Present status of radiochromic techniques for nuclear radiation measurements

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Various developmental stages of radiochromic dosimetry in kGy to mGy range depending on its applications in radiation processing industries, radiological safety, medical sciences, nuclear or dirty bomb exposition and radiation accident have been described. Leuco dyes, pH sensitive dye with halogen containing compound and radiation induced solid state polymerization are the basic chemical methods presently in use for radiochromic techniques. The present status including achievements, limitations and R&D required for further improvements of accurate and precision measurements has also been highlighted. The reader system for mapping of radiation distributions in patient dosimetry and accurate measurements of personal doses in any nuclear or radiological accident scenario are also elaborated.

Keywords: Radiation processing, Radiochromic film, Leuco dyes, Dosimetry

1 Introduction

The major virtue of radiochromic dosimeters is their simple mode of operation. They can provide an immediate estimate of doses. The advancement in radiation technology i.e., sterilization of medical products, preservation of eatable items, shelf life extension of fruits and vegetables, production and quality enhancement of seeds by gene mutations, has played an important role. The improvement in quality of electrical cables, large scale nano materials production, and smart and stealth materials fabrication by gamma or electron irradiation has also proved the prime importance of radiation technology. The delivery of proper doses for quality of product is an essential requirement. The requirements can be only fulfilled if the proper radiation indicator is displayed on the samples to be irradiated. The coloured indicator will assure the delivery of true doses to the irradiated products. In the early part of 20th century, barium platinocynide, pastille discs were used along with colour wheels to quantify absorbed dose which could change from green to a dark yellow orange when exposed to X-rays. Since that time a host of other materials which also turn colour upon irradiation and which require no subsequent processing have been developed and used in radiation processing dosimetry. Unfortunately, for the most part these films are too insensitive for applications in medical dosimetry as well as accident dosimetry. There are two ways to fabricate radiochromic films i.e., (1) Radiation sensitive leuco dyes and/or pH sensitive dyes with a halogen containing compound and (2) colourless photo monomer molecule, initiating colour formation through chemical changes.

2 Physical-Chemical Behaviour of Leuco and Diacetylenes based Radiochromism

2.1 Leuco dye based radiochromism

Photochromism mechanism of Leuco form is shown in Fig. 1. The spiro form of an oxazine is a colourless leuco dye. The conjugated system of the oxazine and another aromatic part of the molecule is separated by a sp3-hybridized "spiro" carbon. After protonating a part of the molecule, irradiation with UV light (photochromism), or introducing other kind of such change, the bond between the spiro carbon and the oxazine interrupts and the ring opens. The spiro carbon achieves sp2 hybridization and becomes planar. The aromatic group rotates, aligns its pi orbitals with the rest of the molecule. A conjugated system forms, with ability to absorb photons of visible light, and therefore appears colourful.

Fig. 1 — Transformation between leuco and coloured form induced ultraviolet radiation
The mechanism of the radiation induced colour change of the LMG from colourless to green may be explained as similar to malachite green cyanide which has similar optical absorption spectrum as shown in Fig. 2. The RC-H bond (similar to RC–N) in LMG may get broken by irradiation, and it results in the structure rearrangement at one of the triarylmethane groups leading to the quinonoid chromophore structure of the deep colour source as a part of the resonant unsaturated carbon ion².

2.2 Diacetylene based radiochromism

A number of different classes of organic compounds undergo photopolymerization if irradiated by UV-light as bulk crystalline material. The preparative and technical aspects of such solid state polymerizations have received much attention. Among the many different reactions known, only two systems have been studied to greater depth because they belong to the class of the so-called topochemical reactions and provide a means of direct synthesis of highly crystalline polymers. These two reactions are: the "Four-Center-Type" photopolymerization of diolefins and leads to polymers with a cyclobutane ring in the base unit and the topochemical polymerization of monomers with conjugated triple bonds. The latter reaction has been found and studied by Wegner³. The expression topochemical polymerization is sometimes regarded as synonymous with solid-state-polymerization or topotactic polymerization. The most general term is solid-state polymerization. It implies that a polymerization proceeds starting from the bulk of the solid crystalline monomer or complex of the monomer with host molecules. Solid-state polymerization is thus a more or less concise description of the experimental technique similar as bulk-polymerization or solution-polymerization. Organic crystals are build-up by packing molecules into a three dimensionally regular lattice. Individual molecules are separated from each other by Van der Waal’s distances which are much too large as to allow the formation of the transition state of a chemical reaction. Reactivity can only come about if the molecules are mobile enough to approach each other to a distance of less than approximately 3Å. Solid-state polymerizations can be regarded as phase transitions from the crystalline phase of the monomer to the phase of the growing polymer. The solid state polymerization implies a direct transition from the monomer molecules to polymer chains without destruction of the crystal lattice and without formation of non-crystalline intermediates⁴.

Substituted diacetylenes (DAs) undergo 1,4-addition reaction in the solid state to give polydiacetylenes (PDAs) (Fig. 3). The reaction can be initiated thermally, photochemically or by gamma irradiation. The reaction is topochemically controlled wherein the packing arrangements of the molecules in the monomer crystal lattice must satisfy the requirements for solid-state polymerization. The packing arrangement of a diacetylene monomer is the determining factor for its solid-state reactivity, manipulation of this to promote reactivity is most desired. In disubstituted diacetylenes, the only possible variations which can be effected, as far as molecular engineering is concerned, are manipulation of the side group⁵.

When the monomer in the crystal has appropriate geometry, i.e. where the distance d and the angle w are approximately 5 Å and 45⁰, respectively, it can be polymerised via topochemical 1,4-addition. It may
be possible to choose side groups such that the corresponding polymer contains the desired properties. In this manner, computer modeling should be useful for predicting the chemical and optical properties of DAs and their polymers. Such models can save time and labour in the laboratory by screening compounds which polymerize from those which do not.

Cystallized diacetylene exists in two phases, active phase and in active phase. The inactive phase polymerization is not occurred due to photo exposure. Active phase is highly sensitive to photo exposure e.g., UV, heat or ionizing radiations. A phase which polymerizes rapidly upon irradiation is referred to as a radiation active phase. By selecting a proper solvent system, some diacetylenes, such as diacetylene -344 [R–C.dbd.C–C.dbd.C—R where R.dbd.OCONH (CH.sub.2).sub.3CH.sub.2] can be crystallized into a phase which would have extremely low thermal reactivity to provide long shelf-life and high radiation reactivity to monitor low dose, such as a few cGy, by developing a noticeable colour. Symmetrical diacetylene is more radiation reactive than asymmetrical diacetylene and is also less expensive. UV-induced polymerization is faster by about one order of magnitude than ionizing radiations^5.

3 Radiochromic Film in Radiation Processing

Thin film dosimeters are still of interest for use in radiation processing because of their convenient characteristics. The most frequently used commercially available film dosimeters are cellulose triacetate, radiochromic thin film dosimeters and Gaf Chromic dosimetry media. Most of these thin films dosimeters have been developed for use in the kGy range. These types of radiochromic films are based on radiation sensitive dyes. The commonly used radiation sensitive dyes are Leuco malachite green, TLA-454, crystal violet lactone, green diaminofluoran, orange aminofuran and black fluoran having absorption peak in the range of 552.0 to 635.0 nm. Among all the above radiochromic dyes leuco malachite green is more radiation reactive in comparison to other dyes^6. There are seven common transparent plastics that are potential candidates for a dosimeter matrix and they are acrylics, epoxies, polycarbonates, polyesters, polystyrene, polyurethanes, and polyvinylchlorides. Polyvinylchlorides weren’t further considered since their Z_{eff} values are not tissue substitutes with Z_{eff} 14.2. The acrylates, polyesters, polystyrenes and polycarbonates were also dropped from further consideration due to the relatively high heat (>100°C) measured during their polymerization, which degrade leuco dyes. The remaining two plastics further studied were epoxies and polyurethanes and from these polyurethanes show the greatest versatility as a 3D dosimeter matrix by generating the least exotherm and the greatest dose sensitivity. 2% LMG polyurethane formulation was reported linearity from 10 cGy to 60 Gy. A new PVB-based film dosimeter is capable for dose measurement of a few hundreds Gy levels of gamma rays, X-rays and electron beams using leuco malachite green (LMG) dye. Chloride materials were chosen as additives because of practical easiness to control their content in films^7. Acetoacenitile leuco dye (Leuco crystal violet) has also been reported for gamma ray detection system with halo carbons. The significant change in colour observed by naked eye is about 10 Gy. But change in absorbance is also reported above 1 Gy using spectrophotometer. The response is linear from 1 to 100 Gy (Ref. 6). The radiochromic films commercially available from M/s Far west Technology (Goleta,CA) is based on hydro-phobic substituted triphenylmethan leucocyanides, and is most commonly used for high dose applications e.g., 0.5-200 kGy. The wavelength in general use is 510 or 600 or 605 nm (Ref. 7). M/s GEX Corporation, USA also supplies GEX B3 dosimeter of the range 1.0-140 kGy as per user requirements. Because of the broad peak of the B3 film, measurement at any fixed wavelength between 550-555 nm is considered acceptable^8.

3.1 Medical radiochromic film

Recently, another form of radiochromic film based on polydiacetylene has been introduced for medical applications. These films were previously supplied in two types, Gaf Chromic DM-1260 (also known as HD-810) and single-layer Gaf Chromic MD-55 for the absorbed dose ranges 50-2500 and 10-100 Gy, respectively (The single-layer Gaf Chromic film will be designated as MD-55-l). A new double-layer Gaf Chromic MD-55 film has now replaced the other two for medical applications (useful dose range 3-100 Gy). This currently available double-layer Gaf Chromic film will be designated as MD-55-2 (Ref. 9). Each of these film types is colourless before irradiation, consisting of a thin, active microcrystalline monomeric dispersion coated on a flexible polyester film base. It turns progressively blue upon exposure to ionizing radiation. The increase in colour
of radiochromic films is usually measured at a narrow spectral wavelength band with a spectrophotometer or a densitometer. These measurements are expressed in terms of the increase in absorbance $A$ (i.e., optical density) or transmittance, $T$, of the light, where:

$$A = - \log_{10} T$$

Nearly full colour development of all radiochromic formulations is very rapid, generally occurring in a few milliseconds. Colour stability is enhanced for absorbance readings made at either of the two main absorption peaks at 610 and 670 nm Fig. 4. The film was found to be essentially insensitive to light at wavelengths above 300 nm; however, it is sensitive to ultraviolet light at lower wavelengths. It has been suggested that the film be stored in the dark, at temperatures below 25°C and relative humidities below 50% to optimize the useful life of the film. The experimental studies with photon beams show a response of MD-55-2 to be about 40% lower for photons of 20-40 keV than with $^{137}$Cs or $^{60}$Co gamma radiation. MD-55-2 is to be approximately 40% more sensitive than MD-55-1 for megavoltage photon beams and is practically insensitive to UV radiation and visible light above 400 nm. The radiochromic film can be analyzed by submilimeter resolution using a scanner such as He-Ne laser.scanning densitometer. Appropriate laser wavelength, high intensity and low power consumption is a major requirement for scanning purpose.

In the use of two-dimensional imaging systems, a uniform light source illuminates the object being scanned from the rear, and an imaging system (like a camera) is used to measure light transmission from many points on the sample simultaneously. The resolution of the scan is primarily governed by the pixel size of the imaging system only. Such systems have a speed of measurement advantage over traditional systems since data are acquired from all points on the sample simultaneously. The desirable characteristics of radiochromic films are sensitivity, tissue equivalence, dose rate dependence, UV and visible light dependence, environmental stability, uniformity of thickness and coating on the films. All the above parameters are to be optimized prior to use of these films in actual practice.

### 3.2 Radiochromic film (alert indicator)

In the 1950’s faced with a possible need to determine the survivability of troops that had received significant exposures from a nuclear explosion, the US army deployed the colour dosimeter. Each dosimeter employed five glass vials filled with a radiation sensitive solution: brom-cresol purple dissolved in chloroform. An exposure to gamma radiation turned the solution from purple to yellow. Now, the question is what level of radiation, it takes to cause cancer for a healthy person. Some believe it is 20 cGy. Below this dose it is not possible to detect adverse health effects. The Health Physics Society, USA indicates that there are no observable health effects below 10 cGy or 100 mSv. Epidemiological studies and data suggest that risks in 150-200 mSv dose range are very small and difficult to measure. It is also reported that LD$_{50/60}$ (mean lethal dose) for man is 350-400 cGy. Therefore, the selected range of radiochromic dosimeter to measure significant biological effects induced due to radiation in any nuclear or radiological accident can be appropriate in the range 100 mSv or 250-350 mSv (Ref. 11).

The radiochromic film dosimeter was originally developed for medical industry having the active component diacetylene monomer dispersed in polymer matrix and applied to polyester film. When the active monomer is exposed to ionizing radiation, a polymerization reaction immediately produces an intensely coloured dye polymer that changes the appearance of the dosimeter. The amount of dye produced is proportional to the radiation dose. The dye polymer is cyan blue with a major absorbance peak at 635 nm and a minor peak at 585 nm. The radiochromic film badges do not require calibration or maintenance, have no electronics or batteries, and are

![Fig. 4 — Radiation induced absorption spectra of MD-55-2 Medical Radiochromic film](image)
The dosimeter can be read visually by the wearer at the incident scene. Most users would be able to visually estimate the dose to within ±20%. The visual read out does not require darkroom or processing equipment. There are two manufacturers who are supplying these types of films: M/s J.P Laboratory (Middlesex, NJ) and M/s RADēCO, Inc. 509 Norwich Avenue Taftville, CT 06380 having trade name SIRAD and RADview\textsuperscript{13,14}. M/s J P Laboratory claims that laboratory succeeded to develop radiochromic film from 0.01 cGy to 10,000 cGy\textsuperscript{11} whereas RADēCo developed radiochromic film cover the range 0.5 to 100 cGy (Ref. 15). Figures 5 and 6 shows the radiochromic film developed by J P Laboratory and RADēCo.

3.3 Indigenous development

Defence Laboratory, Jodhpur has initiated R&D work in 2009 to develop radiochromic film for radiation processing based on LMG-PVB and diacetylene-polymer matrix formulation (Fig. 7). LMG-PVB formulation observed the significant

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**Fig. 5** — Radiochromic dosimeter, J P Lab

**Fig. 6** — RADēCo Radiochromic dosimeter

**Fig. 7** — Absorption spectra of indigenous developed radiochromic film
colour change at 0.1 kGy onwards. The developed films were sent to BARC, Mumbai, for their evaluation. It is appreciated that the work is commendable and thickness optimization is required to improve the colour reproducibility with gamma dose (Fig. 8). Thus it confirms the utility of above film for gamma dose measurements in the range 0.1 to 4 kGy having linear response for fruit preservation. Further, R&D is in progress for thickness and coating optimization, radiation sensitivity improvement of the above film.

The BCG (bromocresol green)-PVC film as pH sensitive radiochromic film is also useful for radiation industries to measure very high doses. The dose measurements are possible varying the concentrations of BCG from few kGy to 100 kGy. The tailor-made film can be fabricated in the above range with number of permutations and combinations. The same is true for leuco dye films also.

The indigenously developed radiochromic film will provide visual assessment of absorbed radiation dose. The film is tissue equivalent, dose-rate independent. It does not require calibration or maintenance, have no electronics or batteries, and is small and light. A quick visual observation of film allows anyone to assess the absorbed dose. Once an exposure is visually evident, a fully quantitative measurement to confirm the radiation dose can be performed, if required, by optically using reflectance optical densitometer. The film develops a distinctive and characteristic colour upon exposure to ionizing radiation. The radiation sensitive diacetylene monomer dispersed in a polymer matrix. When the active monomer polymer strip is exposed to ionizing radiation, a polymerization reaction immediately produces an intensely coloured dye polymer that changes the appearance of the dosimeter. The amount of dye produced is proportional to the radiation dose. The dye polymer is cyan blue with a major absorbance peak at 675 nm and a minor peak at 625 nm. The developed film indicates progressively darker in proportion to absorbed dose in six different shades i.e. 0, 10, 25, 50cGy, 125 and 350cGy. The progressively increase in darkness of same film is also observed by naked eye at 500cGy, 750cGy and 1500cGy. The dose response (10 - 1500cGy), dose rate response (10 - 1200cGy/hr), sunlight and room light effect on radiochromic film and colour stability with respect to temperature and lapsed time has also been studied (Fig. 9). It is observed that the dosimeter is unaffected by exposures to sunlight or normal room light if radiation sensitive strip is covered by clear transparent UV protective film. The dosimeter will tolerate temperatures up to 50°C studied so far. The expected
shelf life of the film if stored with UV protective cover will be more than one year\textsuperscript{17}.

4 Conclusions

Radiochromic films have wide applications in radiation industries, medical sciences, health physics and radiation dosimetry. The development of radiochromic film specific to quality of radiation and the change in colour in place of shade of single colour are a challenges to developers. Further greater sensitivity for imaging and personnel occupational dosimetry is a requirement. To produce high resolution three dimensional radiographic registrations for CT dose distributions should be taken into consideration for future developments.

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