

Spectral response of some polymers to 14 MeV neutron irradiation

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Four polymers, polyvinyl acetate (PVAc), Kapton, polyvinyl dichloride (PVDC) and ultra high molecular weight polyethylene (UHPE) have been chosen and their absorption as a function of dose has been studied using Cary 2390 spectrophotometer and fast neutrons of 14 MeV obtained from AN-400 Van-de-Graaff accelerator. It has been observed that while UHPE and PVDC are relatively insensitive to fast neutron irradiation, the polymers PVAc and Kapton show that changes in the spectral behavior are largest for an optimum dose. The observation that Kapton undergoes a permanent change on fast neutron irradiation while PVAc shows a recovery characteristic is attributable to the fact that while Kapton monomer is a closed carbon ring type of aromatic compound, PVAc, on the other hand, is open linear carbon chain type of aliphatic compound in its monomeric form.

1 Introduction

Radiation effects induced by ionizing particles like electrons, ions, photons have been largely used recently to modify the chemical and physical properties of polymers¹⁻⁸. Unfortunately these modifications are not yet totally controlled as the result is often a superposition of several mechanisms including the interaction of the incident particle with matter and the different secondary reactions initiated. The statement⁹⁻¹⁰ that the effect of radiation on polymers is same if the same amount of energy is deposited irrespective of the type of radiation passing through it is some what misleading and should be taken carefully. If the radiation is neutral (e.m. waves, neutrons and other light neutral particles) this concept may be true to some extent. However, in the case of charged particles the situation may be different in polymers which are electrical as well as thermal insulators¹¹. These two phenomena can make charged particle modification of polymers more complex as compared to metals and metallic alloys. The radiation environment of the nuclear power reactor has stimulated many investigations of radiation effects on materials¹⁰. Of first concern were the structural metals of the core containment and the ceramic insulators of the primary control equipment and instrumentation. But more recently it has also become evident that polymeric materials which have much lower resistance to radiation damage, are needed for service in equipment located in other areas within the containment where the radiation dose can be appreciable over the design life of the plant. The radiation environment in the containment during normal op-

eration consists of gamma-rays and neutrons that escape through the wall of the reactor core. The gamma-ray energy spectrum in this vicinity ranges from a few keV to about 8 MeV. The energy distribution of the neutrons ranges from thermal neutrons to fission neutrons¹⁰. Although neutron represents one of the main radiations in nuclear power reactors, not much study has been made so far of the effect of fast neutron irradiation on these polymers chosen in the present study. It has been commonly observed that the intrinsic physical and chemical properties of unirradiated polymer films, slowly change with time due to natural aging and finite permeability of polymers to various atmospheric gases. However, some irradiated polymers are found to show stable chemical and physical properties with time, although such irradiation may change some of their intrinsic properties. One such interesting property is the UV absorption characteristic which depends on the chemical bond structure¹² that has been studied in the present work; the chemical modifications can be monitored by UV spectroscopy^{12,13} or by IR spectroscopy¹⁴.

2 Experimental Details

The polymers Kapton, PVAc, PVDC and UHPE of thickness 50, 250, 120 and 50 μm , respectively, were obtained from Messrs Goodfellow, Cambridge, U K, and were used without any further treatment. The polymer samples of size $1 \times 1 \text{ cm}^2$ were mounted in front of our 400 Van-de-Graaff accelerator for irradiating with 14 MeV neutrons produced by bombarding a tritium target with a 250 keV deuteron beam. The neutron flux

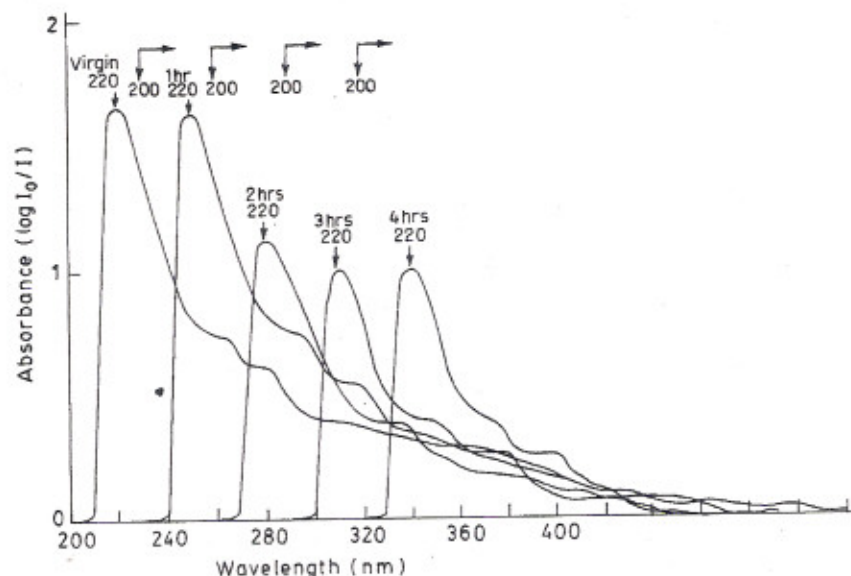


Fig. 1 — UV absorption spectra of 14 MeV neutron irradiated polymer (Kapton)

produced was 3.8×10^7 n/cm²/s. The samples were irradiated for different time intervals, viz, 30 min, 1h, 2h, 3h, and 4h. The spectrophotometry in the UV range, of both the irradiated and virgin samples, was carried out on a Cary 2390 UV-VIS-IR spectrophotometer (Varian/Switzerland) by studying the absorbance (A) which is usually defined as, $A = \log_{10}(I_0/I) = \epsilon cl$, where I_0 and I_t are the intensities of the incident and transmitted light respectively, l is the length of the medium, c is the concentration in moles/litre and ϵ is known as the molar excitation coefficient.

3 Results and Discussion

The series spectra recorded for Kapton, PVAc, PVDC and UHPE are shown in Figs 1,2,3 and 4, respectively. For ease in comparison between the virgin and irradiated samples, the spectra are shifted in x -axis by regular displacements as indicated by short arrows at the top of each individual spectrum.

It can be readily seen from these figures that the changes in spectral response are appreciable for Kapton and PVAc while they are minimal for PVDC and UHPE. A common feature of all the spectra is that in each spectrum, there is a characteristic wave length, λ_{ch} , where the absorbance shows either a point of inflection or a local maximum. The λ_{ch} is different for different polymers. However, the observed λ_{ch} is 220 nm for Kapton, 275 nm for PVAc, 280 nm for PVDC and 246 nm in the case of UHPE.

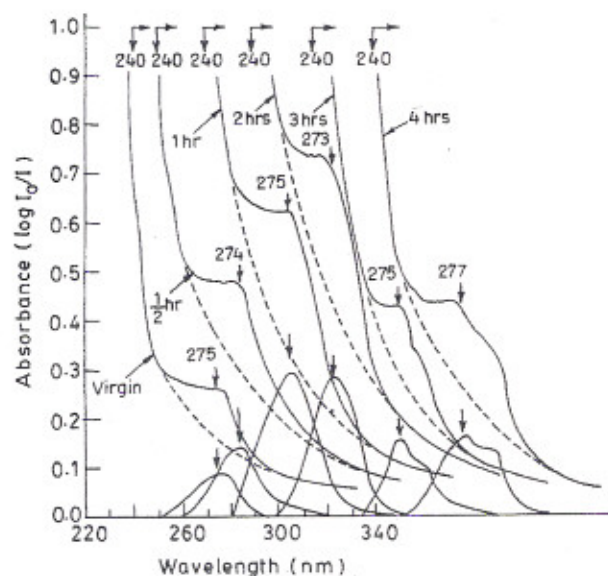


Fig. 2 — UV absorption spectra of 14 MeV neutron irradiated polymer (PVAc)

For a systematic comparison of the spectral behaviour of the four irradiated polymers as a function of the fast neutron dose administered to them, the absorbance at the characteristic wave length λ_{ch} , is plotted as a function of time of irradiation for each polymer separately as shown in Fig.5 (a,b,c,d), respectively. It is interesting to see from Fig 5(c and d) that PVDC and UHPE are scarcely affected by fast neutron irradiation up to 4 hours. From Fig. 5(a), it can be seen that for Kapton the

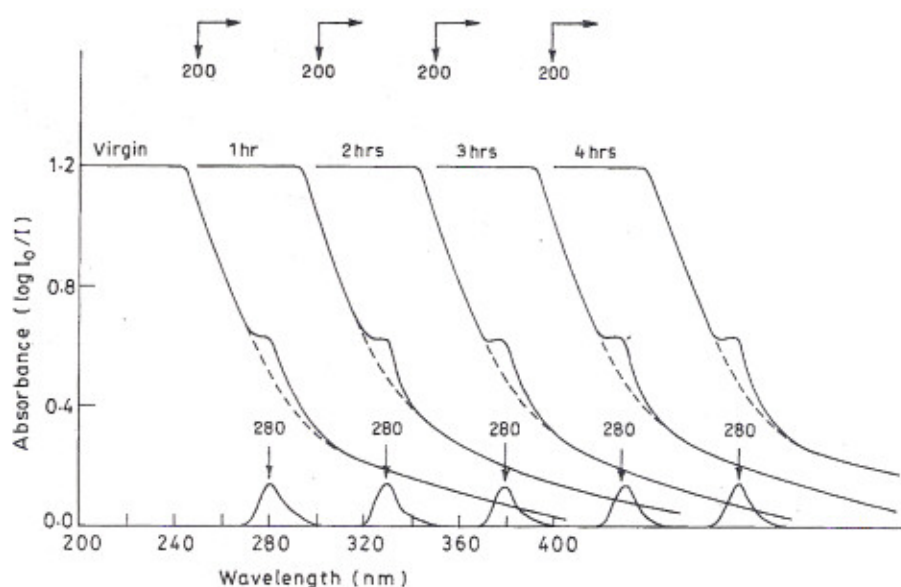


Fig. 3 — UV absorption spectra of 14 MeV neutron irradiated polymer (PVDC)

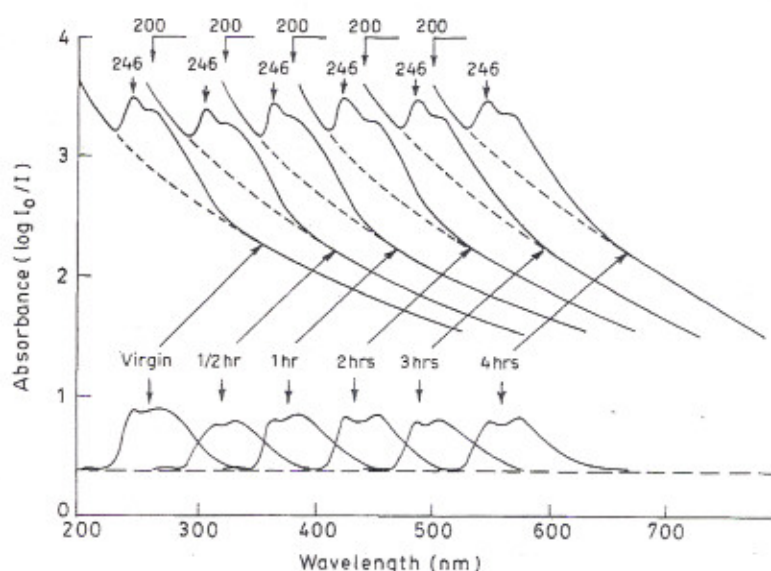


Fig. 4 — UV absorption spectra of 14 MeV neutron irradiated polymer (UHPE)

absorbance decreases rather monotonically from a high value of 1.65 for virgin sample to a final low value of 1.0 for 4 hours of irradiation. This means that there is a permanent change in the absorbency property in UV for Kapton as a result of fast neutron irradiation. It is quite interesting to see from Fig. 5(b) that for PVAc, the absorbance increases from a low value of 0.2 for the virgin sample to a high value of 0.65 for nearly 1.5 hours of irradiation but, for higher doses, falls to a final value

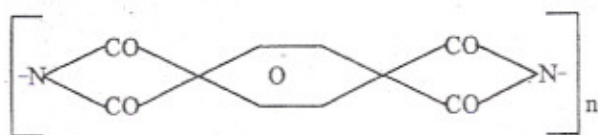
of 0.28 for 4 hours of irradiation. Thus PVAc shows a remarkable recovery characteristic which means that its original properties are more or less restored after long irradiation.

It is well known that the ultraviolet absorption characteristics of an organic molecule are closely linked to the internal bond structure. For example, the conversion of a double bond into a single bond at some location in the structure is likely to shift the absorption maximum;

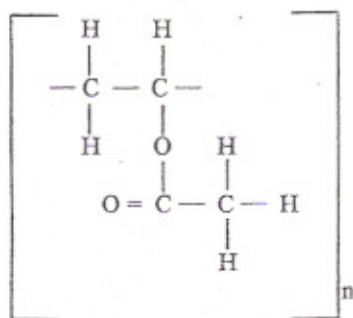
additional peaks in the absorption spectrum may occur due to allotropic modifications in the structure. However, all these changes can be observed experimentally only in pure solutions of the simple organic monomers. In the case of a polymeric substance, particularly in the solid form, it is very difficult to correlate these changes to specific bond locations in the macromolecules which may contain several thousands of monomers in each of them.

It is possible to appreciate, to some extent, the relative spectral responses of different polymers from the composition and structure of their monomers. The structural formulae for four polymers studied in the present work are given below for comparison and contrast:

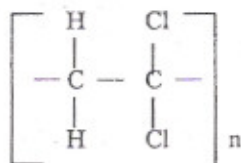
Kapton



PVAc



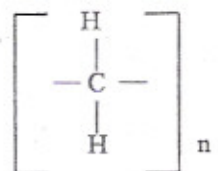
PVDC



From the above representation, it is apparent that the polymers Kapton and PVAc containing oxygen are sensitive to fast neutron irradiation, with respect to ultraviolet absorption properties, while PVDC and UHPE which do not contain oxygen are not. It has already been

established¹³ that many molecules contain electrons that are not directly involved in bonding. These are called non-bonding or *n* electrons and are mainly located in atomic orbitals of oxygen, sulfur, nitrogen and the halogens. The elements contain what are known as non-bonding electrons, which actually do not participate in chemical bonds unlike the σ and π electrons. These *n*-electrons present in atomic orbitals can be more easily excited to σ^* and π^* excited states than σ and π electrons. This makes the oxygen containing polymer more sensitive to ultraviolet absorption than those polymers which do not contain oxygen. The present results indicate that oxygen containing PVAc and Kapton show changes in absorption on fast neutron irradiation while oxygen free PVDC and UHPE are quite stable; thus confirming the above theoretical prediction. It is also interesting to note from Fig. 5 (a & b) that between PVAc and Kapton, both of which are sensitive to neutron irradiation, the aliphatic (linear carbon chain) PVAc shows the recovery characteristic while the aromatic (closed carbon ring) Kapton does not. This can be understood by observing that the probability for the recombination of scission (broken) chains is greater for linear carbon chain polymers (e.g., aliphatic PVAc) than for closed carbon chain polymers (aromatic Kapton). Thus physics and chemistry play an important role in the

UHPE



interaction of radiation with polymers.

Conclusion

The fact that Kapton and PVAc are sensitive to fast neutron irradiation, while PVDC and UHPE are not, may be linked to the fact that the former pair contains oxygen in their structure, while the latter pair does not. The observation that Kapton undergoes a permanent change on fast neutron irradiation while PVAc shows recovery characteristic with modified band-shape may

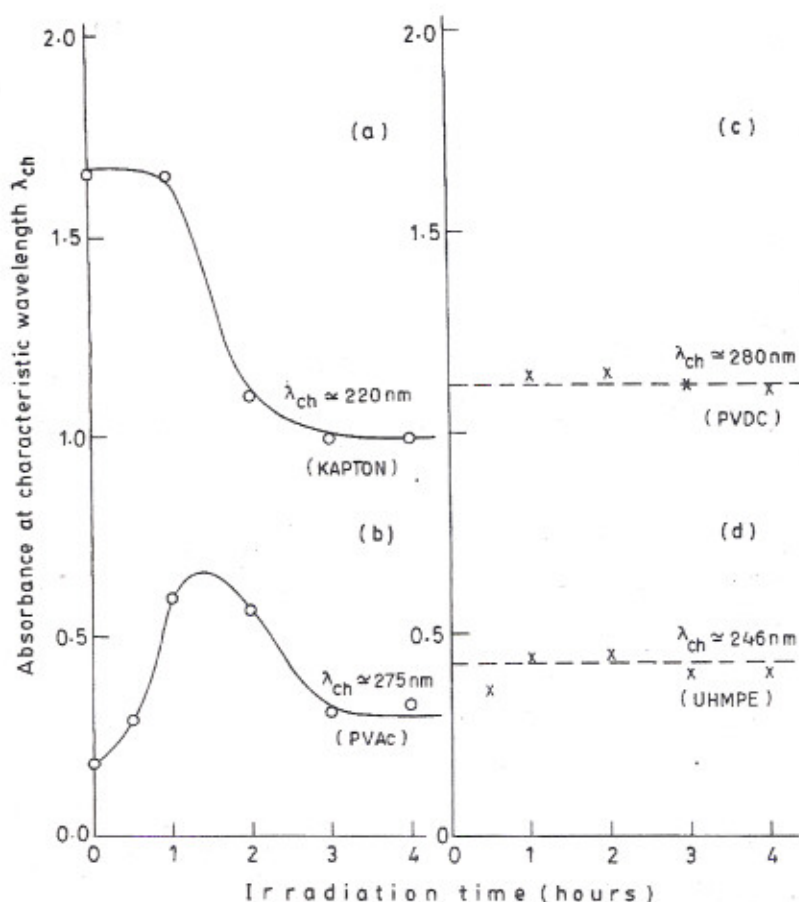


Fig. 5 — Variation of absorbance of polymers due to 14 MeV neutron irradiation at characteristic wavelength (λ_{ch})

be attributed to the fact that while Kapton monomer is a closed carbon ring type of aromatic compound, PVAc, on the other hand, is open linear carbon chain type of aliphatic compound in its monomeric form. The modification in band-shape in the case of PVAc may be due to the allotropic modification occurring in the polymer sample by irradiation. Our experimental results establish that some polymers are insensitive to radiation while others show varying changes in absorptive behaviour under the same irradiation and dose conditions. The spectral response of polymers is dependent on the physics and chemistry of their structural forms.

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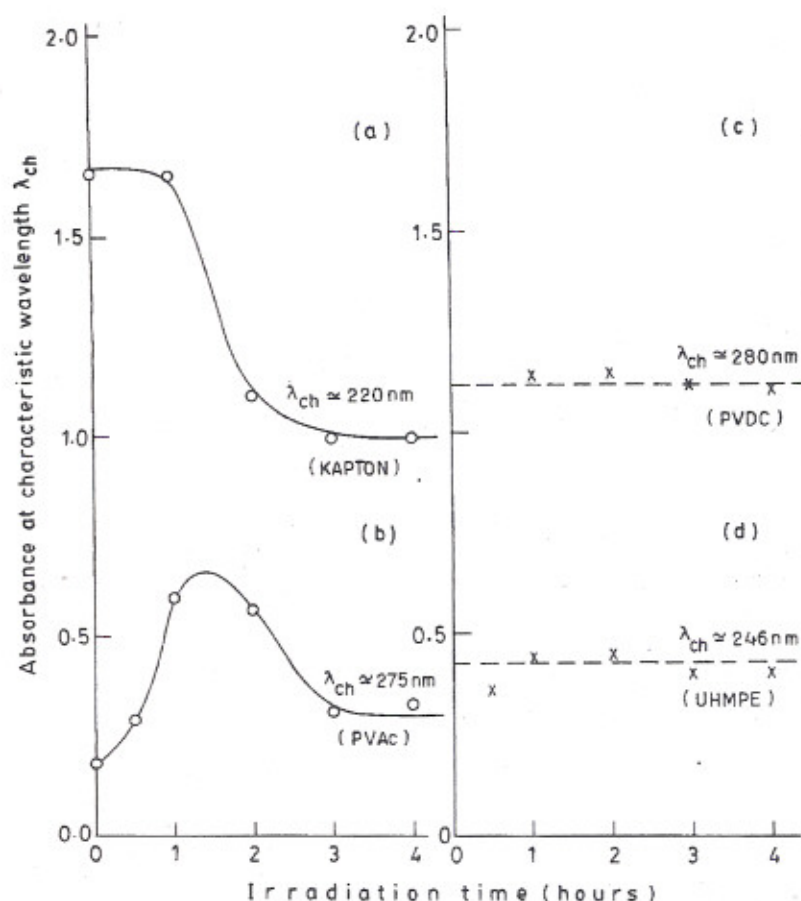


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