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# Variation of Contact Angle with Grafting Parameters for Pure Water on Polyvinylidene Fluoride Film

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**ABSTRACT**
In this work the PVDF film has been grafted by methyl 2-methylpropenoate using benzoyl peroxide as initiator. The effect of changing monomer concentration, molarity of initiator, temperature of reaction and time of reaction on contact angle for pure water on film was studied. The study reveals that grafting of PVDF film by methyl 2-methylpropenoate using benzoyl peroxide as initiator has modified the surface roughness enhancing the contact angle of surface for pure water. The maximum value of contact angle was recorded 81.6 $^0$ for initiator molarity .03M, monomer concentration 15%, temperature of reaction 60 degree Celsius, and time of reaction 60 minutes. Goniometric measurements of pristine and grafted PVDF film were recorded.

**KEYWORDS:** Initiator, roughness, contact angle, film.

## 1. INTRODUCTION-

Polymer has played a very important role in human life and is widely used in science and technologies. In addition to various applications in day to day life in fact anything from clothing to powering a space vehicle and even replacing a human organ. This explains why this age is called "Polymer" age. The extensive utilization of polymeric materials and the rapid development of polymer science have created and increases interest in various problem in physics of polymer. Obviously, polymer has not been discovered overnight. They come out of long and persevering studies by a host of motivated scientists whose work has enriched human life. Hence the knowledge of properties, structure, surface chemistry, morphology and the application of polymers are required to increase the utility. If we modify the polymer surface i.e. its surface chemistry and surface topography, then it can also be used as a non wetting surface i.e. hydrophobic surface and its hydrophobicity can be enhanced by further modification. Super hydrophobic surfaces cannot be obtained with smooth surfaces; it need surface modification by any means. In this regards, surface chemistry and surface roughness play a very important role. Super hydrophobic surface requires high contact angle, low contact angle hysteresis, low surface energy, low contact area, high surface roughness and low bond energy between the molecules of the liquid and the molecules of the solid surface. Scientists have done work to reduce the wettability of solid surface.

Ling et al [1] created a super hydrophobic surface by a simple dip coating method. Lu et al used low density polyethylene for the preparation of super hydrophobic surfaces by thermally induced phase separation. By changing the heat treatment, they have been able to control the structure of the eventual film and finally the wettability of the surfaces [2]. Franco et al fabricated a SH poly propylene membrane by a solvent casting of poly propylene and utilizing the surface roughness and porosity developed with a nano solvent [3]. Yuan et al reported the preparation of a stable super hydrophobic high density polyethylene surface by adding ethanol in a humid atmosphere at 50$^0$C [4].

In the present work the wettability of pvdf film has been reduced by grafting the film under different grafting conditions. The pure water has been used as liquid. The measurement of wettability can be done by measuring contact angle, more is the contact angle less is wettability.. The work shows that contact angle depends on various factors of grafting. The contact angle was found maximum for maximum degree of grafting.

## 2. EXPERIMENTAL:

Polyvinylidene fluoride (PVDF) film (.175mm thickness) was obtained from Good Fellow, Cambridge Limited of Huntingdon (England). Benzoyl peroxide was purchased from SD Fine chemicals (India). 2-methylpropenoate and acetone were obtained from Merck chemicals (India).PVDF film was washed by acetone and dried in an oven. Double distilled water was used as the reaction medium for copolymerization. The film was cut into small pieces of area ranging from $2cm^2$ to 4 $cm^2$. The pieces were weighed by a digital balance of least count .0001gm. Weighed PTFE film was placed in a standard three necked flask fitted with water condenser and thermometer . A definite amount of water (20-35 ml) was added, followed by the addition of a known amount of 2-methylpropenoate (5%-20%V/V) and BPO (.01M-.03M) taken in definite proportions. The mixture was heated for definite time intervals. The grafted film was dried and weight was recorded. The optimum condition of grafting was obtained by changing monomer concentration, molarity of initiator, temperature of reaction, and time of reaction**.** The contact angle was measured for pure water on pristine film and grafted films of various grafting conditions using drop shape analyzer.

## 3. RESULTS AND DISCUSSION:

### 3.1 CHARACTERIZATION OF PRISTINE PVDF FILM:

### (a) FTIR STUDY:

FT-IR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. The FTIR study shows that there is transmittance peak for 3025.89 per cm. The software of FTIR setup matches the film with polyvinylidene fluoride. The spectrum is shown in figure 1.

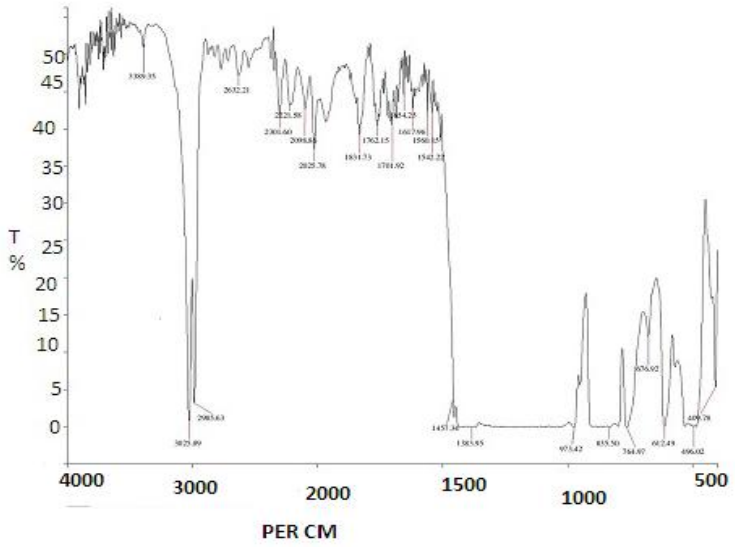


FIGURE 1: FTIR spectrum for pristine PVDF film

**(b) CONTACT ANGLE:**

The contact angle of pristine PVDF film was measured using drop shape analyzer- 25. The syringe volume of water drop was kept at minimum level to minimize the effect of gravity on drop shape. The contact angle of pure water on pristine PVDF film was recorded 63.8 degree. The drop shape of pure water on PVDF film is shown in figure 2.

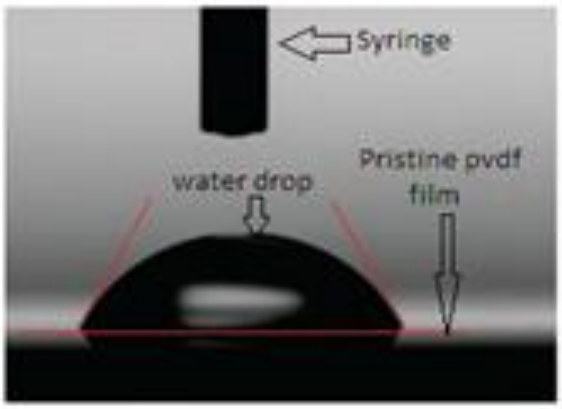


FIGURE 2: Water drop shape on pristine PVDF film.

**3.2 CONTACT ANGLE VARIATION WITH DEGREE OF GRAFTING:**

The rate of grafting depends on various parameters such as monomer concentration, initiator molarity, reaction temperature and time of reaction. The degree of grafting was calculated according to the following expression

$$G\% = (W_G - W_P)\ x100/W_P$$

Where $W_G$ and $W_P$ are the weights of grafted PVDF film and pristine film [5].The study reveals that contact angle increases with the increase in degree of grafting. The variation of contact angle with degree of grafting is shown in figure 3. The increase in contact angle is due to reduction in surface energy of film due to grafting process. The contact angle of pure water on pristine PVDF film was recorded 63.8 degree. The contact angles for grafted samples of film were recorded for monomer concentration 10%, 15% and 20%, temperature of reaction $60^0$C and time of reaction 60 minutes. It is found that maximum contact angle $81.6^0$ is for film grafted at monomer molarity of .03M, monomer concentration 15%, time of reaction 60 minutes and temperature of reaction $60^0$C.

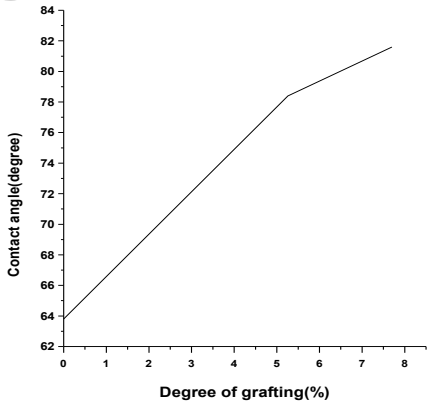


FIGURE 3: Variation of contact angle with degree of grafting.

### 3.3 CONTACT ANGLE VARIATION WITH INITIATOR (BPO) MOLARITY:

The degree of grafting increases to a maximum value of 7.70%with the increase in initiator molarity up to .03M and then decreases. When the concentration of the BPO exceeds a certain value, increased free radical concentration results in serious homopolymerization and decreases the rate of grafting [6,7]. The variation of contact angle with initiator molarity is shown in figure 4. The maximum value of contact angle is for initiator molarity of .03M.

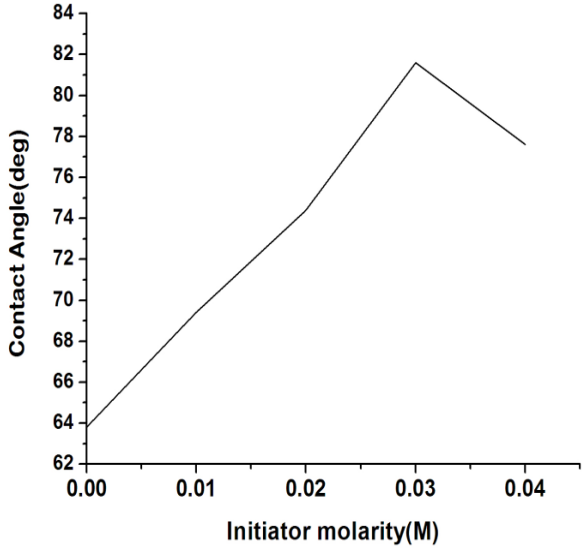


FIGURE 4: Variation of contact angle with Initiator molarity

### 3.4 CONTACT ANGLE VARIATION WITH MONOMER CONCENTRATION:

The contact angle increases initially with monomer concentration up to 15% and then decrease on further increase in concentration of methyl 2-methylpropenoate. At higher concentrations of monomer the free radical sites at PVDF backbone decrease reducing the degree of grafting. The variation of contact angle with monomer concentration has been plotted in figure 5 for initiator molarity of .03M.

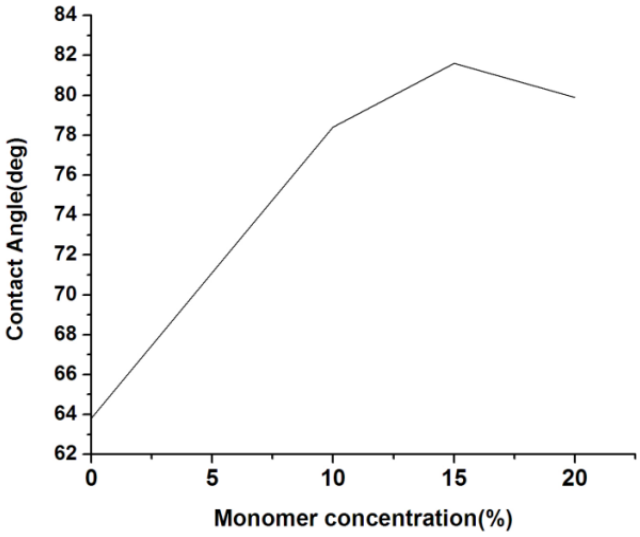


FIGURE 5: Variation of contact angle with monomer concentration

### 3.5 CONTACT ANGLE VARIATION WITH TEMPERATURE OF REACTION:

The temperature of reaction is a key parameter in grafting process. The weights of grafted films were taken for temperature range from $50^0$C to $80^0$C.It is found that the grafting percentage increases up to $60^0$C and then decreases gradually. This may be due to the increase in initiation and propagation rates of copolymerization or due to increase in the decomposition of the initiator leading to the formation of more free radicals and the generation of active sites on the polymeric backbone. However beyond optimum temperature, the grafting rate decreases because the growing polymeric chains are terminated and the chain transfer reactions are occurred. The variation of contact angle with temperature is shown in figure 6 for initiator molarity .03 M and monomer concentration 15%.

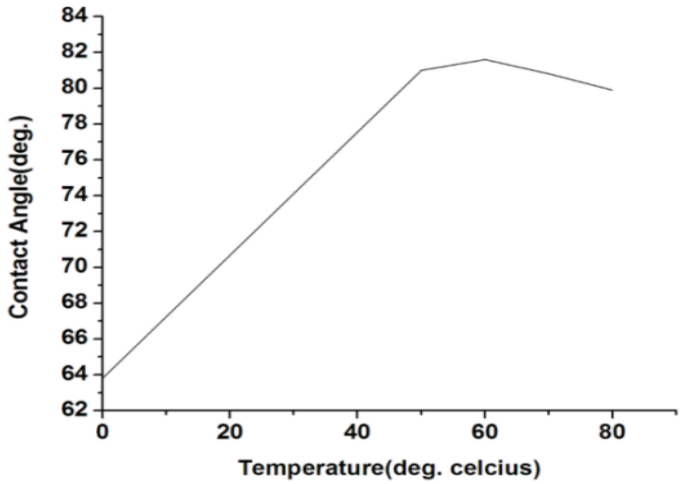


Figure 6.Variation of contact angle with temperature

### 3.6 CONTACT ANGLE VARIATION WITH TIME OF REACTION:

The contact angle is also affected by reaction time. The contact angle is found maximum for reaction time of 60 minute. It is due the decreasing of concentration of initiator for higher time of reaction. The variation of contact angle with reaction time is shown in figure 7 for initiator molarity .03M, monomer concentration 15%.

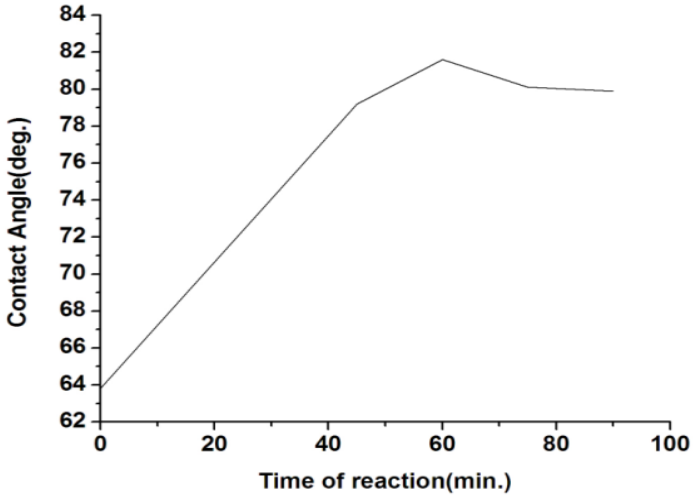


Figure 7.Variation of contact angle with reaction time

## CONCLUSION:

The study reveals that contact angle increases with the increase in grafting percentage of film. The contact angle of pristine film is found $63.8^0$ and $81.6^0$ for maximum grafted film. The study reveals that contact angle is also affected by temperature of reaction, concentration of momomer, molarity of initiator and time of reaction. The increase in hydrophobicity is due to the reduction in surface energy of film surface. The modification in contact angle opens wide applications in automobile and aviation industry [8].

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