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DEVELOPMENT AND DOSIMETRIC CHARACTERIZATION OF INDIGENOUS PADC FOR PERSONNEL NEUTRON DOSIMETRY

by

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CR-39 is a solid state nuclear track detector, chemically known as poly-allyl-diglycol-carbonate, widely used for personnel neutron monitoring because of its sensitivity to neutrons, excellent optical properties that facilitate the analysis and sufficiently long shelf life. Presently, this detector is imported and is being used for the personnel neutron monitoring programme in India. Hence, an effort was made towards the indigenous development of these detectors. Different chemical processes for the indigenous development of the poly-allyl-diglycol-carbonate detector, such as the synthesis of allyl-diglycol-carbonate monomer and isopropyl-peroxydicarbonate as initiators for the polymerization process, were carried out and are reported in this paper. A method for casting unbroken poly-allyl-diglycol-carbonate sheets sized 25 cm $\times$ 15 cm and of a thickness between 500 μm and 800 μm was developed. A longer polymerization process also helps to increase neutron sensitivity, reduce the minimum detection limit and increase the signal-to-noise ratio of the detector. The study suggests that it is possible to develop indigenous poly-allyl-diglycol-carbonate detectors with a minimum detection limit of 0.1 mSv and signal-to-noise ratio of 8.0.

Key words: poly-allyl-diglycol-carbonate, electrochemical etching, neutron dosimetry

INTRODUCTION

There are many techniques for neutron dosimetry based on classical concepts like elastic scattering, neutron activation and absorptive reactions [1-3]. For personnel neutron monitoring, bubble detectors, albedo dosimeters based on thermoluminescent dosimeters such as TLD 600 and TLD 700, electronic pocket dosimeters and CR-39 based neutron dosimeters are used. These neutron dosimeters have different detection mechanisms with their merits and demerits. Most of them are passive and require post-irradiation processing to evaluate the dose. For more than four decades, solid state nuclear track detectors (SSNTD) are in use for neutron dosimetry [4]. SSNTD are dielectric materials that include crystals, glasses and plastics, of which CR-39 ($C_{12}H_{18}O_7)_n$ was found to be the most sensitive and useful. In 1978, Cartwright *et al.*, discovered the proton registration properties of CR-39 [5].

Damage caused by secondary charged particles due to the interaction of neutrons with the detector material/radiator can be seen as tracks. As the detectors and radiators used are organic polymers, the elastic recoils of elements such as H, C, O, and N give rise to tracks in detector materials, along with the tracks due to non-elastic (n, p) and (n, α) processes.

Poly-allyl-diglycol-carbonate (PADC), popularly called CR-39, is the material of choice in personnel neutron monitoring [6-8] as it is the most sensitive track detector discovered so far and responds to a wide range of neutron energies using the recoil proton mechanism. CR-39 satisfies most of the requirements of an ideal track detector and is found to show proton sensitivity over a wide range of energies. It is preferred for personnel neutron monitoring owing to its larger cross-section for (n, p) scattering, greater ranges of recoil protons and a greater possibility of neutron energy transfer to protons. It is almost insensitive to beta and gamma radiation doses. The post-irradiation fading of damaged tracks due to environmental conditions in CR-39 is insignificant. All these favourable properties

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of CR-39 make it a versatile neutron detector as neutrons are always accompanied by gamma radiation. Its lower energy threshold at 100 keV for neutrons makes it suitable for reactor personnel neutron monitoring, fuel reprocessing facilities and accelerator environments [9, 10]. The limiting factors of CR-39 are its background tracks which increase with time. These background tracks are due to manufacturing defects and the nonuniformity of the surface. Background tracks are important parameters in the manufacture of dosimetric grade CR-39.

In India, CR-39 based neutron dosimeters have been in use in personnel monitoring since 1995. At present, CR-39 is imported from overseas manufacturers. To cater to the needs of a fast growing personnel neutron monitoring programme in the country, around 10000-12000 neutron badges are required annually, equivalent to 120 CR-39 sheets per year, measuring 30 cm   48 cm. Hence, there is an urgent need for manufacture of PADC sheets within the country, to be used in various applications, including the neutron monitoring programme. In the present paper, the characteristic of the PADC detector, including its preparation process, are discussed in detail.

MATERIALS AND METHODS

The casting of PADC sheets in the present study involves following processes:
– synthesis of allyl diglycol carbonate (ADC) monomer & isopropyl peroxydicarbonate (IPP) initiator,
– assembling of the mould, and,
– polymerization of ADC.

The polymerized PADC sheets were characterised for neutron dosimetry using the following method:
– preparation of neutron dosimeters and irradiation,
– processing of dosimeters, and
– counting of tracks produced on irradiated dosimeters

Synthesis of ADC monomer

The synthesis of an ADC monomer can be carried out via two different routes; (a) in a transesterification-based mode [11] or (b) a phosgene-based one [12]. Both routes have been used in the present work. The process of synthesis of an ADC monomer is briefly described below.

ADC via transesterification: A carbonate ester was converted into another carbonate ester. *i. e*., diallyl carbonate through ester interchange, and was further transesterified with diethylene glycol to give ADC [13]. The product was finally distilled under reduced pressure of $1.0 \cdot 10^{-2}$ mbar at 39 °C to get pure

diallyl carbonate in a 80 % yield with respect to dimethyl carbonate. Diallyl carbonate and diethylene glycol were mixed and stirred under a continuous and constant nitrogen flow. The KOH in the catalytic amount was then added to the reaction mixture and the mixture constantly stirred to thereby remove the allyl alcohol. It was then extracted in diethyl ether and crude ADC was vacuum distilled at a $2.0 \cdot 10^{-2}$ mbar pressure at 160 °C to yield pure ADC. The product obtained was colorless and the yield obtained was 90 % based on the glycol feed. Unsaturation analysis was carried out to confirm the purity of the monomer. The process was scaled up to obtain up to 100 gm of ADC at a time.

ADC via phosgene/condensation method: For synthesizing larger quantities of ADC simultaneously in order to cast many large- sized PADC sheets, one generally requires to follow the phosgene route. In this method, allyl chloroformate (either commercially available or prepared by reacting allyl alcohol and phosgene or triphosgene) was condensed to form an ADC monomer. In this process, diethylene glycol (DEG) was dissolved in acetone followed by the addition of pyridine. The temperature of the bath was maintained between 0-5 °C. To this mixture, allyl chloroformate was added slowly and, after complete addition, it was stirred for an hour. After the completion of the reaction monitored by TLC, the acetone was removed and the product was extracted in diethyl ether. To purify the product, three to four times water washings were given to it and an organic layer was passed over the anhydrous sodium sulfate to obtain crude ADC. Finally, it was vacuum distilled to yield the pure ADC product.

A purified ADC prepared by both of the methods was confirmed with Fourier transform infrared spectroscopy (FTIR) and ^{1}H nuclear magnetic resonance spectra (^{1}H NMR), as shown in figs. 1 and 2. FTIR spectroscopy helps in identifying the presence of particular functional groups, whereas, ^{1}H NMR spectroscopy indicates the presence of protons in various chemical environments in the compound. The FTIR spectrum of the purified ADC monomer in fig. 1 shows   peak characteristics of functional groups: =C-H stretching (3086.11 cm^{-1}), C=O stretching (1747.51 cm^{-1}), and C=C stretching (1649.14 cm^{-1}). For recording the ^{1}H NMR spectrum, a purified ADC monomer (not soluble in water) was dissolved in CDCl$_3$ solvent. ^{1}H NMR spectral data of this sample, as shown in fig. 2, have peaks at

δ (peak shift) = Ha = 6.00 – 5.90 ppm (=CH-, 2H, m)
 = Hb & Hc = 5.34 ppm (H$_2$C=, 4H, dd)
 = Hd = 4.65 ppm (=CH-CH$_2$, 4H, d)
 = He = 4.32 ppm, (-OCO$_2$-CH$_2$- 4H, t)
 = Hf = 3.75 ppm (-O-CH$_2$-, 4H, t)

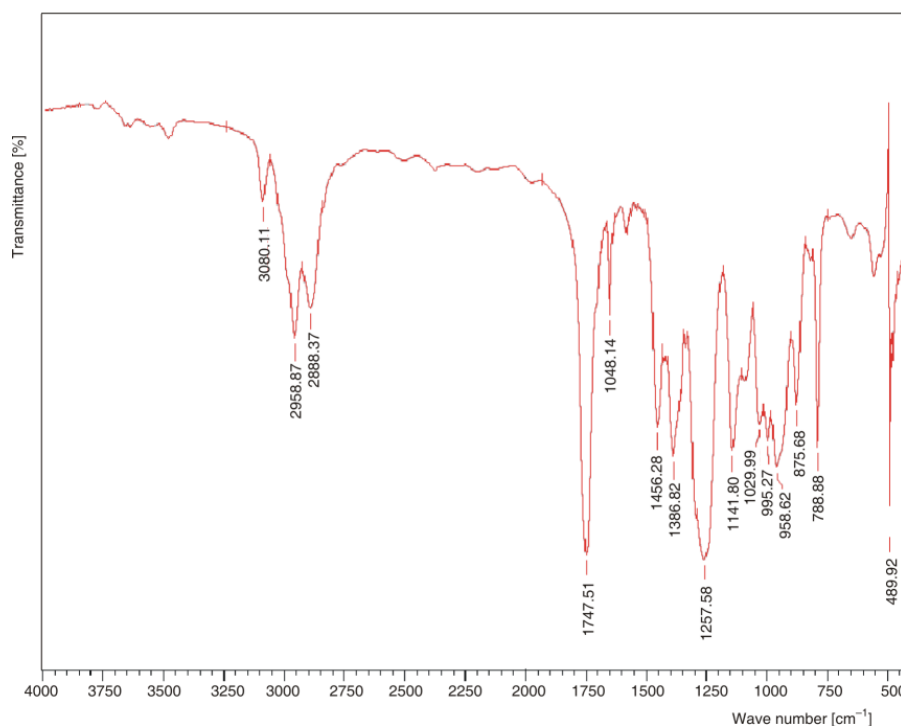Proton positions from Ha to Hf have been shown in the structure of ADC, fig. 2.

Figure 1. FTIR spectrum of purified ADC monomer
Note: The carbonyl stretching peak of the carbonate at 1747.51 cm^{-1}, =C-H stretching peak at 3086.11 cm^{-1},
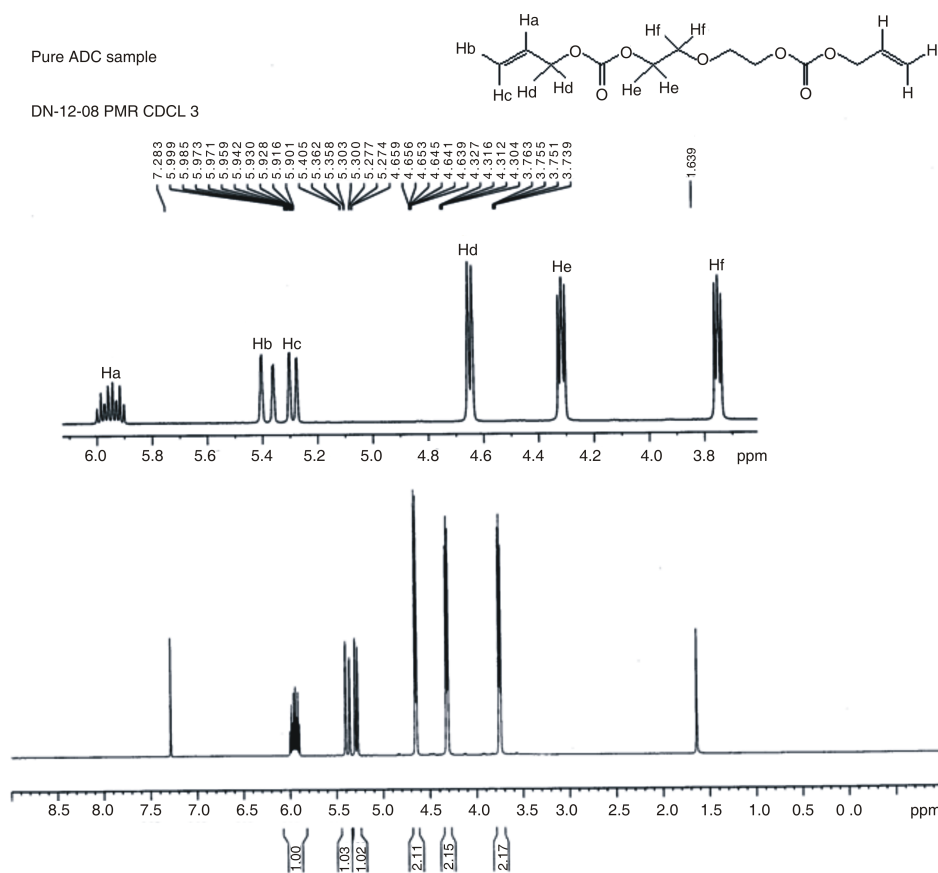*C = C stretching at 1649.14 cm^{-1}*

Figure 2. ^{1}H NMR spectra of purified ADC monomer in CDCI$_3$ solvent at 400 MHz and 22 °C
Note: The y-axis is showing intensity of absorption (arbitrary units) against the chemical peak shift position d (in ppm) of various protons in ADC with an internal reference signal position taken at 0 ppm with respect to tetramethyl silane (TMS) which is used as the internal standard. The peak shifts due to respective proton positions (Ha-Hf) have been denoted in the ADC chemical structure

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Preparation of initiator isopropyl peroxydicarbonate (IPP): The initiator IPP used during the polymerization of ADC is a highly unstable compound above 0 °C and, hence, its commercial supply is not possible. Further, in larger quantities, its transportation could result in explosions. IPP was synthesized from an intermediate Isopropyl chloroformate (IPCL), which is synthesized from isopropyl alcohol and phosgene/triphosgene. Triphosgene is a relatively stable compound that can be transported. The triphosgene was dissolved in dichloromethane and cooled to 0 °C. Isopropyl alcohol and pyridine were injected through the rubber septum in the reaction flask at such a rate that pyridine always remain in excess in the reaction mixture. Dichloromethane was slowly removed by fractional distillation. This crude product was vacuum distilled at 40 °C with very low vacuum to afford pure intermediate IPCL in a 70 % yield. The final product, IPP, was prepared by the condensation of IPCL with sodium peroxide [14, 15]. Its purity was analyzed by volumetric titration. The process to synthesize about 5-7 gm of IPP at a time has been standardized.

Assembling the mould for PADC polymerization

It is well known that during polymerization ADC undergoes a volume shrinkage of about 14 %. This causes the PADC sheet to bend inside the mould and eventually leads to a broken sheet or even pulverization. This is avoided by pressurizing the mould gradually, so that the mould plates are brought closer to each other, thereby stopping the bending of the sheet. Excess of pressure can result in the breakage of glass plates of the moulds. In the cast polymerization method, the mould is assembled and kept in the polymer press for uniform curing and pressure.

Mould design

Optical glass plates were used to assemble the mould. The assembling of the mould for casting small sized (9 cm × 9 cm) PADC sheets has been reported earlier [16-20]. In order to cast large (25 cm × 15 cm) sheets, few modifications were required to make the mould sturdy. It was observed that a float glass 6 mm thick developed cracks in larger moulds. Hence, commercially available 6 mm thick, toughened glass (Pyran S, Schott, Germany) sheets sized 30 cm × 20 cm, were optimised for the mould. It was assembled using a teflon gasket with an inner window of 25 cm × 15 cm sandwiched between the two glass plates, as shown in fig. 3. The plates were cleaned with solvents and then wiped with an anti-dust cloth to assure that they were clean and dust free. A commercial teflon sheet (500 μm or 700 μm thick as per requirement) was heated under pressure to remove the wrinkles on its surface. It was
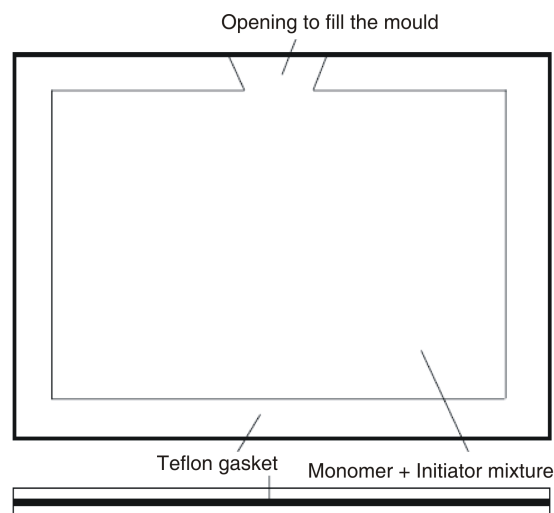

Figure 3. Design of the gasket and mould

then cut in a square shaped gasket 2.5 cm wide and a small opening. The mould was initially kept under a polymer press overnight to avoid leakage during the filling of the monomer. It was found that during filling monomer bubbles get trapped at the opening of the mould which could result in the cracking, as well as the coloring of the sheets. Therefore, the design of the teflon gasket was modified by introducing tapering at the opening to avoid leakage. This resulted in a smooth filling of the mould. The monomer containing the IPP initiator (~45 ml) was introduced into the mould using a syringe pump.

Filling the mould

The purified monomer was first filtered through a teflon filter of 500 μm, followed by a 200 μm filter to remove the suspended particles/solids, if any. The monomer was then subjected to a vacuum for about 5 minutes after which dry nitrogen was flushed for further 20 minutes or so. The process was repeated twice, so as to completely remove the dissolved oxygen from the monomer. The initiator and the plasticizer were added to the flask and the contents homogenized by mixing. The polymerization mixture was carefully injected into the mould through the opening in the teflon gasket, avoiding the formation of air bubbles, and the opening sealed.

Polymerization of the ADC using Polymer press

A polymer press was fabricated using two surface ground mild steel plates (platens) sized 30 cm × 30 cm, 6 mm thick. The plate at the bottom was fitted over a fixed stand and a screw placed at the top plate so that the distance between the plates could be adjusted using screw movement. Heating blocks were

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fabricated using 12 mm thick aluminum plates equipped with hot water lines to circulate the hot water for heating purposes. A polymerization mould can be placed between the two plates and a slight pressure applied by tightening the screw. We have used three blocks so as to be able to place two of the moulds at the time of heating. It was noticed that a perfect parallel alignment of platens and heating blocks was required to avoid the cracking of the polymer films. The heating of aluminum blocks and, in turn, that of the polymer mould, was done by circulating hot water through a programmable circulating water bath model, Julabo F25. A tiny hole (6 mm in diameter and 8 cm in length) was drilled in the heating block to place the sensor for monitoring the temperature. Using this press and the appropriate mould, PADC films of size up to 25 cm   15 cm could be fabricated.

Heating the mould: The mould was placed in a polymer press for heating and the heating was done using a programmable circulating water bath. Two moulds could be kept in the space between the heating blocks. A sensor was inserted into the middle block to measure the temperature of the blocks. For general heating purposes, water was circulated through the blocks to maintain a uniform temperature between the two blocks where the filled mould was placed for polymerisation. The moulds were slightly pressurized during polymerization. Upon the completion of 50 %-55 % polymerization, the pressure on the mould was increased slightly and the polymerization cycle continued till the completion of 12 h. The mould was opened after being naturally cooled at room temperature (natural cooling took about 12 h) and subsequently placed in warm water for 2-3 h to obtain an unbroken sheet of PADC with a fine surface.

Since the allylic or vinyl polymerization process is highly exothermic, the autoacceleration of polymerization is possible over the course of ADC polymerization. The gradual formation of polymer (gel) state is a poor conductor of heat and, hence, if too much heat evolves suddenly, a crack may be observed, as shown
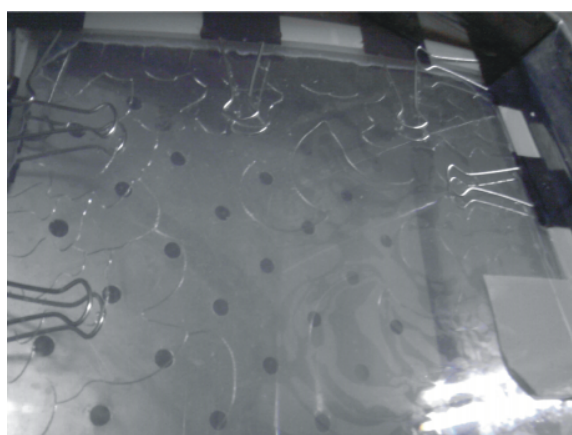

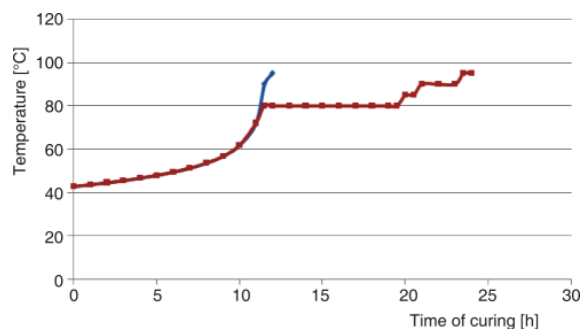**Figure 4. Photograph indicating cracked PADC sheets**

Figure 5. Graph showing optimized 12 h and 24 h curing cycle for indigenous PADC

in fig. 4. In order to avoid such problems, a process of constant rate polymerization was suggested by Dial *et al* [21]. They studied the kinetics of ADC polymerization and proposed an equation for calculating the temperature of the polymerization bath to be maintained at a given time under constant rate conditions. This prevents excess heating of the mould at any given time and a smooth evolution of heat during polymerization. Based on our dosimetric test results, a heating profile for 12 h and 24 h curing was optimized. The curing cycle of 12 and 24 h is shown in fig. 5. There are reports available indicating that heating the sheets at around 80-90 °C for a longer time removes residual unsaturated ADC and produces a polymerized sheet (PADC) which is very smooth, inspite prolonged etching. Hence, upon the ending of a normal 12 h profile, it was decided to keep the moulds at a constant temperature of 80 °C for about 8 hours, followed by a slow rise in temperature of up to 95 °C for the remaining period, until the 24 h heating cycle is over.

We have also noted that the thickness of the PADC sheets depends on the variations in the thickness of glass plates used (from one to the other end (near their edges), as well as on the variation in the thickness of the teflon gasket. As both of these materials are imported, control over their thickness was not possible. The variations amounted up to 50-70 μm. Nevertheless, inspite of the arrangements cited, we managed to produce polymerized sheets with uniform surfaces and without any cracks.

Preparation of neutron dosimeters from PADC sheets

Preparation of dosimeters: The PADC sheets developed with different curing cycles had thicknesses ranging from 500 to up to 800 μm. Initially, a few sample detectors from these sheets were examined under a microscope. The PADC sheets were then manually cut into dimensions of 3 cm   3 cm, so as to avoid any breakage to the sheets. A PADC detector with a 1 mm polyethylene radiator of similar dimensions was loaded in an airtight, triple- laminated aluminized

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pouch. The top and bottom sides of the sheets were marked and the control (unexposed) pieces of both samples utilized in a background study envisioned to check and ascertain the surface while utilizing a lower background. The thicknesses of these pieces were measured at all four edges. The polyethylene radiator provides enhanced sensitivity for track detection due to recoil protons produced by the interaction of neutrons with the radiator. The aluminized pouch protects the detector from ambient conditions, renders it dust-free during handling and prevents entry of atmospheric radon/alpha particles which may result in tracks. For comparison of neutron sensitivity, the CR-39 sheets procured by M/s Pershore Moulding, U. K,. were used as a reference.

Detector irradiations: The irradiations of the detectors were performed in air, in a low-scattering irradiation laboratory. To study the neutron sensitivity, a set of 5 PADC and CR-39 detectors, were irradiated to a 1 mSv neutron dose equivalent from a [241]Am-Be neutron source in air, at a distance of 50 cm, with the radiator side facing the source for sensitivity of PADC detectors. For dose linearity studies, a set of 5 dosimeters were irradiated in air to dose equivalents of 0.5, 1, 2, and 3 mSv in [241]Am-Be neutron source.

Processing of neutron dosimeters

Etching techniques: There are several etching techniques such as chemical etching (CE), electrochemical etching (ECE) and a combination of both chemical and electrochemical techniques. These techniques can be used for enhancing the damaged tracks and counted with an appropriate imaging system. At Bhabha Atomic Research Centre (BARC), the two-step elevated temperature electrochemical etching (ECE) developed by Tommasino *et al.,* is followed by an additional chemical pre-etch step. It was observed that chemical pre-etching (CPE) followed by the ECE technique lowers background tracks [22]. This technique is known as the combined etching technique (CPE+ECE). It removes the superficial shallow defects which may produce background tracks and is standardized [23].

Chemical pretching followed by electrochemical etching(CPE+ECE): Tracks of varying depths are produced depending upon the proton recoil energy. The application of the electric field to chemical etching enlarges tracks even at small depths and makes them visible for counting at low magnification. The combined etching technique significantly improves the energy response of PADC detectors and brings the energy threshold down to 100 keV. PADC detectors are processed by mounting them in a custom-built electrochemical etching cell which can hold 25 detectors at a time, with 7N KOH as the etchant solution

[24].The combined etching technique comprises the following steps:

Step-1: the pre-etch step where the etching cell is placed in the incubator at 60 °C for 90 min, without applying voltage.

Step-2: The etching cell is connected to the power supply for electrochemical etching. Etching at low frequency is carried out for 3 h, where the power supply operates at a low frequency of 100 Hz at 1250 V constant potential (appropriate voltage depending on the thickness of the sheet).

Step-3: Etching at a high frequency of 3.5 kHz for 40 min.

The combined etching technique has been used for the dosimetric characterization of PADC. The typical field strength used for the etching of the PADC detector was 20-25 kVcm^{-1}. The voltage applied was varied, based on the thickness of the sheet.

Track counting using image analysis system

 The manual method of counting has-limited capability when measurements with higher accuracy and reproducibility are required. PC-based image analyzers can overcome these shortcomings. Since there is a strong correlation between measurable track parameters (area, diameter, eccentricity, *etc*.) and the property of the particle inducing the track, it is important to use image analyzers that are capable of measuring the necessary parameter in a reproducible manner.

A PC- based automatic image analysis system developed indigenously at BARC has been used for the counting of tracks of the PADC detector. A photograph of an image taken by the imaging system for exposed tracks is shown in fig. 6. The details of the image analyzer are available in literature [25]. Images and
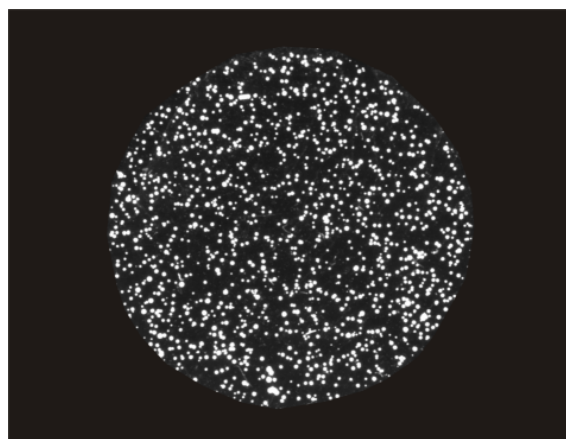

Figure 6. Image of track on the PADC detector exposed to 2 mSv after ECE processing, as seen through the image analysis system

data can be stored against the detector number as a file in the existing system. The basic parameters computed for the tracks in the binary image are: area, perimeter and the roundness factor. The tracks that are produced due to irradiation should ideally be round in shape and have a roundness factor close to that of a circle. The software parameters are set so that, only the tracks that fall within the set area range and roundness factor are counted. This method of shape-based filtering is employed to filter out the tracks that are elongated. These elongated tracks may be present due to scratches and other damages that occur on the PADC detector during the etching process and are not considered for counting. The lower and upper limits of the diameter and roundness factors of acceptable tracks are 60 μm to 250 μm and 0.7 to 2.0, respectively.

RESULTS AND DISCUSSION

Parameters for dosimetric characterization of indigenous PADC sheets

Minimum detection limit (MDL): The minimum detectable limit for a dosimetric system is defined as the dose equivalent at which the signal is significantly greater than the background. It is given by the following equation [26]

$$MDL \text{ [mSv]} \quad N_B \, 3 \, \sigma$$

where N_B is the calibration factor (mSv/tracks cm^{-2}) for a PADC detector and σ is the standard deviation of the background signal (number of tracks cm^{-2} of unirradiated detectors) obtained from the average of the 20 unirradiated and processed detectors.

Sensitivity of a PADC detector: Sensitivity is defined as the number of tracks per unit area per unit dose.

Dose linearity: The linear relation between the response of a PADC detector with an increase in dose equivalent is expressed through dose linearity.

Testing and characterization of indigenous PADC sheets

PADC sheets developed in different phases were tested for the dosimetric parameters such as MDL, sensitivity and the signal-to-noise ratio. A satisfactory performance of the PADC sheets developed in this study was chosen based on the following parameters of the reference CR-39 sheet: (a) background track density (20-70 tracks cm^{-2}), (b) net track density (>100 tracks cm^{-2} mSv^{-1}), and (c) signal-to-noise ratio (>3.0). Based on these parameters, improvements in the polymerization process have been evolved to develop a dosimetric grade PADC sheet.

Phase I

In the initial testing, two sheets (labeled as A & B) of thicknesses 530 μm and 600 μm were polymerized. The sheets were very brittle and would break during removal from glass plates. Nine and fifteen pieces sized 3 cm   3 cm could be cut for studies on their neutron sensitivity. The results are shown in tab. 1. It was observed that, in sheet A, the background tracks were very high. Although the background of sheet B was comparable to reference CR-39, its sensitivity to neutrons was poor, with a signal- to- noise ratio of 1.6, as compared to 7.5 of reference CR-39.

During the preparation of PADC sheets in phase I, nonuniformity of pressure in the hydraulic press led to the cracking of sheets. The cause of higher background tracks and low sensitivity could also be due to the improper polymerization process and impurity in the starting chemicals. In order to improve the quality of the sheets, following precautions were taken, namely (a) use of highly pure monomer samples, (b) improving surface uniformity by application of uniform pressure and temperature, (c) maintaining clean environment during polymerization of the sheet, and (d) careful washing of the glass plates.

Phase II

In phase-II, the PADC sheets were prepared after the rectification of the polymer press carried out to maintain uniform pressure and temperature. Also, the environment of the laboratory was made clean. Two sheets (labeled C and D) were prepared in this phase. Sheet C and D were 800 μm thick. Only nine pieces of 3 cm x 3 cm could be obtained from each sheet. The results on the track density of the control (unirradiated) and exposed detectors are shown in tab. 2. The signal-to-noise ratio of sheet C was found to be comparable to

Table 1. Preliminary testing of indigenous PADC with reference CR-39 in phase I

Sheet label	Thickness [μm]	*Average Bkg track density [cm^{-2}]	*Total average track density [cm^{-2}mSv^{-1}]	*Net track density [cm^{-2}mSv^{-1}]	Signal to noise ratio
Reference CR-39	635 30	27 6	229 12	202 3.1	7.48
Sheet A	530 45	1006 54	850 462	–	–
Sheet B	600 62	24 3	64 16	40 4	1.66

Note: *counts are average of three detectors. Bkg stands for background

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Table 2. Results of the neutron sensitivity and background track density of sheets in phase II

Sheet label	Thickness [μm]		*Average Bkg track density [cm^{-2}]		*Total average track density [cm^{-2}mSv^{-1}]		*Net track density [cm^{-2}mSv^{-1}]		Signal to noise ratio
Sheet C	800	25	24	12	202	7	74	14	3.08
Sheet D	800	30	20	7	109	8	37	20	1.85
Sheet E	600	34	607	67	798	27	95	72	0.15
Sheet F	500	46	97	36	487	10	195	37	2.01
Sheet G	600	30	93	46	118	38	10.4	59	0.11
Reference CR-39	625	34	54	9	250	8	196	12	3.63

Note: *counts are average of three detectors. Bkg stands for background

that of the reference sheet whereas, for sheet D, the signal-to-noise ratio was 1.85 (tab. 2). Based on the above results, it was decided to prepare more sheets of a thickness in the range of 600 μm (thickness of PADC sheet comparable to reference CR-39 sheet) to generate good statistical data on neutron sensitivity and MDL.

In the second lot of phase II, three sheets (labelled E to G, as shown in tab. 2) were prepared.. The results are shown in the tab. 2. It was found that the signal-to-noise ratio of sheet F was close to reference CR-39, but other sheets were not of dosimetric grade in terms of sensitivity. The achievement in this phase was that the sheets could be prepared without any cracks and with an uniform surface, but their sensitivity was not comparable to that of reference CR-39 sheet. Further, in order to have PADC sheets with higher neutron sensitivity, it was decided to use 0.1 % DOP instead of 1 % DOP used in the sheets prepared and tested previously.

Phase III

Two batches were prepared in the final phase of testing comprised of eight and six intact sheets of 25 cm 15 cm. A photograph of the intact sheets is shown in fig. 7. These sheets were physically clear, transparent and strong. They were cut into 3 cm 3 cm

Figure 7. A typical photograph of the intact sheets

pieces and their thicknesses measured at all four edges. The sheets showed varying thicknesses, as shown in tab. 3. They were divided into two groups based on the thicknesses, so that an appropriate voltage for etching could be applied. In the first batch, eight sheets labeled from H to M and were placed in one group having a thickness of 520 μm 31 μm, whereas sheets N and O were placed in the second group with a thickness of 730 28 μm. The etching

Table 3. Results on track density and signal to noise ration of eight PADC sheets in phase III

Sheet label	Thickness [μm]		Etching voltage [V]	*Average Bkg track density [cm^{-2}]		*Net track density [cm^{-2}mSv^{-1}]		Signal to noise ratio	No. of detectors with acceptable control (30-100 tracks cm^{-2}]	No. of detectors acceptable based on signal to noise ratio (>3.0)	Performance of the sheet
H	505	48	1150	270	156	156.3	40	0.58	0	0	Unsatisfactory
I	494	25	1150	98	47	119.3	30	1.22	3	0	Not dosimetric grade
J	550	50	1150	37	26	143.2	20	3.86	3	3	Dosimetric grade
K	482	55	1150	154	102	194.9	60	1.26	1	0	Not dosimetric grade
L	560	38	1150	85.6	16.8	136	18	1.6	5	6	Not dosimetric grade
M	530	56	1150	45.8	11.9	39	13.0	0.7	3	10	Unsatisfactory
N	750	37	1600	33	5	136.5	8	4.09	4	3	Dosimetric grade
O	710	58	1600	273	44	18.6	40	0.07	0	0	Unsatisfactory

Note: *counts are average of three experiments with five detectors. Bkg stands for background. All the sheets were polymerized with 12 h curing cycle

voltages used were 1150 V (for 520 µm) and 1600 V (for 730 µm), respectively, based on the average thickness keeping the electric field strength at 22 kVcm^{-1}. A total of 108 detectors were used for the testing. Out of a total of 108, 53 detectors were kept as control, while 55 were exposed to a 2 mSv neutron dose equivalent. The etching of these detectors was carried out in groups of equal number of control and concurrently exposed (3 detectors each) in order to observe the consistency of their neutron sensitivity/response.

The results on neutron sensitivity and background tracks of these detectors are shown in tab. 3. Out of the eight sheets only J and N have acceptable control, net track density and good signal-to-noise ratio (>3). Sheets H and M have a high background (>100 tracks cm^{-2}) and a lesser signal to noise ratio. Sheet O was unsatisfactory, due to negligible sensitivity. As for sheets I, K, and L, although the signal was good, their signal- to-noise ratio was poor (around 1.5) and they were, hence, not considered to be of dosimetric grade. Only in sheets J and N, the average signal-to-noise ratio was around 3.0, near to the reference CR-39 detector used in neutron monitoring. With regard to sheets J and N, two trials of processing produced consistent results. All sheets tested in this lot were polymerized within a 12 h curing cycle. In order to further improve their performance, it was decided to increase the duration of the sheet curing cycle to 24 h.

In the second batch of Phase III, six sheets labeled from P to U were tested. In order to investigate the variation in the background with respect to the two surfaces of individual sheets, the top and bottom sides of each sheet were marked as S1 and S2. The sheets were cut into 3 cm 3 cm and the thickness measured at all the four edges. They were divided into three groups, based on their thicknesses. Sheets P and T were placed in one group, sheets Q and R in the second and sheets S and U were allotted to the third group, as shown in tab. 4, along with their etching voltages. Sheets T and U were polymerized within a 24 h curing cycle, while the rest were prepared within a 12 h curing cycle. Three PADC detectors were packed and irradiated on the S1 side and three on the S2 side and etched along the control (taken from both sides) for background and sensitivity. The surface of each sheet with a lower background was identified and that particular surface was then used for further studies on the reproducibility of results and dose linearity. Out of the 142 detectors, 54 were kept as control, while 88 were exposed to different doses.

Table 4 provides the details of the performance of the detector in terms of track density, background track density and the signal-to-noise ratio, *etc.*, for each sheet with respect to its side. It shows the average results of the three etchings carried out to verify the consistency regarding the sensitivity of the sheets. In sheets P and Q, the S2 side showed a lower background. However, their MDL was around 0.4 and 0.3 mSv, respectively. The signal-to-noise ratio amounted to around 4.7. Although, the background and signal- to-noise-ratio was acceptable, the MDL was high due to, which the sheets could not be used for lo -dose measurements, as required in personnel monitoring. The said sheets can be used in high-dose experimental measurements. Their performance was considered satisfactory. Sheet R showed dosimetric quality on the S2 side. Side S1 was satisfactory. All the other sheets from S to U were tested and found to be of dosimetric grade (criteria for dosimetric quality is that the signal- to-noise-ratio should be greater than 3 and MDL 0.2 mSv). Both sides of sheets from S-U were acceptable, as they exhibited lower background track density and a high signal-to-noise ratio. Figure 8 presents the total number of control detectors used in the study. It can be seen that all control detectors of sheets from R-U have acceptable background tracks. Figure 9 presents the total number of detectors exposed, along with the ones with an acceptable sensitivity (sheets P-U). It is obvious that sheets R-U have an acceptable net-track density (signal-to-noise ratio

Table 4. Results of second lot of six PADC sheets in phase III

Sheet label	Thickness [µm]	Curing details [h]	Etching voltage [V]	Sheet side with less [Bkg]	*Average Bkg track density [cm^{-2}]	*Net track density [cm^{-2}mSv^{-1}]	Signal to noise ratio	MDL [mSv]	Performance of the sheet
P	470 48.2	12	1050	S2	58 40	275.9 63	4.7	0.4	Satisfactory
Q	540 57.9	12	1200	S2	53 27	255.4 29	4.8	0.3	Satisfactory
R	5405 2.2	12	1200	S1	54 26	233.8 5	4.4	0.3	Good dosimetric quality on S2 side
				S2	46 19	260.4 4	5.7	0.2	
S	560 53.4	12	1250	S1	64 14	217.7 8	3.2	0.2	Good dosimetric quality
				S2	52 16	276.9 28	5.3	0.2	
T	480 9.46	24	1050	S1	29 7	256.7 10	9.0	0.08	Good dosimetric quality
				S2	46 17	239.6 19	5.2	0.2	
U	570 46.1	24	1250	S1	60 3	215.0 29	3.6	0.04	Good dosimetric quality
				S2	32 8	264.7 33	8.3	0.09	

Note: *counts are average of three experiments with five detectors. Bkg stands for background. Sheets labeled P, Q, R, S were polymerized with 12 h curing cycle where as sheets labeled T and U were polymerized with 24 h curing cycle
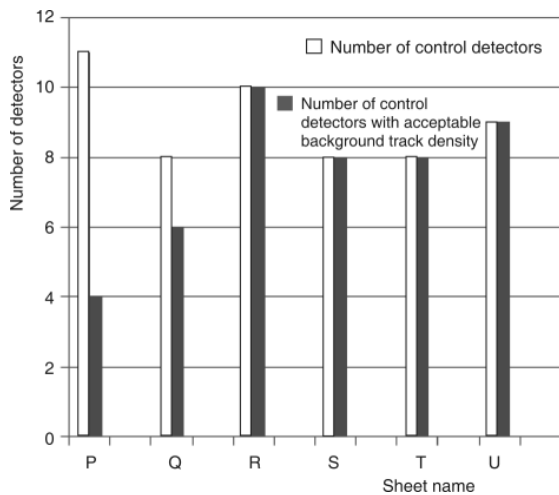
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Figure 8. Total number of control detectors used in the study, along wityh control detectors with an acceptable background track density of sheets developed in phase III
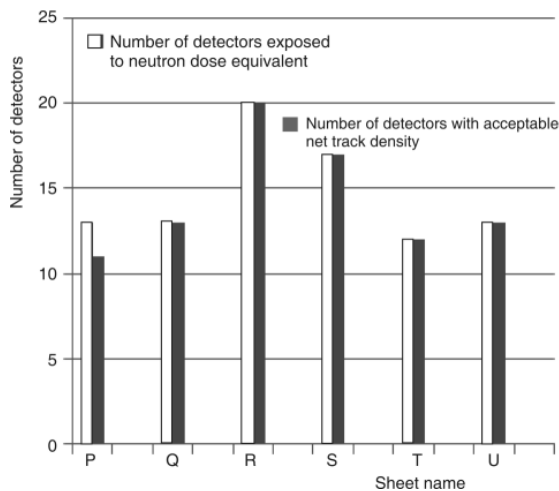

Figure 9. Total number of detectors exposed in the study along with numbers of detectors with acceptable net track density of the sheets developed in phase III

>3.0). It can also be observed from paragraphs given in figs. 8 and 9 that all the control and exposed detectors of sheets R-U used in this study produce an acceptable background and net-track density . The MDL was also up to 0.2 mSv, as required for personnel monitoring. These sheets were promising, as they meet the acceptance criteria and, hence, the dose linearity studies carried out on them, as shown in fig. 10. The dose linearity for sheets R through to U has been established as being   30 %.

As for sheets R and S, a 12 h curing cycle was carried out, whereas T and U were polymerized with a 24 h curing cycle. The sheets exhibited good dosimetric characteristics, comparable to the   reference CR-39 detector. The quality of the PADC sheet depends on the purity of the monomer, the most impor-

tant ingredient of every PADC and. hence, it it is essential to have stringent checks on the purity of the monomer. As can be observed from tab. 3, in case of 12 h curing, out of eight sheets, only two were of dosimetric quality and as observed from tab. 4, out of six sheets, two were satisfactory and four were of dosimetric grade. In case of 24 h curing, only two sheets were prepared, both of dosimetric quality. Therefore, it can be predicted that 24 h curing has a better chance of providing dosimetric grade sheets, due to a prolonged and slow polymerization which leads to sheets with an uniform surface. The sheets prepared with a 24 h curing cycle are promising for personnel neutron monitoring.

This continuous improvement of the curing cycle over a period of three years has finally succeeded in producing dosimetric grade PADC which can be used for neutron monitoring. Sheets of larger size utilizing a large polymer press can now be polymerized without cracking. PADC sheets with an uniform surface can also be made.

CONCLUSIONS

Intact PADC sheets of dosimetric grade sized 25 cm   15 cm were produced in the present study and a curing cycle of 12 h and 24 h standardized. The entire process of evaluating indigenous PADC sheets, starting from detector preparation, irradiation, etching, and counting, was standardized in BARC. It was observed that polymerization over a longer period, *i. e.*, 24 h, results in better quality dosimetric grade detector sheets. A curing cycle of 24 h could produce PADC sheets with a MDL of 0.1 mSv and a signal-to-noise ratio of 8, similar to reference CR-39.

AUTHOR CONTRIBUTIONS

Experimental work was carried out by the team consisting of R. Pal, V. S. Nadkarni, D. Naik, and M Beck. V. S. Nadkarni and D. Naik have contributed towards the development of the indigenous ADC monomer and PADC polymeric detector sheets. The dosimeter preparation, irradiation and, etching was conducted by M. Beck and R. Pal. The
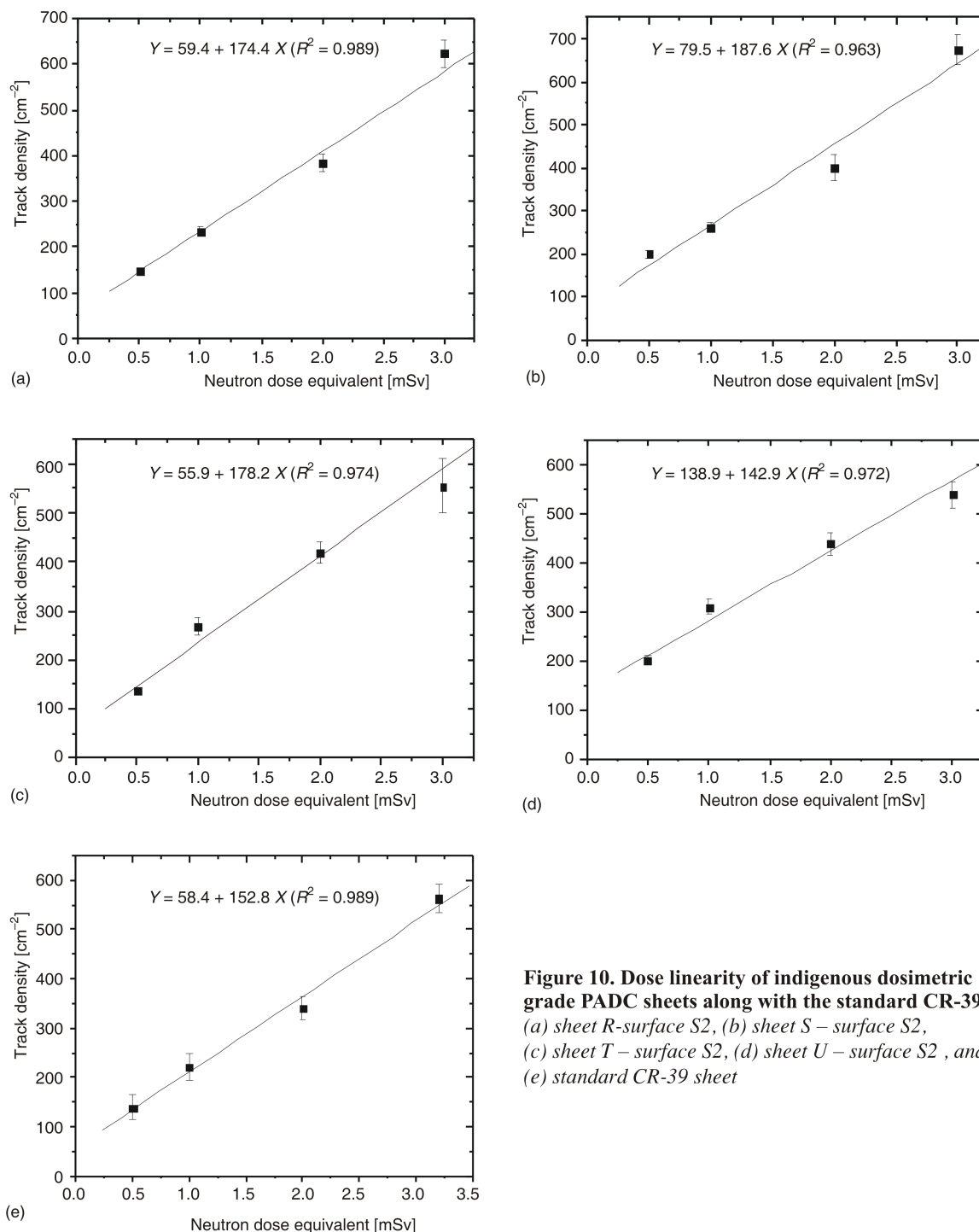
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Figure 10. Dose linearity of indigenous dosimetric grade PADC sheets along with the standard CR-39 sheet;
(a) sheet R-surface S2, (b) sheet S – surface S2,
(c) sheet T – surface S2, (d) sheet U – surface S2 , and
(e) standard CR-39 sheet

analysis was done by R. Pal. The manuscript was written by R. Pal, V. S. Nadkarni, and A. K. Bakshi and the figures prepared by R. Pal and V. S. Nadkarni. M. P. Chougaonkar, G. Chourasiya, Y. S. Mayya, and D. A. R. Babu gave valuable suggestions during each phase of the work and important scientific inputs while writing the manuscript. All authors have contributed to the analysis of results.

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РАЗВОЈ И ДОЗИМЕТРИЈСКА КАРАКТЕРИЗАЦИЈА ДОМАЋЕГ PADC ДОЗИМЕТРА ЗА ЛИЧНУ НЕУТРОНСКУ ДОЗИМЕТРИЈУ

CR-39 је нуклеарни траг детектор, познат под хемијским називом поли-алил-дигликол-карбонат, са широком применом у личном мониторингу због своје осетљивости на неутроне и одличних оптичких својстава која олакшавају анализе и дуг радни век. Данас се ови детектори увозе и користе за програм личног мониторинга у Индији, те је стога уложен труд у њихов домаћи развој. Спроведени су различити хемијски процеси као што су синтеза алил-дигликол-карбонат мономера и изопропил-пероксид карбоната као иницијатора процеса полимеризације и резултати овог поступка приказани су у овом раду. Развијен је метод за прављење неиспрекиданих плоча поли-алил-дигликол-карбоната димензија 25 cm   15 cm и дебљине 500-800 μm. Дужи процес полимеризације доприноси већој осетљивости на неутроне, снижава границу минималне детекције и побољшава однос сигнал-шум. Резултати показују да је могуће развити PADC детектор са минималном детекцијом од 0.1 mSv и односом сингал-шум од 8.0.

Кључне речи: поли-алил-дигликол-карбонат, електрохемијско нагризање, неутронска дозиметрија