The mechanical and optical properties of the PDMS-FCS-MeOH-HMDZ composites are also relatively better, as compared to those of PDMS-FCS-Water-HMDZ. Overall, the present study underlines the importance of choosing suitable precursor dispersions of CS despite similar type of functionalization involving the type of functionalizing agent and the conditions of functionalization. The choice of the precursor dispersions of CS can influence the extent of surface functionalization of CS which in turn affects the dispersion of FCS within the PDMS matrix and the reinforcing ability of FCS.