Characterization of Conductive Nanographite Melamine Composites

Claudia Pretschuh¹, Clemens Schwarzinger¹*, Ahmed A. Abdala², Sulafudin Vukusic²

¹Institute for Chemical Technology of Organic Materials, Johannes Kepler University, Linz, Austria; ²The Petroleum Institute, Abu Dhabi, UAE.
Email: *clemens.schwarzinger@jku.at

Received October 21st, 2013; revised November 21st, 2013; accepted November 28th, 2013

ABSTRACT

Composites based on melamine formaldehyde resins filled with exfoliated graphite or so called nanographite have been prepared to achieve electrical conductivity and improve mechanical strength and thermal stability. The nanographite was synthesized by thermal treatment of oxidized graphite and the incorporation into the melamine matrix was accomplished during the melamine formaldehyde reaction. A homogenous dispersion of the filler in the matrix and the forming of a connecting network based on graphite sheets were proved by SEM images. The graphite filler was able to increase the flexural strength of molded testing specimens compared to unfilled resins and electrical conductivity was achieved starting at 2 wt% nanographite.

KEYWORDS

Nanographite; Melamine; Conductive Melamine Resin

1. Introduction

Conductive polymer composites with fillers like flake graphite, carbon black or metal powder are of great interest due to their functional applications, for example as antistatic material or for electromagnetic shielding. But the mechanical properties of the polymer matrix are often decreased by fillers in micrometer scale. Therefore polymer composites filled with conductive particles in nanometer scale have recently attracted considerable attention. If such a filler is sufficiently homogenous dispersed in the polymer matrix, a conductive network can be formed with a very low filler content.

Natural graphite is often used as conductive filler [1-4] and exhibits a high electrical conductivity (104 S cm⁻¹ at room temperature), derived from delocalized π bonds of sp² hybridized carbon atoms. The natural graphite is consisting of alternating graphene layers bonded by weak Van der Waals forces, offering the possibility for molecules and ions to intercalate between the layers. Thereby the interplanar spacing is increased from 0.335 nm to approximately 0.789 nm [5] and graphite intercalation compounds are obtained. If these compounds are subjected to rapid thermal treatment, the intercalated molecules decompose and expanded graphite, or also called nano-graphite (NG) can be formed. During this exfoliation process, the layer spacing is expanded and the initial volume of the compound is extensively increasing. The layer spacing and accordingly the exfoliation volume are increasing with a higher expansion temperature [6]. The obtained NG is composed of incoherent layers in nanometer scale, so called “nanosheets”, which can sometimes stick together; and it shows functionality due to many pores with different sizes.

Mass-produced NG is used in various fields, for example for batteries, ultracapacitors [7], fire retardants [8], for sealing applications and heating elements [9], and for thermal energy storage [10]. Due to its pore structure and surface functionality, NG additionally turned out to be an adequate filler material for polymers. Therefore, expanded graphite has been used in the last decade as conductive filler for different polymers, like poly(methyl methacrylate) [11-13], polyamide-6 [5], polypropylene [14,15],
polystyrene [16,17], polystyrene acrylonitrile copolymer [18], epoxy resins [19,20], polyphenylene sulfide [21], polyaniline [22] and unsaturated polyester resins [23]. Composites from phenol formaldehyde resins with fillers like graphite powder [1] carbon nanotubes [24] or expanded graphite [25] in order to obtain electrical conductivity have been reported too; however in aminoplastic resins, graphite was not yet applied as conductive filler.

The production of the NG filled composites is usually carried out by an in situ polymerization to improve the dispersion of the NG in the polymer matrix. The dispersion can be supported by ultrasonic treatment. For example, NG can be well dispersed in polar aprotic solvents like N-methyl-2-pyrrolidone, dimethylformamide, dichlorobenzene and tetrahydrofurane (THF) [26].

With increasing filler content, most of the composites showed an improvement in electrical conductivity and some in thermal and mechanical treatments, too. Only 1 to 3 wt% NG [13,16,21-23,25] were needed to reach the percolation threshold, representing the insulator to conductor transition.

In this study, we used NG as conductive filler in melamine formaldehyde resins and as reinforcement material for improved mechanical and thermal properties. Melamine formaldehyde resins are transparent and isolators for improved mechanical and thermal properties. Melamine formaldehyde resins and as reinforcement material cannot be homogenous dispersed in water, so THF was used as solvent. For improved curing, the used melamine to formaldehyde molar ratio was 1 to 3. Curing agents were not added to avoid possibly occurring influences.

100 g melamine with 0.1 - 3 g carbon were suspended—characterized by a change from a white-grey to pH 8) was added. After the melamine was completely dissolved—characterized by a change from a white-grey suspension to a clear black solution, the reaction was carried out for further 15 minutes.

To obtain samples for scanning electron microscopy (SEM) the obtained black resin solution was cured in a drying oven at a minimum temperature of 140°C. To get solid resin particles, the solvent was evaporated under reduced pressure and the obtained residue was powdered and sieved. The obtained grey solid resin particles were then filled into a mould, cold pressed and then cured by hot pressing at 160°C and 2 MPa for 5 - 10 minutes to prepare composite samples for the performance of mechanical tests.
the analysis of graphite oxide and NG.

Scanning electron microscopy (1540 XB Zeiss) was used in order to define the particle size and the structure of NG and to represent its inclusion into the melamine formaldehyde resin. In order to avoid charging, a static inhibitor was added to the melamine formaldehyde resins during their synthesis. The cured resin samples were sputter-coated with gold.

The thermal stability of the NG filled melamine resins was characterized by thermogravimetric analysis (TGA) on a Shimadzu TGA 50 at 20 °C min⁻¹ in helium atmosphere.

Flexural tests on the prepared NG melamine composites were performed on a universal testing machine (Zwick Roell Z1020) in three-point-bending modus. The composites were cut into test specimens with a dimension of 7 cm × 0.8 cm × 0.9 cm. For each set of conditions fifteen specimens were tested at a speed of 2 mm min⁻¹.

The specific electrical resistance of the NG melamine composites was measured by a digital multiplier (Alcron DT 130). An average resistance was calculated by measuring 30 samples.

Mass spectra of the resins were recorded in acetonitrile/water solution on a Thermo Deca XP plus mass spectrometer equipped with an electrospray ionization source in positive mode. HPLC was performed on a Thermo Scientific Surveyor HPLC system with a diode array detector and the Deca XP plus mass spectrometer. Separation was accomplished on a Thermo Scientific ODS Hypersil column (250 × 2.1 mm) using a binary gradient of 0.1% trifluoroacetic acid in acetonitrile/water 4/1 (B): 100% A (1 min) - 95% A (5 min) - 87% A (25 min) - 65% A (30 min) at a flow rate of 200 µL min⁻¹.

3. Results and Discussion

3.1. Characterization of Nanographite

A successful expansion process of graphite, which means that the graphene layers are completely split up, is indicated by four aspects: 1) by a hundredfold volume expansion of graphite oxide after thermal treatment; 2) by an increasing surface area; 3) by an elimination of all diffraction peaks of the NG and 4) by a formation of a porous worm-like nano-structure existing of nanosheets. The graphite was expanded 100 to 150 times and the obtained NG exhibits a specific volume of 200 to 300 m³ g⁻¹ and a specific surface area of 550 to 600 m² g⁻¹ (measured by BET adsorption method). These values for exfoliation are comparable with other studies describing a volume expansion ratio from 200 up to 300 times [21, 29,31] or 50 to 100 times [13] and a surface area of 600 - 800 m² g⁻¹ [26].

XRD was applied for a further determination of the degree of exfoliation. For an expansion it was first necessary to increase the interplanar spacing by oxidation from 0.34 nm to 0.7 nm. The XRD patterns of flake graphite, graphite oxide and expanded graphite (Figure 1) shows the changes in the graphite structure, in particular the increasing of the c-axis spacing. Flake graphite has two strong peaks at 26° and 55° and graphite oxide two weak peaks at 13° and 26°. The peak at 13° results from the increasing of the layer spacing during oxidation and is corresponding to the 0.7 nm spacing, whereas the native peak at 26° decreases. Due to the rapid high thermal treatment, the intercalated molecules were evaporated and the layers were completely split up. The XRD pattern shows this expansion in an elimination of all peaks.

The expanded graphite was obtained as fluffy and highly agglomerating powder. SEM was employed to examine the nanostructure of NG, in order to recognize the size of the graphene sheets and to further characterize the degree of exfoliation. The collapsed layers are observed either as loose and easily agglomerating sheets or are irregular arranged forming a network structure like folded paper with pores of different sizes that indicates the extremely low density of the NG powder. Representative SEM images of NG in different magnifications are shown in Figure 2. The estimated average diameter of an obtained single NG sheet was about 5 µm. The thickness of the nanosheets was in nanometer scale and ranged from 100 to 400 nm. Several groups [13,14,21,23,31] reported similar sheet sizes of 1 - 20 µm and sheet thicknesses ranged from 50 - 100 nm. The structure and size of a NG particle is strongly depending on the degree of exfoliation which is primarily affected by the exfoliation time and temperature. It is referred that a higher temperature leads to smaller particle sizes [6] and further sonication could also reduce the NG particle size [31].
Figure 2. SEM images of NG showing the irregular network structure of NG similar to folded paper (upper); loose but easily agglomerating NG sheets with an average size of about 5 µm (middle); higher magnification shows the graphite nanosheet structure. The graphite was completely collapsed resulting in tiny sheet fragments (lower).
3.2. Characterization of the Melamine Resin

Melamine resins can be characterized very well by simple electrospray ionization mass spectrometry (ESI-MS) [32,33] in just a few seconds or to give more detailed information, especially on the distribution of isobaric structures, HPLC/MS is used. Figure 3 shows the results obtained from both methods and Table 1 lists the components identified. Whereas ESI-MS gives a good overview over the average content of formaldehyde and the degree of condensation, HPLC is necessary to differentiate between the various isobaric structures.

3.3. Characterization of Nanographite Melamine Composites

NG filled melamine formaldehyde resins were prepared and their mechanical, thermal and electrical behavior analyzed. Samples of unfilled melamine formaldehyde resins and samples with activated carbon were produced as reference materials to the resins filled with NG.

SEM was used to present the incorporation of NG in

Figure 3. Upper: ESI-MS of the melamine-formaldehyde resin; Lower: HPLC/UV of the same resin. Structures corresponding to the m/z values are listed in Table 1.
the melamine formaldehyde resin matrix. Figure 3 illustrates samples without carbon and samples with a percentage of 2.5 wt% of activated carbon, 2.5 wt% of NG and a molded sample with 2 wt% NG. The unfilled melamine resins show a glassy surface with intense cracks (Figure 4(a)). By addition of activated carbon a regular distribution of the grains can be observed, but the grains are unlinked and not incorporated into the matrix and cracks still exist (Figure 4(b)). Only by using NG as filler the quantity and size of the cracks could be drastically reduced and the NG sheets are smoothly embedded into the matrix material (Figure 4(c)). The dispersion of NG and its smooth incorporation into the matrix were approved (Figures 4(d) and (e)). Generally graphite nanosheets tend to agglomerate and are difficultly dispersed in polymer matrices, but the figures show that the NG sheets are homogenous dispersed and that they are not strongly agglomerating in the melamine formaldehyde matrix. So the ultrasonication of the NG sheets in THF presents an adequate method for dispersing the sheets previous to the reaction. The monomers can diffuse into the space between the nanosheets during the resin synthesis and the curing and cross-linking of the monomers results in a fixing of the graphite sheets. Because macromolecules need more space than monomers, the graphite nanosheets can be further expanded during the polymerization process [25]. The SEM image of a molded testing specimen containing 2 wt% of NG (Figure 4(f)) proves the interconnecting of the graphite sheets and their building of a conductive graphite network after the hot pressing process. The network of NG sheets is covered and embedded in the melamine formaldehyde resin matrix.

TGA was performed for testing the thermal decomposition of the prepared NG melamine composites. As shown in Figure 5 the addition of NG results in a noticeable enhanced thermal stability. The mass loss of melamine resins up to 450°C is related to further cross-linking of hydroxymethyl groups under release of water and formaldehyde. It can be seen, that the weight loss curves of NG melamine composites appear in this range above the curve of a pure melamine resin. This can be attributed to a slightly inhibited further cross-linking and a prevention of water and formaldehyde release by the presence of the NG network. At 450°C the melamine resins spontaneously pyrolyze and form methylmelamines [32], indicating the largest mass loss. The onset of degradation temperature does not increase with the NG content. At temperatures above 800°C a higher amount of thermally stable char is received by incorporation of NG.

The mechanical properties of NG melamine resins were determined by using the three-point flexure test. The pressing conditions of the composites were optimized in reference to the flexural strength and modulus of the pure melamine formaldehyde resin. Pressing temperature of 160°C and a pressing time of 6 minutes turned out to be practicable. Remarkably the black and with NG filled obtained materials possesses a high density of 1.3 - 1.5 g cm⁻³ compared to 1.1 g cm⁻³ of an unfilled melamine formaldehyde resins. The flexural strength and modulus of elasticity of the melamine resins at different NG loadings are shown in Figure 6. The indicated values for flexure modulus and flexural strength are the average values of fifteen samples for each composition which were referred to the density of the individual testing specimen. It can be seen that the addition of NG increases both the flexural modulus and the flexural strength compared to unfilled resins. NG improves the mechanical properties of melamine resins effectively even at very low loadings, but it is not so successful at higher contents. Although the standard deviations for the tested specimens are rather high, a clear maximum of mechanical strength and

### Table 1. Trivial and IUPAC Names and MH⁺ ions of the melamine resin components.

<table>
<thead>
<tr>
<th>Name</th>
<th>MH⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomethyl melamine</td>
<td>157</td>
</tr>
<tr>
<td>2-(Hydroxymethylamino)-4,6-diamino-1,3,5-triazine</td>
<td>187</td>
</tr>
<tr>
<td>(I)</td>
<td></td>
</tr>
<tr>
<td>Dimethylol melamines</td>
<td></td>
</tr>
<tr>
<td>2-Amino-4,6-bis(hydroxymethylamino)-1,3,5-triazine</td>
<td>217</td>
</tr>
<tr>
<td>(2a)</td>
<td></td>
</tr>
<tr>
<td>2-(Dihydroxymethylamino)-4,6-diamino-1,3,5-triazine</td>
<td>247</td>
</tr>
<tr>
<td>(2b)</td>
<td></td>
</tr>
<tr>
<td>Trimethylol melamines</td>
<td></td>
</tr>
<tr>
<td>2,4,6-Tris(hydroxymethyl)amino-1,3,5-triazine (3a)</td>
<td>277</td>
</tr>
<tr>
<td>2-Amino-4-(hydroxymethylamino)-6-(dihydroxymethyl)amino-1,3,5-triazine (3b)</td>
<td></td>
</tr>
<tr>
<td>Tetramethylol melamines</td>
<td></td>
</tr>
<tr>
<td>2,4-Bis(hydroxymethylamino)-6-(dihydroxymethyl)amino-1,3,5-triazine (4a)</td>
<td>307</td>
</tr>
<tr>
<td>2-Amino-4,6-bis(dihydroxymethylamino)-1,3,5-triazine (4b)</td>
<td></td>
</tr>
<tr>
<td>Pentamethylol melamine</td>
<td></td>
</tr>
<tr>
<td>4,6-Bis(dihydroxymethylamino)-2-(hydroxymethyl)amino-1,3,5-triazine (5)</td>
<td></td>
</tr>
<tr>
<td>Hexamethylol melamine</td>
<td></td>
</tr>
<tr>
<td>2,4,6-Tris(dihydroxymethylamino)-1,3,5-triazine (6)</td>
<td></td>
</tr>
</tbody>
</table>
Characterization of Conductive Nanographite Melamine Composites

Figure 4. SEM images of (a) An unfilled melamine formaldehyde resin showing a completely smooth surface apart from intense cracks; (b) A melamine formaldehyde resin filled with 2.5 wt% of activated carbon. It is observable that the surface is not smoothly but equipped with the activated grains supporting further cracks; (c) Melamine formaldehyde resin filled with 2.5 wt% NG. The graphite is sufficiently homogenous dispersed in the melamine formaldehyde resin matrix, the surface appears smooth and intense cracks are generally reduced resulting in less breaking of the materials; (d) and (e) Melamine resins filled with 2.5 wt% NG showing its incorporation into the matrix material. The sheet structure and the pores of NG are apparent. It is observed that the resin matrix diffuses between the graphite sheets. The inclusion of NG is not resulting in cracks; (f) Fracture surface SEM image of molded and conductive testing specimen filled with 2 wt% of NG presenting the forming of an effective conductive graphite network in the melamine formaldehyde resin matrix.
Characterization of Conductive Nanographite Melamine Composites

Figure 5. TGA curves of melamine formaldehyde resins unfilled and filled with 1.8 wt%, 2.5 wt% and 3 wt% of NG. The NG containing resins show a slightly improved heat resistance between 200°C and 300°C compared to the reference sample of a pure melamine resin.

Figure 6. Flexural strength and flexural modulus of graphite melamine formaldehyde resins as a function of NG content. The addition of NG leads to increased mechanical properties. Maximum flexural strength and a maximum flexural modulus are obtained at NG percentage between 1 - 1.5 wt%.

The modulus at 1.0 - 1.5 wt% graphite load can be found. A maximum flexural modulus of 2500 MPa and a flexural strength of 12 MPa are obtained. Usually different forms of wood particles are used as filler for aminoplastic resins and a content of more than 30 wt% wood is normally necessary for similar mechanical strength. In comparison with unfilled melamine formaldehyde resin testing samples show an average flexural modulus of 1250 MPa and flexural strength of 4 MPa. This enhancement of mechanical strength at low NG filler content is a result of the extremely high specific volume of the NG filler and the forming of a stable graphite sheet network in the resin.
matrix. The decreasing flexure strength at NG content above 1.5% is potentially caused by an inhibition of sufficient matrix cross-linking by the presence of agglomerating graphite sheets. Maybe the melamine resin matrix cannot sufficiently diffuse into the pores of the graphite network at these high filler values.

The most important effect of NG addition is observed in electrical conductivity. Nanocomposites with excellent electrical conductivity were prepared by our process. In general melamine formaldehyde resins are insulators like most polymers. The introduction of NG offers the possibility of electrically conductive melamine resins. At low filler contents (less than 2 wt%) the conductivity was still negligible and similar to that of an insulator. But at slightly higher filler contents the composites show an abrupt transition from not measurable conductivity to conductivity similar with that of a semiconductor. The sharp increase in conductivity is of particular importance. The transition occurs at a defined filler content known as the percolation threshold. According to the classical percolation theory [34] the percolation threshold corresponds to the onset of the transition from an insulator to an electrical semiconductor. Percolation is seen as a highly change in the effective permittivity of a mixture of spheres. Percolation threshold occurs when the macroscopic permittivity starts to increase rapidly when the mixture is completely filled with inclusions. Bruggeman’s mixing formula [35] for the effective permittivity of a mixture of spheres show percolation threshold as high as at a volume filling ratio around 0.3 [36].

The average values of the measurable electrical conductivity and the resistance of the graphite melamine composites depending on the NG filler content are shown in Table 2. Silver coated fracture pieces of the prepared material testing specimens were used as testing material. The measurements were accomplished on 30 fragments for each sample at room temperature and the measured electrical resistance was related to the dimensions of the individual samples. The melamine composites indicated electrical conductivity by starting from 2 wt% NG. In Table 2 it is shown that the electrical conductivity increases and the specific electrical resistance of the composites decreases with increasing NG filler content. Conductivity of $6.6 \times 10^{-4} \text{ S/cm}$ was achieved for melamine composites containing 2 wt% NG corresponding to a specific resistance of $15.2 \mu \Omega \text{m}$. When 3 wt% NG were incorporated into the melamine resin the electrical resistance of the prepared composites was $3.9 \Omega \text{m}$ and the conductivity of the composites at 3 wt% NG reached about $2.6 \times 10^{-3} \text{ S/cm}$, one magnitude higher than with 2 wt%. Lower filler percentages than 2 wt% NG are not presented in the table because the conductivity of NG composite with a graphite content of 1.8 wt% was out of the detectable range of the used instruments. Therefore the electrical conductivity of the resins must have been increased in order of a few magnitudes by the addition from 1.8 wt% NG to 2.0 wt% NG. So this suggests that the NG melamine composites exhibit a percolation threshold lower than 2 wt%. Whereas prepared melamine composites filled with 3 wt% activated carbon did not show electrical conductivity.

The enormous increase in conductivity by addition of NG already at low loading levels is obvious. The high conductivity can be explained in agreement with the percolation theory by a well dispersion of the graphite nano sheets and their formation to a conducting network in the melamine resin matrix. The very low percolation threshold is indicating that the NG sheets were sufficiently dispersed as proved by SEM images and the graphene sheets gives a completely connecting network at low filling levels. Conductive bridges and network structures can be easier formed when the graphite sheets are better dispersed.

Similar results were reported for the percolation threshold of NG composites prepared with other polymers. Lower percolation thresholds around 1.0 - 1.5 wt% expanded graphite were referred for composites based on unsaturated polyester [23], for polyaniline composites [22], polystyrene composites [16,31] and poly(methyl methacrylate) composites [13]. Percolation threshold of 2 wt% graphite were described for composites on polyphenylene sulfide [21] and a percolation threshold at 3 wt% for thermosetting phenol formaldehyde resin composites [25]. This result shows that NG melamine composites exhibit a lower percolation threshold than phenol formaldehyde composites filled with expanded graphite.

The percolation threshold depends further on the geometry of the conducting fillers. Fillers with elongated or expanded geometry like fibers or sheets possess lower percolation thresholds because they can better form conducting networks in a polymer matrix. Therefore it is obviously that composites with expanded nano graphene sheets require a much lower percolation threshold than composites with activated carbon or graphite powder. In comparison, polystyrene composites filled with graphite powder exhibit a significantly higher percolation threshold of 6 - 7 wt% [16,31]. Poly(methyl methacrylate) composites filled with graphite powder show a percolation threshold below 5 wt%, whereas carbon filled poly (methyl methacrylate) composites possess a threshold as

### Table 2. Specific electrical resistance and electrical conductivity of graphite melamine resin composites.

<table>
<thead>
<tr>
<th>NG [%]</th>
<th>Specific resistance [Ωm]</th>
<th>Conductivity [S·cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>15.2</td>
<td>$6.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>2.5</td>
<td>14.5</td>
<td>$6.9 \times 10^{-4}$</td>
</tr>
<tr>
<td>3.0</td>
<td>3.9</td>
<td>$2.6 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
high as 8 wt% [13].

4. Conclusions

NG sheets are prepared by thermal treatment of graphite oxide at 900°C and exhibit a specific volume of 300 mL·g⁻¹ and a specific surface area of 600 m²·g⁻¹. Graphite oxide as intercalation compound was obtained by oxidation of graphite with potassium chlorate in concentrated sulfuric and nitric acid. Due to the intercalation of oxygen containing groups, the interplanar spacing of the graphite layers was increased according to XRD. SEM images show that the NG sheets possess an average diameter of 5 µm and a thickness of about 100 nm.

Melamine nanocomposites consisting of NG sheets were successfully produced by an in situ process. NG was added during the melamine formaldehyde reaction by using THF as solvent. The homogenous dispersion of NG and its smooth incorporation into the melamine matrix were approved by SEM images. In contrast to unmodified NG and its smooth incorporation into the melamine matrix, the composites show a higher density, significantly increased mechanical strength and increased thermal stability compared to unmodified resins. Furthermore the composites show a higher density, significantly increased mechanical strength and increased thermal stability compared to unmodified resins.

REFERENCES


Characterization of Conductive Nanographite Melamine Composites

http://dx.doi.org/10.1016/S0002-3861(00)00819-3


