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Photo Induced Structural Changes in Insecticide Incorporated Mosquito Net Material

Neha Sharma, Vijay Veer**, Ashwani Kumar Shrivastava* and R.S. Chauhan****

*SOS in Physics, Jiwaji University, Gwalior, (MP) India,
**DRDO Laboratory, Tejpur, India,
***Center for Environment and Social Engineering, Gwalior, (MP) India.

(Corresponding author: R.S. Chauhan)
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ABSTRACT: This Paper reports changes in the mechanical properties and other morphological details of indigenously developed mosquito net filament and granules from which filaments were made. Mechanical properties of exposed filaments registered loss in strength and elongation at break due to susceptibility of polymer structure to imposed stress by solar radiation. Raman studies on polyethylene granules showed enhanced intensity after exposure due to increase in crystalline domain and increased number of scattering units due to scission of chain molecules. Shrinkage measurements indicated relaxation of longitudinal stress set in during the drawing of filaments. Lower shrinkage of solar exposed filaments indicates relaxation of stress as well as filling of amorphous regions to some extent. Scanning electron micrographs revealed interesting surface relief in the form of tiny nodular structure.

Keywords: Deltamethrin, Polyethylene, tensile strength, Raman spectroscopy, Shrinkage, Scanning Electron Microscopy

I. INTRODUCTION

Polymers present one of the most significant supports to our current life style including health care. Currently, polyester, Nylon and Polyethylene (PE) have been roped into to fight the menace of malaria in the form of net material. It is known that malaria inflicts a huge health care burden in terms of mortality and morbidity worldwide, and mosquito net provides first line of defence against mosquito bites [1]. In order to ensure that mosquito do not stay even on the surface of the net and find their way inside into the net, various chemicals have been tried to make the net repellant to mosquitoes [2-3]. To fortify the protection behavior of mosquito net, WHO recommended treatment of nets with pyrethroids like deltamethrin. In several endemic area of the world including India, laboratory and field trials showed better protection with treated mosquito nets as compared to untreated nets [4-5].

Initially mosquito repellent nets were made by externally treating the net material with pyrethroids. However these nets became cause of environmental concern due to the leaching of chemicals during washing and in turn also became less effective. As a result, Long Lasting Insecticide Treated Nets (LLIN) was developed by incorporating the insecticide in to the net material during the extrusion of net filaments. Mosquito nets are made from polymer filaments. It is known that certain residual impurities remain in the polymer during its synthesis.

When polymer chips are converted into filament, oxidative impurities also get introduced inadvertently as the polymer is subjected to heat, oxygen and shear forces. All these factors lead to deleterious effect on the macromolecular structure [6-8]. These impurities are known to impart an element of degradability to an otherwise non-degradable polyethylene molecule [8-10]. Many studies proposed different chemical mechanisms to explain the processes of degradation of polyethylene, by light heat or weathering conditions [11]. The degradation and stabilization of polyethylene has been studied for a long time but continued knowledge in this field is still needed today particularly when virgin polymers are processed at small scale industries. It is imperative that in absence of standard operating procedure and processing controls, poor product development may result in at many small scale polymer units. While the mosquito repellant material is doped into net material, addition of `extra impurities' is ensured in the form of weak sites, unsaturated groups and branching which decrease the dissociation energy of C–C bonds [6,8]. These additives may further enhance the photo-degradability of polyethylene net material. With this logic in view, physical properties of deltamethrin-doped polyethylene filaments, exposed to UV and solar radiations were evaluated along with their respective controls, since the mosquito net is likely to last a couple of years.

As far as authors are concerned no study appears to have been documented in the literature on the aspects of photo degradation of LLIN material and the resultant changes in physical properties.

II. MATERIALS AND METHODS

Deltamethrin (DM) is a broad-spectrum synthetic dibromo - pyrethroid. It is stable to light, heat (for 6 months at 40°C), and air, but unstable in alkaline media [12].

Deltamethrin doped and UV stabilized polyethylene (PE) filaments along with un-doped ones having a diameter of 145 ± 15 µm were obtained from one of the laboratories of DRDO. These were subjected to X-ray diffraction studies to confirm the type of polymer. The peak at $2\Theta = 21°$ of the samples corresponded to polyethylene.

A. Solar Exposure

PE Filaments were exposed to solar radiations by placing them at the roof top of a building at Gwalior, India situated at the latitude of 26° 13' N and longitude of 78° 13' for 250 days between January to September where the temperature can vary between 5° to 48°C. During summer season the surface temperature of roof can easily go beyond 55°C.

B. UV Exposure

Filaments were exposed to UV radiation (ATLAS UV-2000, Wave length 280-310nm, Irradiance 0.63 W/ M^2, Temperature 60°C, UV light cycle 8hrs, condensation cycle 4 hrs). The exposure was carried out at 30% RH as per the ISO method. The total UV exposure time was 150h for tensile strength measurement and 250 days for Raman spectroscopic studies.

C. Shrinkage Measurement

Measured length of control as well deltamethrin incorporated PE filaments, were subjected to 15 minutes boiling in distilled water. Similarly their corresponding solar exposed samples were exposed to boiling water for 15 minutes. After drying their lengths were recorded. From these measurements the extent of shrinkage was calculated.

D. Mechanical Properties

Tensile strengths of control films and solar-exposed films were recorded on an Instron tensile tester with a cross-head speed of 150 mm/min. Test specimens of 50 mm long was used. For each test 10 specimens were taken. The loss in strength and elongation was computed from their respective unexposed samples.

E. Laser Raman Spectroscopy

Renishaw In via Raman Microscope was used to obtain Raman spectra of films before and after the solar exposure. A solid diode laser operating at $\lambda = 785$ nm was used as the excitation source with a laser power of 25 mW. The Rayleigh lines were eliminated from the scattering by a holographic notch filter. The samples were mounted on an X-Y scanning stage controlled by a stepper motor. The laser beam was focused via a microscope onto the sample. The system has a variable aperture for confocal acquisition of images. Signals were detected using a charged couple device (CCD) camera at a spectral resolution of $4 cm^{-1}$. The instrumental parameters like laser power, exposure time, and number of accumulations were kept constant for all the experiments. The instrument was used in the normal mode with a 50X objective for the Raman mapping.

F. Scanning Electron Microscopy

Electron microscopic studies were performed with a FEI Quanta-400; SEM. Samples were coated with a thin layer of gold produced by ion sputtering in Ion Sputter JFC-1100 before observing these in the electron microscope at various accelerating voltages.

III. RESULTS AND DISCUSSION

Table 1 presents strength and elongation data for control (undoped) polyethylene filaments before and after solar exposure. Exposure to solar radiations for 250 days results in the loss of 34.87% strength and 37.80 % elongation.

Table 1: Mechanical Properties of Pe Net-Filaments.

Poly-ethylene	Tensile Strength MPa	Standard Deviation SD	Loss in Strength (%)	% Elongation	Standard Deviation SD	Loss in elongation (%)
Control	**398.9**	**10.3**	**34.87**	**34.76**	**3.6**	**37.80**
Solar Exposed	**260.5**	**13.0**		**21.60**	**5.2**	

Table 2 shows the similar data for the deltamethrin doped polyethylene filament. Incorporation of deltamethrin along with UV stabilizer tends to lower the strength of filament as compared to its corresponding unfilled specimens. The doped filament registered tensile strength of 288.00 MPa as against 398.9 MPa for the control. However loss in strength of control filament is higher (34.8%) as compared to deltamethrin filled filaments after the exposure (27.4%). The loss in elongation is higher for the solar exposed deltamethrin doped filament and is to the tune of 48.8% whereas it is 37.86 % for the solar exposed control filaments. The extension at break reduces after the solar exposure for both kinds of samples. The addition of mosquito repellant ingredients to filaments may lead to non uniform distribution of the added ingredients across the length of filaments. This uneven distribution will add to non uniform distribution of stress in filaments under tensile loading resulting into lower tensile strength. A polymer matrix, that has strong intermolecular forces, otherwise contains large constrained regions [8, 13, 14]. These constrained regions become more susceptible to imposed stresses in the form of solar energy and day-night temperature fluctuations. Coupled with solar radiation, the humidity, rains and elevated temperatures during the day can influence the destructive effects of solar radiation, by accelerating the rate of secondary reactions and introduction of micro-discontinuities on the surface [14, 15]. It is known that deformation under tensile load initiates from surface flaws and micro-discontinuities and weathering for 250 days may have initiated many such flaws [14].

Table 2: Mechanical Properties of Deltamethrin Doped Net Filaments.

DM (PE)	Tensile Strength MPa	Standard Deviation SD	Loss in strength (%)	% Elongation	Standard Deviation SD	Loss in elongation (%)
Control	**288**	**11.8**	**27.4**	**42.5**	**4.5**	**48.8**
Solar Exposed	**209**	**14.0**		**22.0**	**6.5**	

Fig. 1 shows the Raman Spectra of PE granule from which the filaments were drawn. The spectra show characteristic peaks of polyethylene [13, 15] around 380cm^{-1}, 1062cm^{-1}, 1080cm^{-1}, 1129cm^{-1}, 1169cm^{-1}, 1295cm^{-1}, 1360cm^{-1}, 1414cm^{-1}, 1440cm^{-1}, 1470cm^{-1}, 2848cm^{-1} and 2882cm^{-1}.

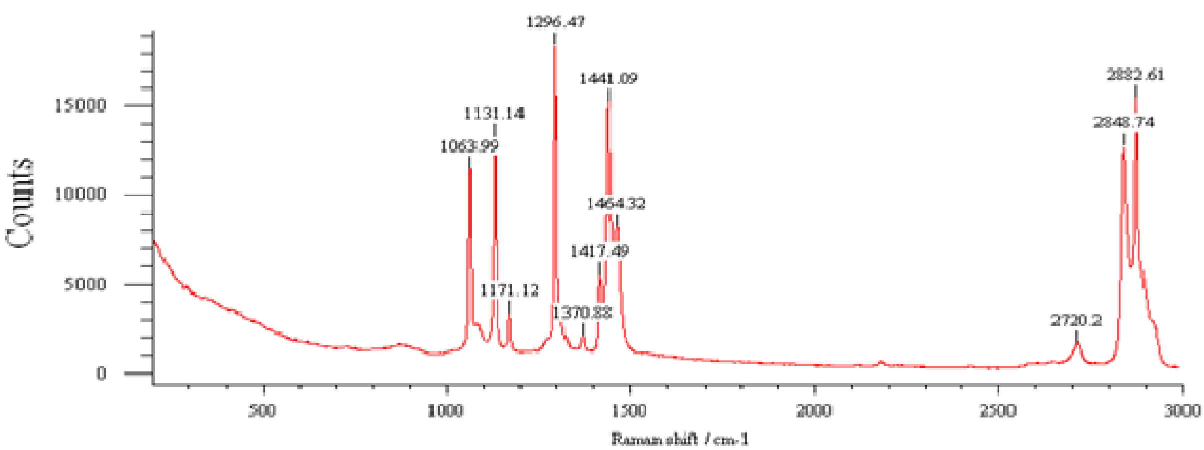

Fig.1. Polyethylene (Control).

Exposure to solar radiations for 250 days results in Fig. 2 substantial change in intensity at 380cm^{-1} and 1371cm^{-1}. The peak at 1371cm^{-1} appears to have components of CH_2 twisting and bending. Authors could not assign the peak at 380cm^{-1}. The other intensities at 1171cm^{-1}, 1441cm^{-1}, 1464cm^{-1} and 2720cm^{-1} decreased marginally to about 11 to 15 percent. However there is an increase in intensities at 1064cm^{-1}, 1131cm^{-1}, 1296cm^{-1}, 1417cm^{-1}, 2828cm^{-1} and 2882cm^{-1} after exposure to solar radiations.

Peaks around $1064cm^{-1}$ and $1130cm^{-1}$ corresponds to C-C stretching mode in crystalline region. Peak at $1296cm^{-1}$ which corresponds to crystalline domain is considered anisotropic in nature. Intensity enhancement of these peaks, indicate changes in crystalline regions.

The peak at $1441cm^{-1}$ corresponding to CH_2 deformation in the region where both crystalline and amorphous phases contribute for Raman scattering registered about 12% decrease over the unexposed granule. The Raman at $1464cm^{-1}$ that has been assigned to CH_2 rocking mode registered lower intensity.

The peaks around $2847cm^{-1}$ and $2882cm^{-1}$, corresponding to symmetric C-H stretching and anti symmetric C-H stretching showed relatively higher scattering. It is established that exposure to solar radiations triggers complex weathering process in polyethylene, involving macromolecular mobility, diffusion-controlled reactions, free-radical formation and chain scission as well as cross-linking [10,16]. These solar induced complex changes results into variety of Raman scattering affecting back-bone vibrations to different extent.

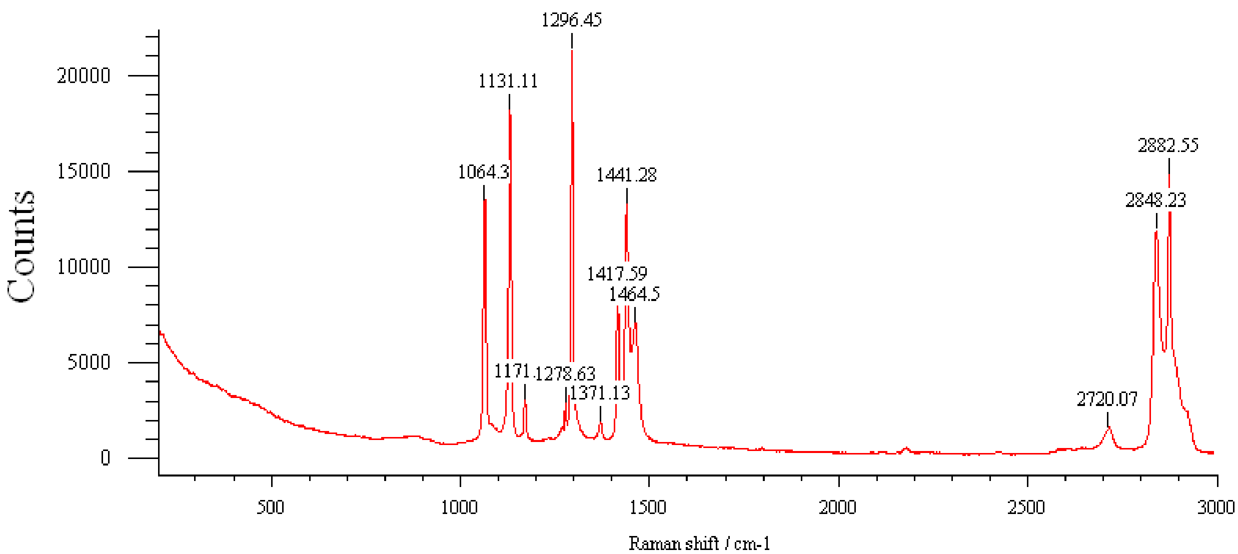

Fig. 2. Polyethylene (Solar exposed).

Fig. 3 and 4 presents Raman spectra of Deltamethrin incorporated PE granules exposed to solar radiations for 250 days. It is interesting to note that almost all the characteristic peaks of PE registered substantial increase after solar exposure as compared to control PE and 250 days exposed PE.

The intensity of Raman band is also governed by the change in polarisability, as atoms pass through their equilibrium positions as a result of incident energy. The solar exposed granules indicate change in polarisability as indicated by the Raman spectra.

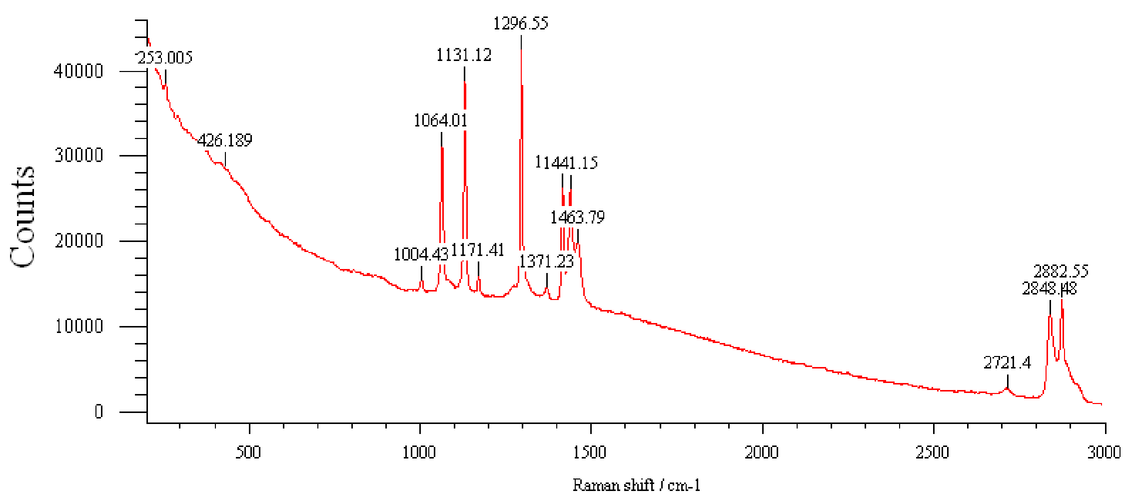

Fig. 3. DM incorporated PE (control).

This increase in Raman scattering could results from the incorporation of deltamethrin during the making of PE granules with deltamethrin as well. Deltamethrin is known to crystallize with nano sized crystallites ranging between 6.9 nm to 47 nm after subjecting to heat and on subsequent cooling [12].

In an another study on thermal behavior of deltamethrin in our laboratory, it has been noted that with increasing temperature from 90^{O}C to 250^{O}C the Raman scattering continuously registers higher absolute intensity for almost all the peaks (to be published elsewhere). Thus while the deltamethrin is processed along with PE to prepare pellets with deltamethrin for subsequent processing into filament, crystallization of deltamethrin results and that leads to enhancement of Raman scattering.

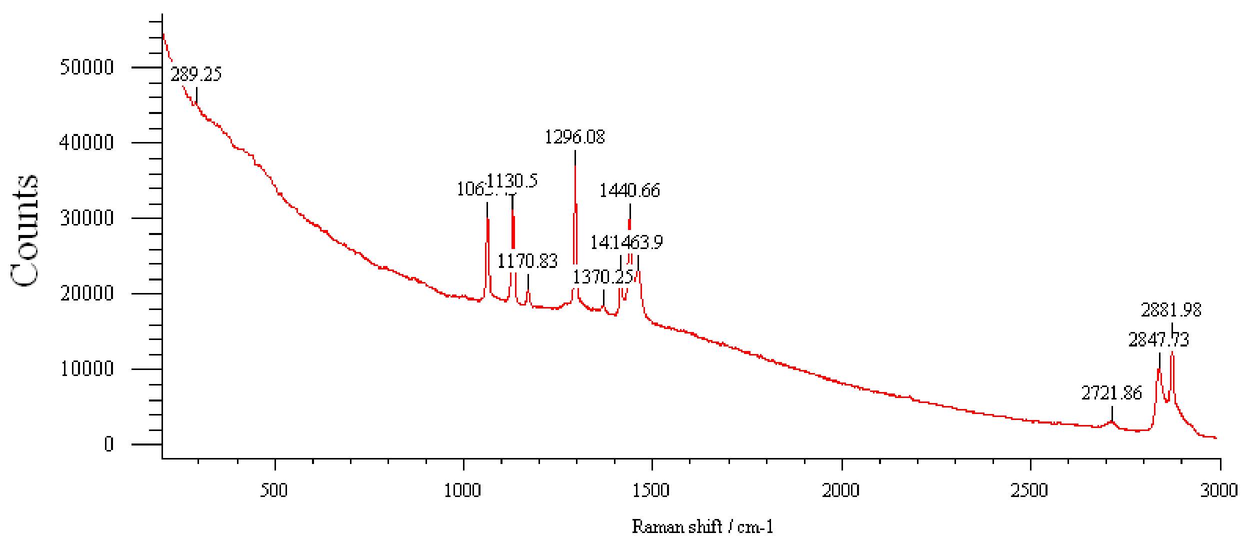

Fig. 4. DM incorporated PE (Solar Exposed).

Table 3 shows the extent of shrinkage experienced by polyethylene filaments after boiling in distilled water. Un-doped control filaments registered shrinkage of 10% and the corresponding UV exposed specimens registered 8.8 % shrinkage. The shrinkage provides insight into relaxation of longitudinal stress imposed on filaments during their formation. It is known that the polymer is subjected to the effect of heat, shear and oxygen in all thermoplastic processing technologies. As an effect of these factors chemical reactions take place in the processing machine with a number of consequences.

Polymer molecules in filamentous form are invariably twisted, folded, bent, intertwined and associated with one another leading to stress build up. Shrinkage in the length of filament indicates that a certain amount of stress relaxation sets in the structure after subjecting them to boiling water heat. The UV exposed sample showed lower change in length perhaps due to the development of crystallinity and filling of amorphous regions as a result of solar energy. Previous studies on polyolefin indicate that exposure leads to development of crystallinity at the expense of amorphous regions [7, 13, and 15].

Table 3: Shrinkage Data on these Filaments.

	Unexposed	**UV Exposed**
Polyethylene	**10%**	**8.8%**
Deltamethrin	**8.0%**	**2.9%**

Fig. (1a) shows a Scanning electron micrographs of deltamethrin doped unexposed polyethylene filament. The surface shows grove marks and lines caused perhaps by spinneret during spinning of filaments. The surface appeared smooth with few dust particles. Surface details of solar exposed deltamethrin filament are shown in Fig.1b. The surface looks similar to the unexposed filament except that a few more surface deposits appear due to environmental exposure. However at higher magnification Fig. 1c the surface revealed small nodular structural throughout the surface caused by the combine effects of heat, day-night temperature variations and other stresses. These dots like structure were present throughout the exposed length of filaments. In order to confirm whether these nodules are superfluous or part of the morphology, these filaments were treated xylene.

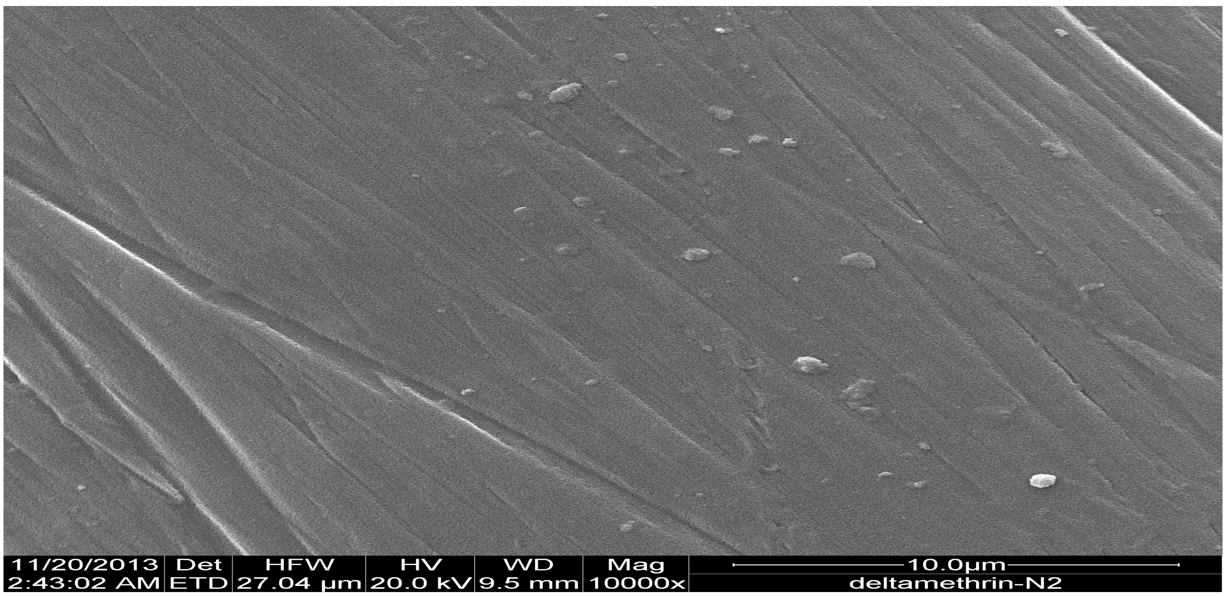

Fig. 1(a) SEM of DM doped unexposed polyethylene filament.

Fig. 1(b) SEM of Solar Exposed DM Filament.

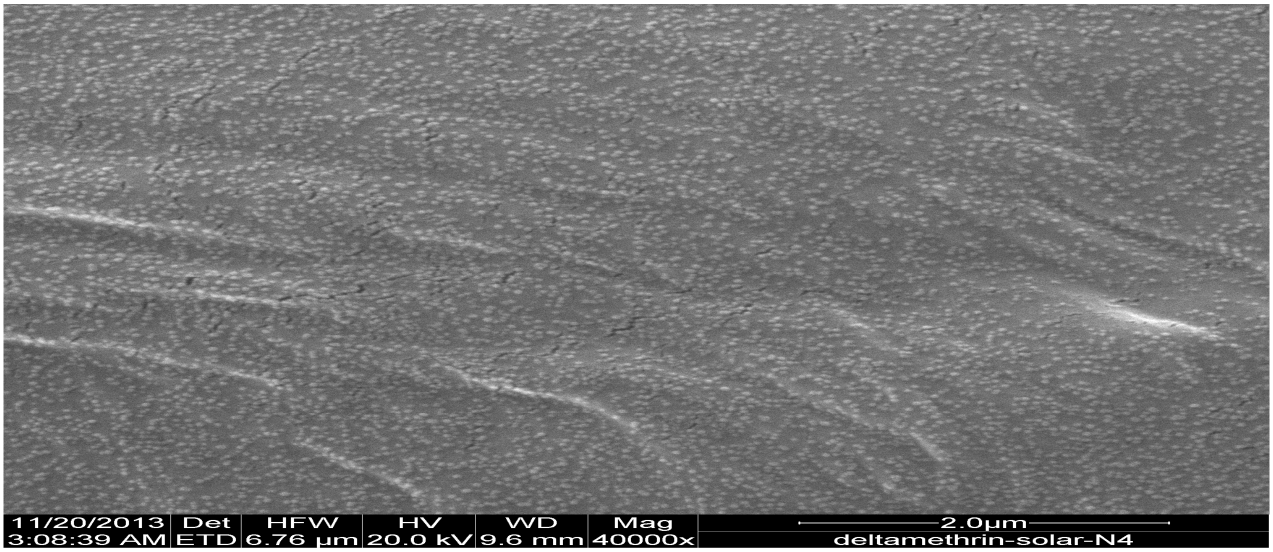

Fig. 1(c) SEM of Solar Exposed DM Filament.

Fig.1d depicts the surface details of solar exposed filament that has been treated with Xylene for 10 hour. Xylene is known to act as an etching agent for polyethylene. Due to the etching effect a number of nodular eruptions were dissolved and underneath cracks and other surface irregularity appeared. These micrographs revealed subtle surface damages induced by the solar exposure to these filaments.

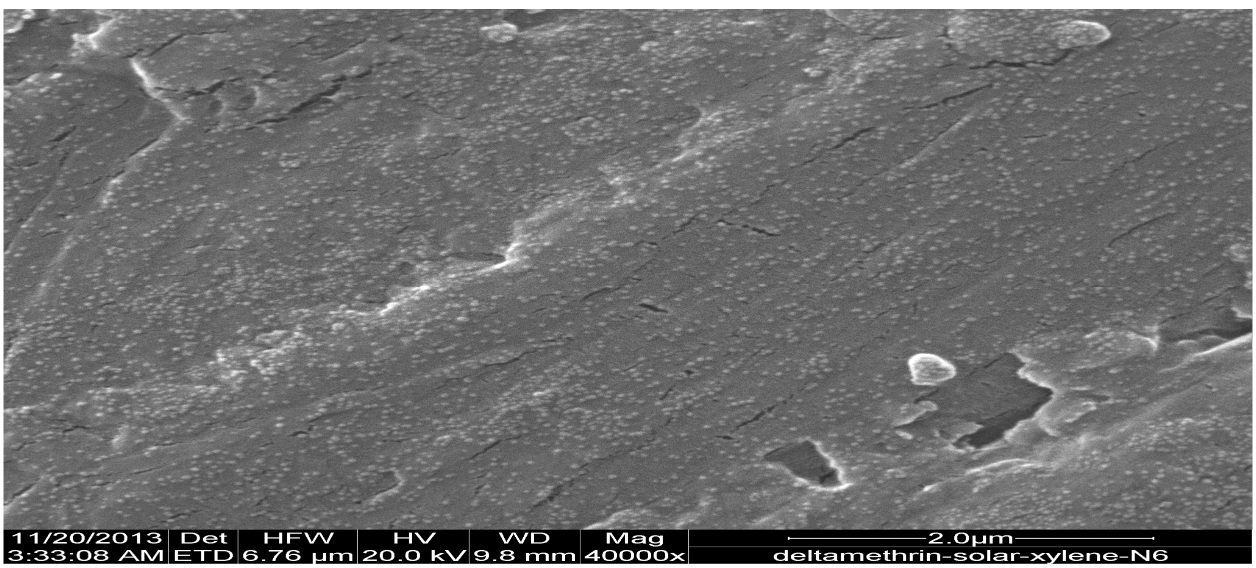

Fig. 1(d) SEM of Solar Exposed xylene treated DM Filament.

IV. CONCLUSIONS

The study brings out the effects of solar radiations on certain physical and mechanical properties of deltamethrin incorporated mosquito net filaments. Mechanical properties of exposed filaments registered loss in strength and elongation at break due to susceptibility of polymer structure to imposed stress in the form of temperature fluctuations, humidity variation, wind and rains. Raman studies carried out on polyethylene granules showed enhanced intensity due to increase in crystalline domain and increased number of scattering units due to scission of chain molecules.

The intensity of Raman band is also governed by the change in polarisability, as atoms pass through their equilibrium positions as a result of incident energy. The solar exposed granules indicate change in polarisability as indicated by the Raman spectra. Shrinkage measurements indicated relaxation of longitudinal stress set in during the drawing of filaments. Lower shrinkage of solar exposed filaments indicates relaxation of stress as well as filling of amorphous regions to some extent. Scanning electron micrographs revealed interesting surface relief in the form of tiny nodular structure.

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