

# Electron Spin Resonance on polyurethanes – Vapor grown carbon nanofiber composites



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## ABSTRACT

Electron Spin Resonance investigations on polyurethane – vapor grown carbon nanofiber composites are reported. The research focuses on the free radicals generated during the processing step and on the ESR spectrum of the conducting electrons delocalized over the carbon nanofiber. The deactivation of free radicals due to their interaction with the electrons residing on carbon nanofiber was analyzed and related to the enhanced stability of these composites. The dependence of the resonance line parameters on the concentration of the nanofiller is studied in detail. Experimental data indicates that the electrical conductivity is due to uncoupled electrons delocalized over the conducting domains of the nanofiller and suggests that the electrical conductivity is dominated by polarons. The percolation of the electrical conductivity is also reflected in the ESR data. The interactions between uncoupled electronic spins, as revealed by the line width dependence on the concentration of carbon nanofibers are discussed in detail.

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## 1. Introduction

Polyurethanes are extremely interesting materials due to their shape memory capabilities [1]. The addition of carbon nanotubes or nanofibers enhances their mechanical properties (and in particular increases of the Young modulus [2,3,4], hardness [5], elongation at break [2,4], and stress at break [4]), improves the thermal conductivity [6,7], augments the thermal stability of the polymeric matrix [4,6,8], and adds electrically conducting capabilities [7,9,10]. High concentration of carbon nanotubes (typically above 10% phr; where phr stands for parts per hundred parts of matrix, which frequently is a resin) may result in the decrease of the elongation at break. Typically, the tensile strength is enhanced as the loading is increased [2,5,8]. However, nanofillers may destroy or lower the memory shape capabilities of the polymeric matrix.

Electron Spin Resonance (ESR) spectroscopy is a powerful technique in the study of uncoupled electronic spins (such as free radicals and conducting electrons residing on carbon nanotubes or nanofibers) [11]. The ESR spectrum reflects the resonant absorption

of energy from an ensemble of uncoupled electronic spins placed in a magnetic field of intensity  $H$ . The energy is absorbed from the magnetic component of an electromagnetic field of frequency  $\nu$ . For most commercially available spectrometers, the frequency lies in the microwave range (X band or  $9 \times 10^9$  Hz). The consequence of this resonant absorption is the flip of the electronic spin. The resonant condition equals the splitting of the energy level (Zeman levels) in the external magnetic field to the energy of the electromagnetic radiation;

$$h\nu = g\mu_B B$$

where  $h$  is the Planck's constant,  $\mu_B$  is the Bohr's magneton for the electron,  $B$  is the intensity of the external magnetic field, and  $g$  is the so called  $g$  factor, Lande factor, or gyromagnetic factor. For a free uncoupled electronic spin, without relativistic corrections  $g = 2.00$ .

The study of conducting electrons by ESR is frequently referred as Conduction Electron Spin Resonance [11,12]. Typically, the ESR spectrometer records both the spectra of free radicals and of conduction electrons, if both are present in the system under investigation. ESR spectroscopy has just recently started to be utilized in the study of carbon-based nanostructures, as cleaner materials became available [13]. Early carbon nanostructures contained an important fraction of magnetic residues originating from catalyst's

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residues [14]. In many cases, the ESR spectrum of carbon nanostructures is a convolution of spectra originating from magnetic impurities, free radicals (paramagnetic defects) in the graphitic component, and delocalized conduction electrons [13,10].

Recent studies revealed that multiwalled carbon nanotubes acts as free radical scavengers in irradiated polymer-based nanocomposites [15–18]. The possibility of interactions between the electronic spins delocalized over carbon nanotubes and the electronic spins of a conducting polymer (region regular poly 3 hexylthiophene) has been suggested [19].

This research is focused on ESR investigations on polyurethane – vapor grown carbon nanofibers (PU-VGCNF) composites, in a tentative to understand the role of free radicals in the stability of these composites and to obtain additional information about the electrical conduction in these nanocomposites.

## 2. Experimental methods

The polymeric matrix is Irogran PS455-203 purchased from Huntsman Polyurethane. According to the manufacturer, Irogran has a density of  $1190 \text{ kg/m}^3$ , a glass transition temperature of  $-45^\circ\text{C}$ , and a melting temperature of  $48^\circ\text{C}$ , as measured by DSC.

The filler of choice is the vapor-grown carbon nanofiber (PR-19-HHT) from Applied Science Incorporated. Vapor grown carbon nanofibers (VGCNFs) have a density of  $2100 \text{ kg/m}^3$ , an average diameter of about  $100 \text{ nm}$  and an average length greater than  $10 \mu\text{m}$ , as determined from scanning electron microscopy. PR-19-HHT contains 99.9% carbon with hydrogen, nitrogen and catalyst residues (iron) levels below 0.1%, 0.1% and 0.024%, respectively.

Nanocomposites PU-VGCNFs have been obtained by solution mixing using a stirring device operating at 14,000 rotations per minute.

ESR spectra have been obtained by using a Bruker JEOL-ESR spectrometer operating in X-band (at about  $10 \text{ GHz}$ ). The as received pristine PU polymer does not show any ESR spectrum (within the experimental errors). The ESR spectrum of pristine processed PU (PPU), is actually originating from pristine PU after being subjected to the same processing conditions as the as obtained PU-VGCNF nanocomposites.

## 3. Experimental results and discussions

The research focuses on the free radical generation during the synthesis/processing of PU-VGCNF composites and on the analysis of the ESR spectra of VGCNF dispersed within PU (actually CESR spectra).

### 3.1. Free radicals in PU-VGCNF composites

The spectrum of PPU is shown in Fig. 1. The resonance spectrum is weak and the hyperfine splitting is not very well resolved. The symmetry of the spectrum suggests that it originates either from an uncoupled electronic spin ( $S = 1/2$ ) delocalized over  $I = 1$  nuclei or from an uncoupled electronic spin delocalized over an even number of nuclear spins characterized by  $I = 1/2$ . The degradation of PU under various conditions suggested the following free radicals: a)  $\cdot\text{CH}_2\text{-CH}_2\text{-}$  free radicals where “” identifies the uncoupled free electrons. Such a structure is responsible for a five-line ESR line with an intensity ratio 1:3:1:3:1 and a hyperfine splitting of  $2.5 \text{ mT}$  [20]. Both the hyperfine spectrum structure and the hyperfine splitting constant are not compatible with the as recorded spectrum (in this case the central line should be a weak line). b)  $\cdot\text{CH}_2\text{-CH}_2\text{-}$  free radicals with an intensity ratio 1:4:6:4:1 and a hyperfine splitting of  $2.5 \text{ mT}$  (assuming equal alpha and beta splitting [20]). The structure of the spectrum can explain the recorded ESR

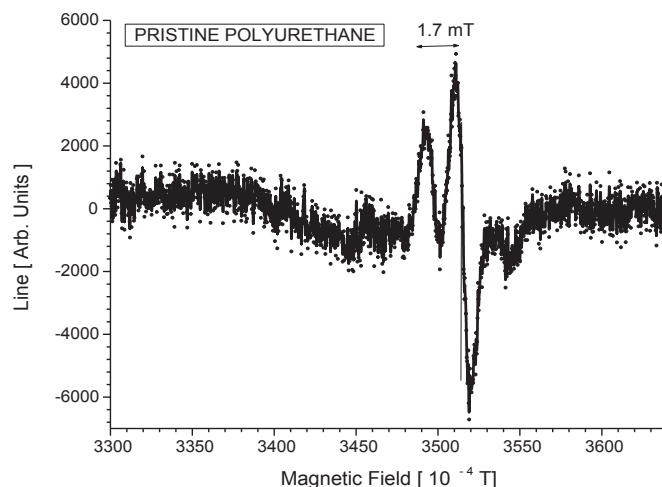


Fig. 1. The ESR spectrum of the pristine polymer (PPU) subjected to the same processing conditions as all PU-CNF nanocomposites.

spectrum but the value of the hyperfine splitting is too large. c)  $\cdot\text{NH-}$  or  $\cdot\text{N-O-}$  free radicals, responsible for a triplet spectrum with a hyperfine constant of about  $1.7 \text{ mT}$  and intensity ratio of 1:1:1. However, in polymers, a differential broadening mechanism affects the extreme lines, which are becoming smaller and broader [21]. Both the hyperfine splitting and the differential broadening are consistent with a free radical where the uncoupled electronic spin is delocalized over a  $^{14}\text{N}$  nucleus, characterized by a nuclear spin  $I = 1$ , an isotropic hyperfine splitting of about  $1.7 \text{ mT}$ , and a natural abundance of about 93% [11]. It is speculated that the generation mechanism for such free radicals is the cleavage of the N–H bond [22].

In PU-VGCNF nanocomposites that contain a low concentration of filler (VGCNF), this weak signal is still observed. The intensity of this line decreases as the VGCNF content is increased due to two competing processes: 1. Some of the free radicals generated within the polymeric matrices during the processing step are deactivated by the collisions of the macromolecular segments (that carry these radical states) with the carbon nanofibers via the recombination of the free radical with a delocalized free electron. 2. The fraction of polymer that contributes to the resonance line is decreasing while the fraction of VGCNF is increased.

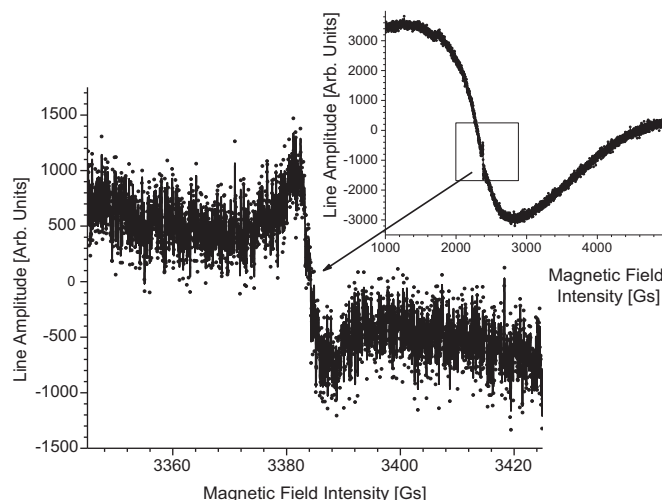


Fig. 2. The ESR spectrum of CNF, where  $10,000 \text{ Gs} = 1\text{T}$ .

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