Dispersion and interaction of graphene oxide in amorphous and semi-crystalline nano-composites: a PALS study

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Abstract. The influence of dispersion and interaction of Graphene Oxide (GO) in semi-crystalline Polyhydroxy butyrate (PHB) and glassy amorphous Poly(tBP-oda) is explored by Positron Annihilation Lifetime Spectroscopy (PALS). The ortho-Positronium lifetimes which represent the main free volume hole size of both polymers are mainly affected by the large differences in internal stresses built up by the shrinkage of the polymers during their preparation, restricted by the platelet structure of GO. The ortho-Positronium intensities, which represent the ortho-Positronium formation probabilities, suggest a strong dependency on the dispersion of the nano-particles and their aspect ratio.

1. Introduction
Two different types of polymers are mixed with Graphene Oxide (GO) to modify their physical properties. The first type, PHB, is a naturally occurring biodegradable semi-crystalline polyester which is produced by bacteria. The second type, glassy amorphous poly(tBP-oda), belongs to the group of Polybenzoxazines which are formed after self-activated polymerization of benzoxazine monomers at high temperatures. Physical properties of both polymers and their nano-composites as a function of GO content are presented elsewhere [1, 2]. Common feature of both systems is the forming of a network structure by the GO particles, characterized by an equilibrium modulus in the melt state for PHB and monomer liquid state for poly(tBP-oda). Two different onsets of percolation volume fractions result from the mixtures of GO in the two polymers.

GO exhibit excellent properties as a nano-filler. High aspect ratio (lateral size on the order of 1 µm and thickness in the order of 1 nm), a Young’s modulus in the range of 200 GPa, and a versatile surface chemistry, possesses a high potential to effectively modify the physical properties of polymer nano-composites. The purpose of this contribution is to search for correlations between structural characteristics of the nano-composites and parameters resulting from Positron Annihilation Lifetime Spectroscopy (PALS) such as ortho-Positronium lifetimes \( \tau_{\text{o}} \) and ortho-Positronium intensities \( I_3 \). The thickness of the GO platelets are in the nm range, suggesting an interaction of GO with radiation chemistry effects in the terminal spur of the positron thermalization track in the nano-composites at low volume fractions.
2. Materials and experimental
GO was prepared according to the procedures of the modified Hummers method from graphite flakes, exfoliated for the PHB nano-composites and dried in an oven at 130 °C [1]. Samples for PALS measurements of PHB nano-composites were compression moulded at 180 °C for 2 min. The detailed description of the preparation of the (tBP-oda) samples is reported elsewhere [2]. The mixtures (150 mg) were pressed into discs with a diameter of 15 mm using a support of a Teflon disc of 2 mm thick and the same diameter. The crosslinking reaction was completed by placing the discs in an oven while heating them in sequences at 100, 120, 140, 160, 180, and 200 °C for 2h each. After cooling to room temperature, the samples were separated from the Teflon support. Standard PALS spectra were collected with about 1.5 million counts per spectrum at 22°C. Five Spectra per sample were recorded and average values of three lifetime components were established with PALSfit. Only averaged ortho-Positronium lifetimes and intensities are reported here.

3. Results and discussion
Figure 1 shows the influence of GO content on the ortho-Positronium lifetime of PHB and poly(tBP-oda). The τ values of the unfilled polymers are 2.33 ± 0.02 for PHB and 1.96 ±0.02 for poly(tBP-oda) respectively. The glass transition temperatures (T_g) of the unfilled glassy amorphous polymer is 150 °C and the T_g of the semi-crystalline PHB is equal to 4 °C, which explains the large difference in lifetimes and corresponding free volume hole sizes when using the Tao-Eldrup relation correlating lifetime and free volume hole size [3, 4]. Remarkable differences can also be observed for the sensitivity of including minor concentrations of GO. The lifetime of tBP-oda is hardly affected by the incorporation of GO, while the lifetime of PHB is strongly increased. Reasons for this behaviour may be found in the large difference in shrinkage of the two nano-composite systems during their preparation.

![Figure 1. Ortho-Positronium lifetimes of PHB and poly(tBP-oda) as a function of wt (%) GO.](image_url)
Polybenzoxazines are well known for their ‘near-zero shrinkage’ behaviour during polymerization [5]. In contrast, PHB crystallizes on cooling from the melt, resulting in a heat of fusion of 91.3 J/g, corresponding to a crystallinity of 63%. An appreciable shrinkage may occur when considering that the PHB amorphous density is 1.178 g/cm³ and crystalline density 1.260 g/cm³ [6]. Platelet fillers, like GO, hinder the shrinkage and reduce the thermal expansion, resulting in hydrostatic tensile stresses on the amorphous phase in semi-crystalline polymers, and tensile stresses on the tie-molecules which bridge the crystal lamellae. Hydrostatic tensile stresses will consequently increase the free volume cavity size.

From rheological dynamic measurements experiments, reported elsewhere, follows that GO shows network formation in both polymeric systems at very low GO concentrations [1, 2]. In rheology this effect is visible by a dynamic equilibrium shear modulus in the terminal zone. In figure 2 these equilibrium moduli are shown for PHB processed by using two different solvents and for the tBP-oda filled systems. For PHB the lowest volume fraction of GO where an equilibrium modulus could be established was 7.1 x 10⁻² %. The corresponding equilibrium modulus was 11.7 Pa. The same equilibrium modulus is reached in the tBP-oda samples at a much higher volume concentration of 1.7 x 10⁻¹ %. According to Ren et al. [7] an aspect ratio $\zeta$ can be established when knowing the percolation volume fraction $\phi_p$, assuming randomly distributed disc-shape nano-fillers. The aspect ratio of the nano-filler $\zeta$, the ratio of width to thickness, is:

$$\zeta = 3 \phi_s / 2 \phi_p$$

Where $\phi_s = 0.29$, the volume fraction at the onset of percolation of interpenetrating, randomly packed spheres. The aspect ratio of GO in PHB is determined 400 and the aspect ratio of GO in (tBP-oda) 165.

![Figure 2. Equilibrium dynamic shear moduli $|G'_{eq}|$ as a function of vol % GO.](image)
In Figure 3 the relative ortho-Positronium intensities $I_3/I_0$ are presented as a function of GO concentration. The decrease of intensity with GO content for both systems is stronger than a weight average decrease assuming no ortho-Positronium formation in the filler particle. This is, in combination with the high aspect ratios and nm thickness of the fillers, a strong indication of inhibition reactions in the terminal spur by the nano-fillers. For the PHB/GO nano-composites a correction for the crystallinity is taken into account. Differences in heat of fusion as presented in Figure 4, and the assumption that only the amorphous phase contributes to the ortho-Positronium intensity, is taken into account for calculation of the PHB ‘amorphous’ presented data.

The influence of inhibition reactions on the ortho-Positronium intensity for nano-filled polymers at low concentrations may be represented by an equation similar to the one presented by Eldrup et al. [8]:

$$I_3 = I_0 [A + (1-A)/(1 + \sigma D)]$$  \hspace{1cm} (2)

$\sigma$ represents an inhibition constant, which is related to the efficiency of the scavengers in comparison to the positronium formation efficiency. Scavengers at the GO surface include electron-attracting moieties such as hydroxyl and epoxy groups. $D = \zeta \cdot \text{wt} \%$ and $A.I_0$ is the saturation value of $I_3$.

Best fitting with $A = 0.59$ gives an efficiency factor for PHB of 0.34 and for poly(tBP-oda) of 0.10. The better dispersed GO particles with larger aspect ratio are thus more efficient in the inhibition process for ortho-Positronium formation in the two nano-filled polymers studied so.

![Graph](image-url)

**Figure 3.** Relative ortho-Positronium intensities $I_3/I_0$ as a function of wt (%) GO.
3. Conclusion

PHB and poly(tBP-oda) nano-composites were prepared with low fractions of GO nano-fillers and studied with Positron Annihilation Lifetime Spectroscopy. Free volume hole sizes, represented by ortho-Positronium lifetimes $\tau_{o-Ps}$, increase with increasing GO content for semi-crystalline PHB samples but are merely independent of GO content for the glassy amorphous poly(tBP-oda). This remarkable difference in behavior is explained by the differences in volume shrinkage of the two polymers, leading to large hydrostatic internal stresses and dilatation of the free volume cavities for the PHB nano-composites.

The ortho-Positronium formation probability, represented by the ortho-Positronium intensities $I_3$, decreases appreciably for both polymers with increasing GO content, pointing to an inhibition of the ortho-Positronium yield by scavengers present at the surfaces of the GO nano-particles. The experimental results show that aspect ratio and dispersion of the GO nano-particles have an appreciable influence on the positronium yield. Earlier hypothesis and the hope that $I_3$ represents a free volume hole density can not be kept in the light of understanding of the mechanism of positronium formation [9]. The present work may contribute to this understanding.

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