Electrical/dielectric measurements for monitoring polymerization, morphology and mechanical integrity in polymer nanocomposites


Abstract

Electrical and dielectric measurements are a powerful tool for following in real time physical and chemical processes, evolution of morphology and mechanical integrity in complex polymeric systems. Here we employ electrical dc measurements and broadband dielectric spectroscopy (DS) to follow the state of polymerization and curing processes in polymer/clay nanocomposites and the quality of filler dispersion, alignment and integrity of carbon nanotubes (CNTs) in various polymer/CNT nanocomposites, focusing on fundamental aspects of the various processes involved.

1. Introduction

The use of DS for monitoring in real time physical and chemical processes in polymeric systems, in particular the state of polymerization and curing, is based on the significant changes of dielectric properties (dielectric function, time scale and strength of the various relaxations present) with the evolution of these processes [1, 2]. The broad frequency range available enables to follow at the same time relaxation processes with very different time scales, which implies also very different spatial scales, from local (secondary) processes over segmental processes to interfacial polarization processes. Thus, the broad frequency range of DS provides the basis for following in real time the evolution of morphology. In many cases also electrical conductivity shows significant changes with the evolution
of the processes mentioned above, rendering dc measurements, which are less sophisticated with respect to equipment and modeling, a valuable and promising tool for industrial applications. Electrical dc measurements may also provide information on morphology, as the moving charge carriers (typically ions) probe local morphology.

In polymer composites and nanocomposites with conducting fillers, such as carbon materials and metal particles, conductivity changes significantly with the dispersion and agglomeration of fillers, which forms the basis for using dc or ac conductivity measurements for assessing the quality of filler dispersion [3], including also alignment of anisotropic conducting fillers, such as carbon nanotubes (CNTs), induced by preparation and processing of the composites [4]. This is particularly true for compositions near and above the percolation threshold, i.e. the composition where the first conducting path is formed and the transition insulator – conductor occurs. It is interesting to note, however, that significant changes of dielectric properties with composition occur also below the percolation threshold due to polarization processes related with the size and shape of filler agglomerates. Finally, the same intrinsic conductivity of fillers and changes of the overall conductivity with the evolution of damage (breaking of conducting paths) are utilized in using the composite itself as sensor (self-sensing) for structural health monitoring [5, 6]. If the filler used for reinforcement is non-conducting, e.g. glass fibers, addition of a small amount of conducting filler, typically CNTs or carbon black (CB), at a fraction above the percolation threshold, may provide the necessary conductivity. In addition to health monitoring based on changes of the overall conductivity during strain and damage, capacitance sensors may be used [5, 6], where the changes of capacitance of the sample during deformation are utilized.

Despite much work in the past, several questions are still open in the topics mentioned above. Here we present results of recent work and work in progress in the use of electrical dc measurements and broadband DS to follow polymerization and curing in polymer/clay nanocomposites, as well as quality of filler dispersion, alignment and structural integrity of the filler itself in various polymer/CNT nanocomposites. We focus on selected examples with particular emphasis on fundamental questions about the processes involved and routes for optimizing composition and processing conditions, rather than specific results of interest for the one or the other polymeric system or application.

2. Experimental

Commercial equipment was used for measuring dc conductivity and dielectric function against time in the course of evolution of the various processes mentioned above in several polymeric systems, including polymerization and curing in nanocomposites of polycyanurate ester and layered silicates (PCN/clay) and quality of filler dispersion in nanocomposites of polypropylene and CNTs (PP/CNT). We refer to previous work for details of the preparation and characterization of the PCN/clay [7] and the PP/CNT [3] systems by various experimental techniques, including dc conductivity and broadband DS. Alignment of CNTs was studied by dc conductivity measurements (next to electron microscopy and Raman spectroscopy) in nanocomposites based on poly(ether ether ketone) (PEEK) and CNTs prepared and processed by various methods. Finally, structural integrity of CNTs, in particular possible damage/breaking during melt processing, was studied by broadband DS (next to electron microscopy) in nanocomposites based on poly(ether ketone) (PEK) and CNTs.

3. Results

3.1. Polymerization and curing of PCN/clay nanocomposites

Polymerization and curing in PCN/clay nanocomposites, using special comb electrodes as sensors, was followed in real time by DS at selected frequencies between 1 kHz and 1 MHz at several temperatures of interest using HP4284A LCR meter in combination with a dielectric sensor IDEX-036S (NETZSCH). The frequencies of measurements were selected rather high in order to ensure fast response. More specifically, the real (G) and the imaginary (B) part of the ac conductance were recorded as functions of time at the frequencies of 1, 10, 100, 500, and 1000 kHz. Fig. 1(a) shows a scheme of the polymerization of the cyanate ester used, whereas a scheme of the dielectric sensor inside the test tube filled with the material under investigation is shown in Fig. 1(b). Examples of measurements (raw data) are shown in Fig. 2 for the neat cyanate ester B10 at the frequency of 1 MHz and several temperatures. Please note that G is the conductance (actually the real part, as mentioned above), whereas B/ω is the capacitance (ω
is the angular frequency of measurement). The peak in $G(t)$ in Fig. 2(a) corresponds to the segmental $\alpha$ relaxation (dynamic glass transition).

The degree of conversion, the gelation time and the vitrification time were calculated from the dielectric data. Using the data in Fig. 2(b), the conversion $\alpha(t)$ was calculated by means of the following equation.

$$\alpha(t) = \alpha_m \frac{\log(\omega / B(t)) - \log(\omega / B_0)}{\log(\omega / B_m) - \log(\omega / B_0)}$$

In this equation $B/\omega$ is the capacitance, $t$ refers to the time of measurement, $m$ to a time just before vitrification, and $0$ to initial time. As an example, Fig. 3(a) shows $\alpha(t)$ for the neat cyanate ester B10 at several temperatures. Fig. 3(b) illustrates again at the example of neat B10 the procedure followed for estimating the gelation time ($t_{gel}$) and the vitrification time ($t_{vitr}$) from the dielectric data.

The methodology described above was followed to study polymerization and curing in several PCN/clay nanocomposites by varying the type (organic modification) and the fraction of clay. The results indicate and allow quantifying the catalytic action of clays, depending on the type of the organic modification used, in good correlation with the results of FTIR and DSC measurements for the same materials in a previous study [7]. Of particular importance for following the evolution of morphology proved interfacial polarization and relaxation processes, arising from the accumulation of charges at the boundaries of phases with different electrical and dielectric properties. Electrical dc measurements (characterized by simplicity and low cost) for the same materials and temperatures were less conclusive with respect to the quantities mentioned above.

3.2. Quality of dispersion and alignment of CNTs

For monitoring the quality of filler dispersion ac conductivity measurements were performed in PP/CNT nanocomposites at fixed compositions and different conditions of mechanical melt mixing (temperature, speed and time of mixing). The results show that changes of ac conductivity with mixing conditions are particularly pronounced at compositions around the percolation threshold, which are also the compositions of interest for many practical applications. An example of measurements is shown in Fig. 4(a). The CNT fraction in this particular example is rather high, so that for all sets of conditions in Fig. 4(a) the mixture is conductive. This is indicated by the appearance of the plateau, i.e. independence of conductivity from the frequency [3]. The plateau value is the dc conductivity, which changes significantly with mixing conditions, reflecting the quality of CNT dispersion. At the same time, the
frequency of change from dc to ac conductivity shifts to higher frequencies with increasing level of dc conductivity and quality of CNT dispersion. Thus, the frequency of change from dc to ac conductivity may be evaluated as an independent measure of the quality of filler dispersion, which is obviously not provided by dc conductivity measurements.

**Fig. 2.** Conductance G (A) and capacitance B/ω (B) at 1 MHz versus time during isothermal curing of B10 at various temperatures indicated on the plot.

It is well established that CNTs act as nucleating agents in the case of a semicrystalline polymer matrix [3], such as PP. Results of DSC measurements in PP/CNT nanocomposites show that the crystallization temperature T_c shifts to higher temperatures in the nanocomposites, reflecting the quality of filler dispersion [3]. The advantage of electrical/dielectric measurements against DSC measurements for monitoring the quality of filler dispersion is that they may be easily used for the on line monitoring during mixing. On the other hand, electrical/dielectric measurements are limited to conducting fillers, this limitation being not necessary in the case of DSC measurements, provided the filler act as nucleating agent increasing the rate of crystallization.
The alignment of CNTs was studied at the example of PEEK/CNT nanocomposites with 3 wt% CNT prepared by calendaring, a special preparation/processing technique, which may promote alignment of CNT parallel to the direction of calendaring [8]. Golden strips were sputtered on the surface of a PEEK/CNT sheet and surface resistance was measured between two parallel strips for different orientations with respect to the calendaring axis. Volume conductivity was measured by using the silver painted opposite faces of the sample cross section as electrodes. For multiple measurements the electrode configuration depicted in Fig. 4(b) proved very effective. Results of measurements of surface resistance between the central electrode and a second electrode on the circumference are given on the plot. Despite scattering of the values, probably related with spatial heterogeneities, alignment of CNTs parallel to the calendaring axis becomes obvious from these and similar measurements, in agreement also with SEM images obtained with the same samples. Please note that Raman spectroscopy could not be used for studying alignment of CNTs in the samples under investigation, due to strong phosphorescence of the commercial PEEK matrix, obviously arising from additives. Quantification of alignment on the basis of the electrical measurements is still under investigation.

![Graph showing conductivity versus frequency for PP/CNT nanocomposites containing 5.3 wt% MWCNT and prepared under various conditions.](image)

**3.3. Structural integrity of CNTs**

Structural integrity of CNTs, in particular possible damage/breaking during melt processing, was studied by broadband DS (next to electron microscopy) in PEK/CNT nanocomposites prepared by hot compaction before calendaring (270°C, 200MPa). Two-electrode configuration measurements were performed on circular samples with gold sputtered circular electrodes on opposite sides using an Alpha Analyzer (Novocontrol).

Fig. 5(a) shows results of measurements at different CNT weight fractions. Values of dc conductivity (plateau values) were then used for the analysis in terms of percolation shown in Fig. 5(b). Using the well-known equation from percolation theory

\[
\sigma_{dc} \propto (\phi - \phi_c)^t
\]

where \(\sigma_{dc}\) is the dc conductivity, \(\phi\) is the volume fraction of the filler, and \(t\) is a critical exponent related with the dimensionality of the investigated system, \(\phi_c=0.13\) vol% (corresponding to \(p_c=0.17\) wt%) was obtained.

The Garboczi model [9] was then employed to study possible damage (breaking) of CNT during processing. This model defines the intrinsic conductivity of a conducting filler in an insulating matrix as
where $\sigma_{\text{red}}$ is the reduced conductivity given by

$$
[\sigma_{\text{red}}] = \frac{\sigma_{\text{eff}} - \sigma_m}{\phi \cdot \sigma_m}
$$

In the above equation, $\sigma_{\text{eff}}$ is the conductivity of the composite, $\sigma_m$ is the conductivity of the matrix, and $\phi$ is the filler volume content. In Fig. 6 the reduced conductivity of the nanocomposites which are above the percolation threshold is plotted against the volume fraction of CNTs. The intrinsic conductivity $[\sigma]$ is then determined by a linear extrapolation of the reduced conductivity to zero volume fraction to $[\sigma] = 9 \times 10^4 \text{S/cm}$. Using the following equation

$$
[\sigma] = \frac{(l/d)^2}{\ln(l/d)}
$$

we obtained then for the aspect ratio of the CNT in the nanocomposites $l/d = 770$. With the value for $d = 9.5 \text{nm}$ for the mean diameter given by the producer (Nanocyl), the mean CNT length is estimated to $l \approx 7.3 \mu \text{m}$, which is of the same order as that given by the producer, $1.5 \mu \text{m}$.

The value calculated above for the percolation threshold, $\phi_c = 0.13 \text{vol}\%$, is very low, especially for a nanocomposite based on a semicrystalline thermoplastic matrix [3], indicative of good dispersion and little or no shortening of CNTs during processing. The estimated values of aspect ratio and of CNT length even exceed those given by the producer for the initial CNTs, which can be explained by the approximate character of the equations used.

Finally, possible attrition of CNTs in the same PEK/CNT nanocomposites was investigated on the basis of a model proposed by Li et al. [10]. According to this model, both individual, perfectly dispersed CNTs and CNT agglomerates usually co-exist in a nanocomposite. Thus, the percolation threshold of such a nanocomposite can be expressed by

$$
\phi_c \approx \frac{\epsilon \pi d}{6} + \frac{(1 - \xi) 27 \pi d^2}{4 l^2}
$$

where $\epsilon$ is the localized volume content of CNTs in an agglomerate and $\xi$ is the volume fraction of agglomerated CNTs. Assuming $\epsilon = 0$ in our nanocomposites, on the basis of the extremely low percolation threshold, we have

$$
\phi_c \approx \frac{27 \pi d^2}{4 l^2}
$$

With $\phi_c = 0.13 \text{ vol}\%$ estimated above, we get $l/d \approx 128$ and from that $l \approx 1.2 \mu \text{m}$, which is very close to the value of $1.5 \mu \text{m}$ given by the producer (Nanocyl) for the initial CNTs. Thus, the results of the analysis indicate little or no attrition of CNTs for the PEK/CNT nanocomposites during the processing described above.
Fig. 5. (a) Real part of ac conductivity $\sigma'$ versus frequency $f$ measured at room temperature for PEK/CNT nanocomposites with the CNT weight fraction indicated on the plot. (b) dc conductivity $\sigma'$ versus CNT volume fraction for the samples in (a).

Fig. 6. Reduced conductivity against CNT fraction for the PEK/CNT nanocomposites of Fig. 5 (for $\sigma_m=10^{-15}$S/cm).

4. Conclusion

The results presented provide additional support for the suitability of electrical dc and DS measurements for following in real time physical and chemical processes, evolution of morphology and mechanical integrity in complex polymeric systems. At the same time, the results indicate the need for additional basic research on the various aspects of the processes involved for optimizing the conditions of measurements and the methods of data analysis.

Acknowledgements

This research has been co-financed by the European Union (European Social Fund, ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF). Research Funding Program: THALES.
References


