POSITRON ANNIHILATION IN ARGONNE ILLINOIS #6 COAL

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Introduction

The electronic structure of coals has received little attention but has been the subject of a recent investigation by Larsen *et al.*.[1] At a molecular level, the coal becomes increasingly more unsaturated with increasing rank, consistent with generation of a pseudo graphitic structure. Electronically the maturing of coal may be visualized as a transformation from an insulator to a semi conductor. Studies of coal have indicated that a decrease in resistance occurs with increasing temperature consistent with coal being classed as a semi conductor.[2] Recently there has been considerable interest in the electrical properties of conducting polymers generated by doping conjugated macromolecules[3-5]. The conductivity of these materials is influenced by the efficiency of electron diffusion within the conjugated chain structure and hopping between chains which usually involves donor-acceptor sites. Conjugated polymers are very poor semi conductors and it is only when they are doped either by the addition of strong Lewis acids or bases or alternatively the incorporation of hetroatoms into the conjugated structure that semi conductor or metallic behaviour is observed. It is reasonable to assume that similar criteria will be operative for coal, the detailed processes being a function of the rank and chemical composition of the coal. If conductivity were to be measured on a block, there would be complications from any cracks present, together with complications from the bedding plane and the local maceral structure. Direct measurement of the conductivity of powders is difficult in itself.

Positron annihilation has been used for a number of years in the investigation of the effects of radiation damage on metals and ceramic and recently in the study of free

volume in polymers and glasses. The generation or occurrence of defects on an atomic scale allows trapping of positrons as positronium. The typical positron annihilation experiment involves firstly the generation of a positron with an energy of approximately 1.28 MeV; and it is this which when it passes through an organic media will induce radiation damage, combining with a free electron and forming positronium [Ps]. In polystyrene, the diffuse Ps becomes thermally equilibrated and trapped in a molecular size void associated with free volume. Positronium can exist in two spin states; ortho [o-] and para [p-] Ps. The pPs state undergoes annihilation via an allowed transition and has a lifetime of 0.125ns, whereas the oPs state which undergoes annihilation via a forbidden transition which has been predicted by Dirac to have a lifetime of 140ns. In a molecular insulator, spin exchange processes shorten the lifetime and a proportionality with the size of the void has ben established. The intensity of the oPs component is a function of the ionization potential of the molecular structure and hence reflects the ability of the thermalizing positron to induce radiation damage. In amorphous polymeric materials, the annihilation spectra are usually composed of three components. The two shortest lifetime components correspond respectively to the self annihilation of p-Ps and free positrons with lifetimes of 0.125ns and 0.4ns. In general, neither of these annihilations will have any significant interaction with media and are independent of its physical and chemical properties. The intensity of the p-Ps will be influenced by the trapping thermalization probability of the positronium which is intimately connected with the occurrence of voids. In the case of a conductor, the positron can interact with the the intrinsic delocalized free electron density and trapping will only occur if the radiation spur is larger than the domain structure of the material. Studies of doped polypyrrole has shown that in contrast with the usual situation in most amorphous polymer insulators, annihilation gives rise to a two component spectrum which contrasts strongly with that of the typical amorphous polymer. In this case the positron is assumed to combine with the delocalized electronic structure of the extended conjugated backbone of polypyrrole and its annihilation is a probe of the spin states of this structure. This paper reports the first positron annihilation studies of coal and attempts to compare these observations with the results of related studies on other amorphous materials.

Results and Discussion

Materials

Illinois #6 was selected from the Argonne premium Coal bank for this study. The coal was used as supplied and was subjected to exhaustive extraction using pyridine. The pyridine was completely removed by rotary evaporation prior to use.

Positron Annihilation Spectroscopy

Figure 1 shows a schematic diagram of the apparatus used. A sealed ^{22}Na source was used to generate 1.28 MeV positrons and an accompanying gamma ray. The source was constructed by the evaporation of a concentrated solution of $^{22}NaCl$ onto a polyamide [Kapton] film. The source was then covered with a second layer of film and the sandwich sealed using a room temperature curing epoxy resin [Araldite]. The positron lifetime was determined from the time delay between the observation of the initial 1.28 MeV gamma ray and the detection of two 0.511 MeV gamma rays which mark the annihilation process. The spectrometer used in this study was a fast-slow coincidence system which incorporates a time-to-pulse height conversion unit and the data is collected using a mutlichannel analyser, Figure 1. The gamma rays are detected using two fast plastic scintillators coupled to fast photomultiplier tubes [PMT]. The processes are characterized by the emissions at 1.28 and 0.511 MeV which are energy selected and provide the start and stop signals respectively. Discrimination between the start and stop pulses is achieved in the slow circuit and removes any ambiguity of the nature of the pulse arriving at the photomultiplier tubes. The positron annihilation spectra used in this study were obtained from an accumulation of 10^5 counts. The spectrum obtained was analysed using the computer programme POSITRONFIT[6]. The timing resolution of the system had previously been determined using the full width at half peak maximum obtained from a ^{60}Co source. The instrumental resolution function was determined by analysing the lifetime spectrum for annihilation in benzophenone which has a single lifetime of 0.33ns. POSITRONFIT EXTENDED uses the results from the calibration experiments and fits the deconvoluted curve to a sum of exponentials:

$$f(t) = \sum_i A_i \exp(1/t_i) \qquad \text{I}$$

where i represents the the number of components present. The relative intensity of

each component is calculated from the area under the corresponding lifetime curve. The adjustable variable in the computer fitting of the data can be altered allowing the selection of the number of components and whether or not each is to be fixed or allowed to be freely adjustable. The quality of the data fit is obtained from the value of σ. For these experiments the powdered coal sample as was loaded into a 5ml vial (diameter 10m) and the ^{22}Na source with its plane perpendicular to the axis of the PMT's. The glass vial was placed coaxially in a second larger vial which was itself inserted between the PMT's[7]. All measurements were carried out at room temperature.

Results and Discussion

Two samples of powdered coal were examined in this initial investigation; a sample of Illinois #6 and a sample of the same coal which has been extracted with pyridine. This extraction removes low molecular mass fractions and may be expected to increase the *free volume* in the material. Ps annihilation spectra for the two samples were obtained and fitted using two component lifetimes. Attempts to fit the data using the traditional three component fits fails, there being no appreciable long lifetime component. The lifetimes and the fits are presented in Table 1. A typical spectrum for the fresh Illinois #6 is shown in Figure 2.

The process of extraction appears to have the effect of increasing the lifetime. Increases in the lifetime of oPs in polymers such as polystyrene can be interpreted in terms of an increase in the lifetime associated with the generation of *free volume* in the matrix. However, in the case of coal the observed spectra resembles more closely that observed in doped polypropylene than that obtained for polystyrene, as shown in Table 2.

Spectra obtained from coal can therefore be seen to resemble those of the semi conducting polymer polypyrrole rather than the insulator polystyrene. The shorter lifetime τ_1 can be associated with free positron annihilation and would not be expected to be significantly influenced by the nature of the matrix. The values of 0.34 and 0.32 ns for the coal and polypyrrole can be assumed to be the same within experimental error. The second component, τ_2 is however clearly a more sensitive probe of the matrix and has a longer time in the coal than in the conducting polymer. The electron mobility may be expected to be greater in the case of the p-toluenesulphonic acid doped polypyrrole than that of the coal. However, these data would suggest that at a microscopic level these values are comparable. Extraction of the low molecular weight fraction appears to

increase slightly the lifetime and this would be consistent with a reduction in the electron mobility. It is probable that the extractable material will not only fill voids in the coal but can also aid electron mobility. Removal of this fraction may generate voids into which the positronium might be trapped and will reduce electron mobility which will further increase the lifetime. It is not possible from these preliminary observations to deduce which of these effects will dominate, however, this data does indicate that positron annihilation may be useful in obtaining information about the nature of the micro-structure of coal.

References

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Table 1 Positron Annihilation Study of Illinois #6 Coal

	τ_1 (ns)	σ_1 (ns)	τ_2 (ns)	σ_2 (ns)	I1 (%)	σ_1 (%)	I_2 (%)	σ_2 (%)
Illinois #6	0.746	0.092	0.345	0.007	10.411	3.273	89.589	3.27
Pyridine Ext. Illinois	0.843	0.101	0.345	0.005	7.987	1.785	92.013	1.78

Table 2 Lifetimes and Intensities for Related Polymer Systems

	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	I_1 (%)	I_2 (%)	I_3 (%)
Polysyrene (room temperature)	0.125	0.450	1.20			
Doped Polypyrrole (room temperature)	0.32	0.68	-	18.0	78.0	-

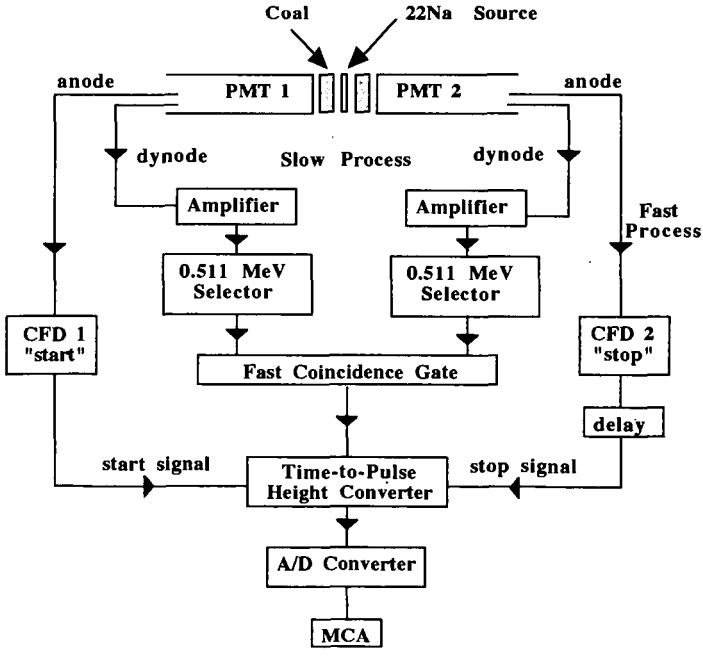
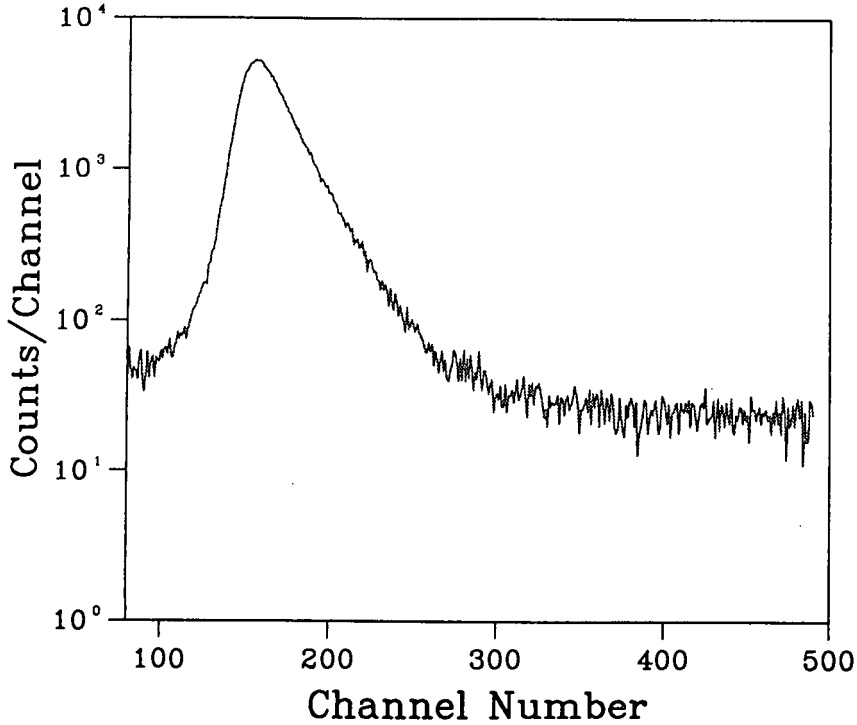


Figure 1 Schematic diagram showing the fast-slow coincidence system


10^4
10^3
10^2
10^1
10^0
Counts/Channel
100
200
300
400
500
Channel Number