1 INTRODUCTION

The quality and homogeneity in properties of hybrid materials with nano-sized fillers depends highly on the quality of dispersion of the fillers in the matrix. Often, the desired properties of the end-material are achieved with a well dispersed filler. For example, the mechanical and optical properties of particle-reinforced hybrid materials strongly correlate with the dispersion quality of filler in the matrix, and so does the electrical conductivity in CNTs composites. Song and Youn investigated different dispersion states of CNTs in epoxy resins [1] and demonstrated that well dispersed CNTs/epoxy composites showed higher tensile modulus than poorly dispersed ones. In a second study, they could prove that if the CNTs were well dispersed in the epoxy matrix, they could form a conductive three-dimensional network even with low filler contents [2]. The wear resistance of transparent nanoparticle-filled polymer-coatings is also influenced by the particle dispersion in the matrix [3, 4]. Filler-agglomerates in the composite may act as stress concentrators and therefore reduce its tensile strength.

Dispersion quality and means to achieve it in hybrid materials has been the object of many studies reported in the literature. One approach to avoid the formation of agglomerates is by functionalisation of the filler. In order to enhance the dispersion of the filler in the matrix, the particle surface can be chemically modified with a dispersant and therefore sterically stabilize the dispersion [5–8]. Another approach is to break down agglomerates by mechanical shearing. In conventional plastics processing the required shear force to individualize particles in the polymer melt is generated by specially shaped twin-screws or shear rolls [9–12]. Another method to enhance the dispersion quality, reported in references [3, 11, 13], proposes to match the refractive index between the filler and the matrix.

Assessment of the Dispersion Quality of Refractive Index-matched Nanodispersions

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Abstract:
Dispersion quality has a large influence on the resulting properties of filled polymers, hybrids and nanocomposites in general. Reducing the van der Waals forces and therefore, matching the refractive index between the filler and the matrix should improve dispersion in hybrid materials. However, in this case the usual light-based techniques cannot be used to assess dispersion quality. In this work, dispersions containing silica nanoparticles and a solvent mixture of 1-butanol and benzyl alcohol were analysed by rheological methods. The refractive index of the solvent was changed by varying the mixing ratio, and thus the effect of index difference on the filler-matrix interaction was investigated. In agreement with theory, a stronger gel network was observed when the refractive index of filler and solvent were matched. If the difference in refractive index of the two materials became too large, particles and solvent interaction was reduced, and agglomerates were formed. This resulted in a weaker gel network.

Keywords:
Complex rheology, Hamaker constant, refractive index, interface, nanoparticle dispersion
tion is confirmed by the model experiments: The matched system shows the largest value for the ratio of the fitting parameter. The value of $A$ decreases with increasing mismatch of the dispersions. To reach reliable results, resting times of up to 20000 s would be needed. Due to partial evaporation of the solvent, this was not possible with the currently used solvent mixture. However, our values measured at long resting times (> 1800 s) gave valuable information about the network strength, and therefore showed that the method of Galindo-Rosales et al. can be applied to the present system [19].

A further analysis can be carried out considering the position and shift of the crossover point. As presented in Figure 10, the lower resting times show rather unreliable results. Again longer resting times, such as 3600 s, and a better match of the refractive indices of solvent mixture and nanoparticles lead to higher values in deformation at the crossover point. The constant value of strain at crossover for the dispersion with refractive index 1.480 indicates the formation of agglomerates in the mixture and thus no or a weak gel network. Whereas the high or still increasing deformations at crossover of the dispersions with refractive indices 1.470 and 1.460 show the build-up of a strong gel network, which can withstand more strain before breaking up. This is in agreement with Ren et al [31], who stated that the crossover point occurs at higher deformations as the gel network strength increases.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A(G'_{c}) \times 10^3$</th>
<th>$A(G''_{\text{MAX}}) \times 10^6$</th>
<th>$A(G'<em>{c})/A(G''</em>{\text{MAX}})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.460</td>
<td>-145.9 ± 31.7</td>
<td>-15.2 ± 0.8</td>
<td>9.6</td>
</tr>
<tr>
<td>1.470</td>
<td>-71.0 ± 11.3</td>
<td>-9.5 ± 3.4</td>
<td>7.4</td>
</tr>
<tr>
<td>1.480</td>
<td>-49.5 ± 7.2</td>
<td>-10.2 ± 0.9</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Table 3: Fitting Parameters and their ratios according to Galindo-Rosales et al. [19].

4 CONCLUSIONS AND OUTLINE

In conclusion, through model experiments with a series of dispersions with increasing mismatch in refractive indices, we have shown by using rheological methods that matching of the refractive indices of both the filler and the matrix leads to a strong gel network, everything else being similar. Mismatched dispersions, on the other hand, showed a weaker gel network, hence a lower dispersion quality and the probable formation of agglomerates. Furthermore, the particle-solvent interaction was reduced compared to that of the matched system. Therefore, we can conclude that, following theory, van der Waals forces are indeed larger in mismatched systems than in matched ones, and transparent suspensions should lead to better dispersion and stronger network formation. The actual size of the agglomerates could not be determined by traditional methods such as static light scattering and photon correlation spectroscopy, although more specific imaging techniques such as Cryo-TEM might be an option for further investigation. Also, care had to be taken to prevent solvent evaporation during testing. Nonetheless, we have also validated the use of rheological methods to assess quality of dispersions, as rather simple to implement and a macroscopic method of analysis.

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