Use of Oleo-Phobic Ion beam Irradiated Grafted Polymer to enhance Transportation of Crude Oil

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Abstract— Flow of crude oil in pipelines leads to deposition of wax on the walls of the pipes in which the oil is transported. This eventually leads to reduction in the diameter of the available area for flow of oil. Also wax offers a cohesive force leading to reduction in speed of flow. Oleo-phobic surfaces may offer effective solutions to many engineering and industrial problems like coating in pipelines for crude transportation which may be responsible for reduction in wax deposition. Oleo-phobic surfaces have been explored due to their self-cleaning character. The multi-functional coating on a grafted polymer surface is the current field of research that has been applied in this paper. The surface morphology of PTFE polymeric surface has been modified by employing two fold methodology for studying the oleophobicity of the PTFE surface with potential application in various engineering processes. First: Increasing the surface roughness by chemical grafting process, under robust conditions and Second: The roughness of the grafted polymeric surface has been further enhanced by irradiating the polymeric surface by low energy Ar^+ ion beam with interaction time of 10s and 100s. The grafting of MMA on PTFE surface has been done at different temperatures, reaction times, monomer concentrations and initiator concentrations, to obtain an optimum value of all these parameters giving maximum grafting yield. To further increase the roughness, the grafted co-polymers were irradiated using 3KeV Ar^+ ions and defocused ion beam for beam time with for interaction time 10s and 100s respectively and again the effect of this treatment on the surface reference and morphology has been studied through FE-SEM, EDS, CAG and XRD analysis.

Key words: Use of Oleo-Phobic Ion beam Irradiated Grafted Polymer, Transportation of Crude Oil

I. Introduction

Oleo-phobic surfaces may offer effective solutions to many engineering and industrial problems like coating in pipelines for crude transportation which may be responsible for reduction in wax deposition. Oleo-phobic surfaces have been explored due to their self-cleaning character. The multi-functional coating on a grafted polymer surface is the current field of research. For obtaining oil-repellent surface, it is necessary to prepare the surface with very small surface tension. These surfaces can be obtained by uniformly applying fluoromethyl (–CF_3) groups on them [1-5]. Thus, the fluorinated compounds usually remain the most common active ingredients for oil-repellent purpose. The basic effect of surface structure on super oil repellency has been well known since the initial publications of Wenzel [6] and Cassie and Baxter [7] model. Both the models have laid emphasis on the geometrical structure of solid surfaces as an important factor in determining the wettability of the surface. Preparation of super oil-repellent surface has been investigated by several publications in the past [8-10]. Starting from Onda *et al.* [11–12] .Such publications have reported a serial achievement that demonstrated that the contact angle of oil droplets on low energy surface increases strongly with growing surface roughness and porosity.

The irradiation of grafted PTFE through low energy (approx. 3 KeV) Ar^+ ion beam is not only responsible to change the surface morphology but also increases the possibility of change in elemental composition. The roughness of the surface is the prime parameter to study the oleo-phobic nature of Teflon surface. The contact angle is quantifiable measurement of roughness of surfaces.

II. Experimental

A. *Materials and Methods*

PTFE film (150 µm thickness) was obtained from Good Fellow, Cambridge, Ltd. Hontingen, England). Benzoyl peroxide (BPO) was procured from S.D. Fine Chem Ltd. (India). MMA and acetone were obtained from Merck Chemicals (India). PTFE films were washed with acetone and dried in an oven. Double-distilled water was used as the reaction medium for graft copolymerization. The processes of graft-polymerization of the samples have been discussed elsewhere. [14]

The ion beam of Ar+ 3KeV Ar^+ ions and defocused ion beam with beam time of 10 and 100s for ion affluence was used in IUAC, Nuclear Science Center, New Delhi.

B. *Chemical Grafting:*

Commercially available polytetrafluoroethylene (Teflon) (Poly-1,1- difluoroethelene) films of thickness 150 µm obtained from Good Fellow, Cambridge Limited of Hontingen, U.K, is used for experimental work. The PTFE films were sliced into square strip of about 2cm x 2cm in size. To remove the organic residue on the surface, the PTFE film was washed with acetone, methanol and double distilled water respectively. The films were dried in air at room temperature and stored in a clean and dry box. Benzoyl peroxide (BPO) [S D Fine-Chem. Limited, India] and acetone (Merck Specialties Private Limited, India) have been used in this work to create active site for grafting Methyl methacrylate (MMA), without further purification.

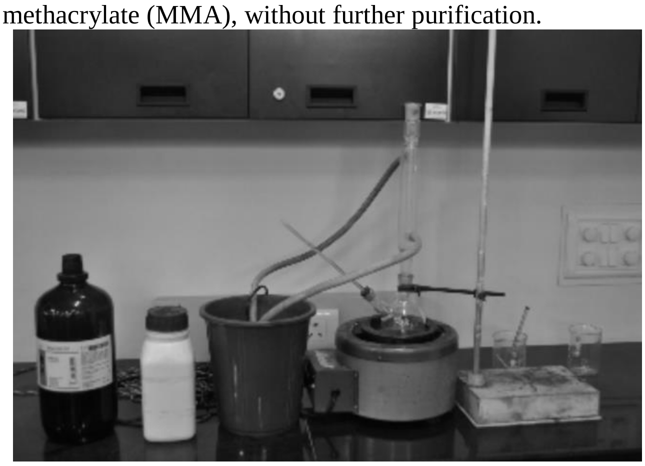

Fig. 1: Chemical Grafting Setup.

The above figure shows chemical grafting set -up designed at chemistry laboratory, University of Petroleum and Energy studies, Dehradun. The Three Neck Flask (T-Flask) apparatus was carefully rinsed with acetone in order to get high degree clean surface. The acetone cleaned Teflon of 2__$._2 cm were weighed through an electronic digital balance (least count 0.001 grams) in dust and dirt free atmosphere. 50 ml of solution was prepared with different concentration of monomer Methyl Methacrylate (MMA) (X %) and was added to (100-X) % of distilled water. The initiator concentration being constant, 0.03gm benzoyl peroxide was dissolved in 10 ml of ethyl alcohol (ethanol). The Teflon film was put in the T-Neck containing monomer MMA, ethanol and BPO solution. One neck of the T-Neck flask was fit with thermometer, second neck was used to keep inserting/taking out PTFE film while the other neck was fit with water cooled condenser which condensed the solution vapour.

C. Ion Beam Irradiation

The Low Energy Ion Beam Facility (LEIBF) at the Inter-University Accelerator Centre, New Delhi, provides Ar+ ion beam of energy 3KeV for irradiating grafted PTFE teflon surface of 150 µm thickness. The LEIBF consists of an Electron Cyclotron Resonance (ECR) ion source (Nanogan from Panteknik) installed on a high voltage deck. This is based on permanent magnet (NdFeB) design for radial and axial confinement of plasma. All the electronic control devices of the ECR source including high power UHF transmitter (10 GHz), are placed on a high voltage deck. These are controlled through optical fiber communication in multiplexed mode. Design and development of the high voltage platform, accelerating system and the beam lines with components thereof like electrostatic quadruple triplet lens, all metal double slit, beam steerers, Faraday cups, all metal pneumatic straight through valve, UHV scattering chamber have been indigenously made. A standard Sputtering method is utilized to generate ion beam - A mechanized arrangement to insert a long thin wire (≈ 0.5mm thick) of Ar element to be introduced into the source plasma volume. The high energy electrons can sputter out the elements present in the wire, ionize them and produce the required beam.

III. RESULTS AND DISCUSSIONS

A. Grafting Data Analysis and Results

Grafting reaction involves the copolymerization of a monomer onto a polymer backbone. The formation of copolymers of various synthetic and natural polymers via graft copolymerization has been extensively studied [11]. Methyl acrylate (MA) and Methyl methacrylate (MMA) have been graft copolymerized with numerous polymeric backbones using various initiating systems. Though there are different number of methods present to change the surface morphology and roughness parameter of polymer surface, but in the present work, the polymer surface is modified by chemical induced graft copolymerization.

In the present work, an attempt has been made to change the surface morphology of PTFE polymer through grafting of monomer Methyl Methacrylate (MMA) through chemical grafting method. In this work, the effect of monomer concentration, initiator concentrations, effect of temperature of the reaction and time of reaction on grafting were discussed and analyzed.

Teflon (PTFE) surface modification after grafting was studied and verified through FE-SEM. Crystallographic changes were analyzed through XRD. Contact angle goniometry applied to measure and analyzed the variation of contact angle.

B. FE-SEM Study

Field Emission Electron Microscope (FEI Quanta 200F model) with resolution of 2nm and possible magnification 500000 X to study the surface morphology of the grafted PTFE film was used. FE-SEM analysis provide qualitative analysis of the surface morphology at various magnification FESEM uses field emission electron gun which provides improved special resolution down to 1.5 nm that is 3 to 6 times better than conventional SEM and minimizes sample charging and damage. The electron beam, which typically has an energy ranging from a few hundred eV to 50 KeV, is focused by two condenser lenses into a beam with a very fine focal spot size of (1 to 5 nm). The basic mechanism of field emission is that a high voltage applied between a pointed cathode and a plate anode causing the current to flow. The field emission tip is generally made of a single crystal tungsten wire sharpened by electrolytic etching. A tip diameter of 100 to 1000 Å is used, with the apparent source size much less than that. The field emission process itself depends on the work function of the metal, which can be affected by adsorbed gases and due to this very high vacuum is required [12]. The contrast in an SEM image reveals information about the surface morphology and composition of the material.

Comparative analysis and to study the optimum roughness condition, two sets of irradiated sample of PTFE was considered (i) irradiated with beam time of 10 sec (ii) irradiated with beam time of 100 sec. For each set, four images at various grafting temperature i.e. 40, 50, 60 and 70°C are considered. Set of Fig. 1 shows the FE-SEM images of irradiated PTFE sample with beam time of 10 sec with various grafting temperature i.e. 50, 60 and 70°C (other conditions remain constant) Fig. 2 is for same set but beam time in these set of figure is 100 sec.

Following conclusions are drawn from these sets of figures:

C. Pristine and Grafted Polymer:

Fig. 1 (a) SEM observation showed that the surface of pristine PTFE has low but uniform roughness without sharp edges. The surface edges are the ones which rarely observe any non-uniform valleys. The surface is more or less uniform and smooth. The dark spots indicate a little irregularity in the height of sample at that particular portion of pristine surface.

D. Grafted and Ion Beam Irradiated polymer

Fig. 1(b) FE-SEM observation of PTFE sample irradiated for 10 Sec and grafted at 50°C. Mild bumps are observed with Shallow irregularities on the surface. The peak to valley height does not exceed 0.5mm. Approximately equal portion of dark and mild spots are present. It indicates that due to irradiation the surface roughness increases. Light crack is also observed at one portion of the image.

Fig. 1(c) and (d) FE SEM observational image of PTFE sample irradiated for 10sec and grafted at 60ºC and

70°C. Deep dark line observed at the surface indicates the possibility of surface cracking and irregularity. Dugs are also observed in the image shown with arrows .There is the possibility of surface distortion.

Approximately similar observation is observed in second set of figure. Fig. 2(b) shows the maximum roughness as portion of dark and mild spots is almost equal and at higher temperature the crack is developed hence it is of no use.

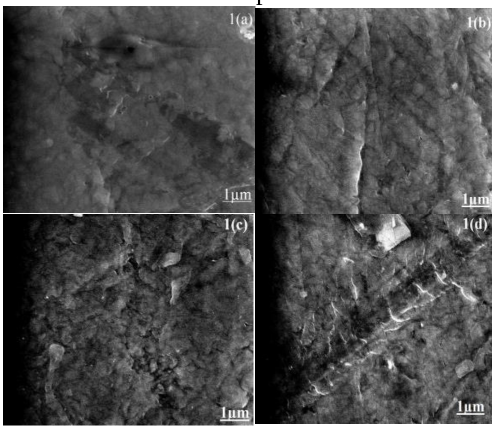

Fig. 1: FE-SEM images of ion-beam treated pristine and grafted PTFE. (a) Pristine (b) Grafted at temperature 50°C (c) Grafted at temperature 60°C (d) Grafted at temperature 70°C. The beam time for all the samples was 10 seconds.

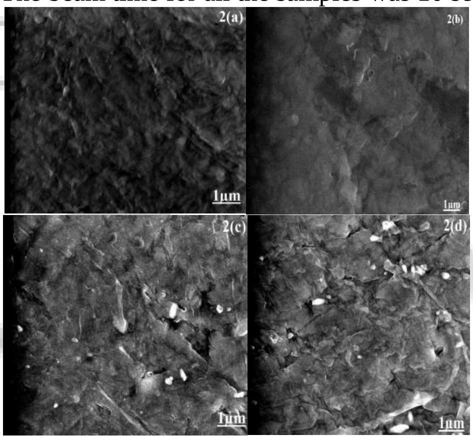

Fig. 2: FE-SEM images of ion-beam treated pristine and grafted PTFE (a) Pristine (b) Grafted at temperature 50°C (c) Grafted at temperature 60°C (d) Grafted at temperature 70°C. The beam time for all the samples was 100 seconds

FE-SEM analysis of the irradiated (for 10 sec.) shows that smoothness of the samples decreases when compared with that of the pristine. With increase in grafting temperature, it was observed that as temperature goes beyond 50^{0}C the sample surface is deformed which is evident from the micro –size cracks in the samples. No such kind of micro cracks were observed in the samples grafted at 50^{0}C except the decrease in smoothness. As increasing the irradiation time by 100 seconds, several micro-sized pits were observed on the sample surface for all grafting temperature.

E. Elemental Analysis of low Energy Ar+ Ion Treated PTFE

Using the energy dispersive x-ray analysis (EDS) attachment with the SEM, elemental composition analysis can be done. An EDS spectrum displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen. Interaction of an electron beam with a sample target produces a variety of emissions, including X-rays. An Energy-Dispersive X-Ray Spectroscopy (EDS) detector is used to separate the characteristic X-rays of different elements into an energy spectrum. EDS system software is used to analyze the energy spectrum in order to determine the abundance of specific elements.

X-ray spectrometers with X-ray tube generators as sources and Si(Li) detectors have been used for X-ray diffraction (XRD).With a radioactive source, an EDS system is easily portable and can be used in the field more easily than most other spectroscopy techniques. With a minimum detection limit (MDL) of 100-200 ppm for most elements, an EDS system is capable of detecting less than a monolayer of metal film on a substrate using Kα lines at moderate accelerating voltages of 5-15KeV.

The experimental set up of EDS is attached to FE-SEM (Model: FEI Quanta 200F, FEI Company Oregon USA) at IIC (IIT, Roorkee). The height of the amplifier output pulse is proportional to the input preamplifier pulse, and hence is proportional to the X-ray energy.

Detectors are maintained under vacuum at liquid nitrogen temperature to reduce electronic noise and to inhibit diffusion of the lithium when the bias voltage is applied. The gold-coated outer surface is usually further protected by a thin window of beryllium or a polymer. Fig. 7.5 and 7.6 represents the output of EDS system. The peaks C(K) F(K) and O(K) are almost same in each figure. The individual weight % is also depicted in each diagram.

There was no change in the composition of the element found via EDS analysis. This clearly shows that the ion beam which is used to increase the oleophobicity of the grafted Teflon has only imparted the energy to decrease the smoothness of the sample. The ion has not got embedded in the sample.

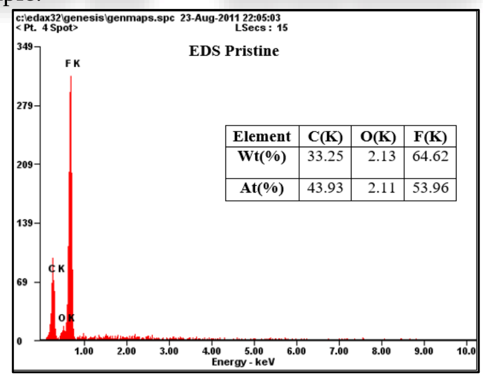

Fig. 3(a): Energy Dispersive Spectrum of Pristine PTFE

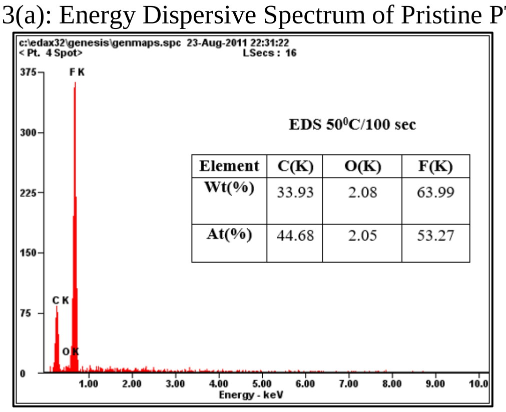

Fig. 3(b): Energy Dispersive Spectrum of treated PTFE (Beam Time=100 sec) with grafting temperature 50°C

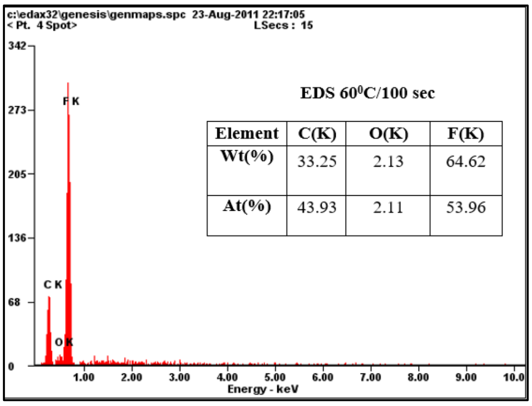

Fig. 3(c): Energy Dispersive Spectrum of treated PTFE (Beam Time=100 sec) with grafting temperature 60°C

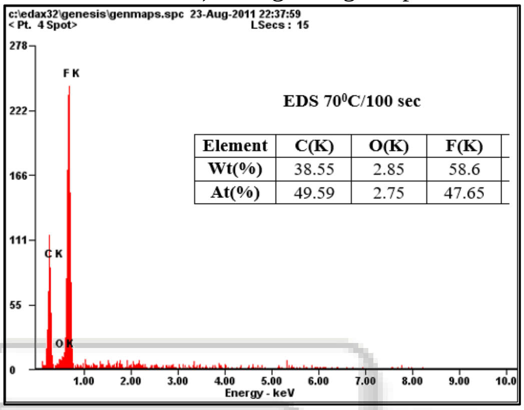

Fig. 3(d): Energy Dispersive Spectrum of treated PTFE (Beam Time=100 sec) with grafting temperature 70°C

F. Irradiated PTFE Surface Analysis through Contact Angle

Grafted Polymer treatment was performed with the ISE 10 ion gun using 3 KeV Ar+ ions and a defocused ion beam with ion affluence of 10^{16} cm^{-2}. After treatment, the samples had to be remove from the vacuum chamber as the contact angle measurements were performed in air. The two sets of four samples of PTFE with different grafting temperatures (i.e. 50°C, 60°C, 70°C and Pristine) were prepared for ion affluence (≈ $10^{16}cm^{-2}$) For first of sample beam time is 10 sec while for other set of samples beam time is 100 sec. The average contact angle was taken as an angle for particular ion affluence. The contact angles θ were calculated by the program using the Young-Laplace function. The software allows to take photographic images of the drop which will be shown in Images.

Static contact angle of methylene iodide CH_3I with treated polymer surface in order to analyze the changes generate in 2 cm x 2 cm (150 μm) grafted PTFE after irradiated through low energy (3 MeV) Ar+ ion beam is determined by contact angle goniometry**.** The Lubricant CH_3I is used to measure contact angle on treated and untreated PTFE. The Oil drop on untreated PTFE is of the form of a bead with the angle θ < 90° i.e. θ ≈ 86.4° . With increasing temperature, the liquid spreads on the treated surface, showing that the olio-philic PTFE surface becomes olio-phobic, when the polymer is irradiated with ions. For the contact angle measurements, the contact angle system called "Easy Drop Standard" from KRUSS, Germany with pre-installed Drop Shape Analysis Software DSA-1 was used at Institute Instrumentation Centre, Indian Institute of Technology (IIT), Roorkee. The Pre-Installed DSA-1 Software is to determine static contact angles using sessile drop method, to control camera, illumination, temperature, dosing modules, table movements, to measure, store and report measured contact angle values. The manual sample table moves the sample to the right position. Single dosing system deposits the drop onto the treated polymer surface by micro-syringe.

Contact angle measurements were done using air as medium. The treated polymers were removed from vacuum and reacted with atmospheric O_2. During these reactions oxygen containing functional groups were formed that influenced the experimental measurements.

Grafted PTFE(150μm) (Ar^+ Treated) Contact Angle(θ)	Degree of Grafting (%)	0%	3.75%	9.77%	8.39%	5.3%
	Temperature	Room Temp.	40˚C	50˚C	60˚C	70˚C
	Pristine	90.4°				
	Grafted	90.4°	92.0°	95.5°	93.3°	93.0°
	Grafted + Irradiated Beam Time = 10 Sec	92.3°	92.6°	104.4°	98.0°	90.2°
	Grafted + Irradiated Beam Time = 100 Sec	90.9°	92.4°	103.2°	96.0°	90.4°

Table 1: Variation of contact angle with % monomer grafted for beam time 10 sec and 100 sec.

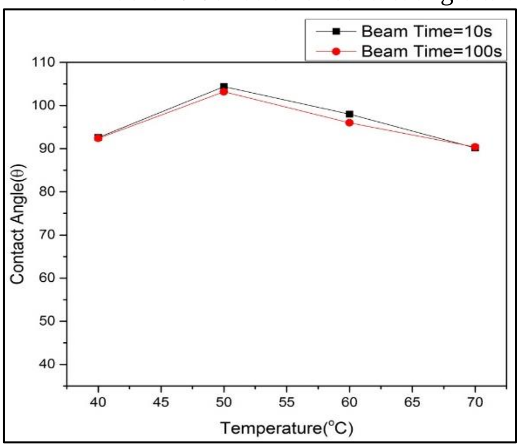

Fig. 4: Variation of contact angle with grafted temperature of PTFE with beam time of 10 sec and 100 sec.

G. Crystallographic Analysis of Irradiated Teflon Polymer through XRD

XRD was direct evidence for the periodic atomic structure of the polymers and is the most powerful tool for determining the structure and orientation of polymers. XRD is a non-destructive technique and is based on Bragg's Law. Bruker D8 Advanced Diffractometer uses Nal scintillation counter as a detector at Institute Instrumentation Center (Indian Institute of Technology, Roorkee) is used for the materialistic characterization of PTFE polymer surface. Fig. 6 represents the output of XRD for pure pristine and PTFE grafted at 50°C and 60°C with irradiated ion beam time of 10 sec. The peak exists at approx. 21° indicating that crystallographic planes of PTFE with grafting temperature 50°C show maximum orientation at this glancing angle. The height of the peak for the sample grafted at 50⁰C is maximum, which indicates that the crystallographic behavior of PTFE grafted at 50°C is maximum in comparison to PTFE sample grafted at 60° and 70°C.With the help of comparative analysis in context of their peaks with the pristine, we reached to a conclusion that the crystallographic changes in PTFE sample grafted at 50°C with 10 sec beam time is maximum.

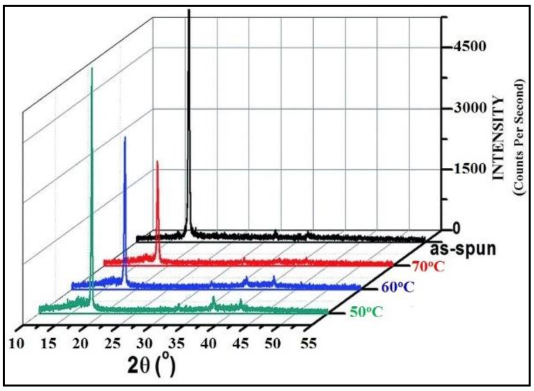

Fig. 5: Comparative analysis of XRD images of pristine with treated PTFE grafted at 50°C, 60°C and 70°C temperature

IV. Conclusion

FE-SEM image of treated PTFE surface (after grafting) revealed that maximum change in surface morphology in context of change in surface roughness was achieved on 50°C grafted PTFE with 3Mev Ar+ ion beam treatment for 10 sec (Fig.8.3). The maximum bumps and white patches appeared in PTFE surfaces is maximum at 50°C sample. Irregularity and non-uniformity without cracking is the evidence of maximum roughness on grafted PTFE after irradiation**.** The contact angle goniometry also revealed that maximum contact angle of 104.4° was achieved on PTFE surfaces which were grafted at 50°C.

Similarly, the XRD analysis output is also in full compliance with the results i.e. maximum number of counts was observed for treated PTFE with grafting temperature of 50°C.

Monomer grafted PTFE sample showed slight increase in contact angle. However, after irradiation further increase of 8-10° was observed. This definite change in contact angle corroborated well with increase in the surface roughness as seen in FE-SEM images.

This hence incorporated the idea of such polymers in fuel transportation lines to reduce any form of wax deposition in the fuel lines which can often be problematic. However the proper application of the polymers in the oil pipelines has to be researched further.

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