Physicochemical and electrochemical characterization of battery separator prepared by radiation induced grafting of acrylic acid onto microporous polypropylene membranes

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Abstract. Mutual radiation grafting technique was used to graft acrylic acid on micrometer thick micro-porous polypropylene membrane using high-energy gamma radiation. Grafting could not be achieved in aqueous acrylic acid solution. The presence of Mohr's salt effectively retarded the homopolymerization of acrylic acid but did not lead to grafting enhancement. Mohr's salt in presence of acids was found to be effective in enhancing the grafting yield. Contact angle measurement studies of the grafted and radiation treated polypropylene showed that initial grafting as well as radiation treatment of poly(propylene) in aqueous medium and in presence of Mohr's salt enhances its affinity towards the grafting solution. The enhancement in the polar component of surface energy of treated polypropylene membrane is the primary cause of grafting enhancement. The membranes grafted to an extent of ~20% were found to perform comparably with the battery separator presently being used by battery industry.

Keywords: polymer membranes, radiation grafting, acrylic acid, contact angle, charge-discharge

1. Introduction

Separator materials for alkaline batteries have received a great deal of attention in last five decades. It is mainly due to the desire to develop high energy per unit weight and volume battery packages that materials are still searched for better separator properties [1]. However because of complexity of inventing new functional materials, the present trend is of modifying existing polymers. The modification of polymers through graft co-polymerization offers an attractive path for introducing desirable properties in existing polymer for various polymer applications [2, 3]. Radiation induced grafting offers some unique advantages over the conventional chemical grafting method

since it results in uniform grafting and it is room a temperature process [4]. Radiation grafted co-polymers have been tried for a wide spectrum of applications like surface modification [5], separation purposes [6], biotechnology [7], electrochemical applications such as electro-dialysis [8], battery separator [9] and solid polymer electrolyte in fuel cells [10]. Ion exchange membranes have been investigated for their suitability as battery separator because of their durability, long life, high charge density and appreciable ion exchange capacity at optimum water content, which is the most desirable property of the separator membranes [11]. Radiation induced grafting of various monomers onto poly(propylene) (PP) by pre irradiation as well as

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post irradiation method has been investigated to improve/introduce certain desired properties. Grafting of hydrophilic monomers onto PP has been of particular interest because of good strength, low cost and easy availability in different forms [12, 13]. The grafted product possesses a hydrophilic surface and is of good strength. These grafted hydrophilic membranes have found promising application in form of a battery separator, since they fulfill basic requirements of a battery separator namely presence of spontaneous, uniform and permanent wettable surface in order to accommodate and fully retain the aqueous electrolyte solution. Also, the battery separator should be dimensionally stable and should not swell or shrink significantly on introduction of the electrolytic solution [14].

In the present work mutual radiation grafting technique has been used to graft acrylic acid onto micrometer thick polypropylene sheet to induce optimum wettability on its surface. Effect of various experimental variables on grafting yield has been studied. The grafted membranes were characterized for their wettability and surface energy by dynamic contact angle measurement. The developed membranes were tested for their performance as separator under actual battery conditions.

2. Materials and methods

2.1. Materials

The polypropylene (PP) micro-porous films (porosity 38%, pore dimensions 0.02–0.20 microns), thickness 2.5 μm in sheet form was supplied by M/s High Energy Batteries Ltd., India. Acrylic acid monomer (purity > 99%) from Fluka was used as received. Mohr's salt and all other chemicals used were of AnalaR (purity > 99%) grade. Doubly distilled water was used for preparation of all solutions and Millipore-Q water (conductivity $0.05 \mu\text{S}\cdot\text{cm}^{-1}$) was used for contact angle studies. Gamma chambers GC-5000 having Co^{60} gamma radiation source, supplied by M/s BRIT, India having dose rate of $5 \text{ kGy}\cdot\text{hr}^{-1}$ as measured by Fricke dosimetry were used for irradiation purpose with suitable lead/steel attenuators.

2.2. Grafting of acrylic acid onto polypropylene

Grafting of acrylic acid (AA) onto polypropylene (PP) films was carried out by mutual radiation grafting technique. PP film of known weight was immersed in grafting solution of known composition in glass-stoppered bottles for an hour. The bottles containing PP, immersed in grafting solution were then irradiated in gamma chambers for required radiation doses. The homopolymer was removed from the grafted samples using water as an extractant by Soxhlet extraction for 8 hours. The grafted samples were vacuum dried at 50°C and stored in desiccator for further use. Grafting yield (G.Y.) was determined gravimetrically using Equation (1):

$$\text{G.Y.}[\%] = \left(\frac{\text{Weight after grafting} - \text{Initial weight}}{\text{Initial weight}} \right) 100 \quad (1)$$

2.3. Characterization of grafted PP membrane

Fourier transformed infrared spectroscopy (FTIR) measurements were performed on a FTIR spectrophotometer from JASCO, model FT/IR-610. Samples were thoroughly ground at liquid nitrogen temperature and mixed with KBr to prepare discs by compression under vacuum. FTIR spectra were obtained in the range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and averaged over 100 scans.

Figure 1. FTIR spectra of a) PP (b) PP grafted to an extent of 2% c) PP grafted to an extent of 8% d) polyacrylic acid

The absorption peaks corresponding to 2970, 2870, 1460, 1376 cm^{-1} wave number were characteristic of $-\text{CH}_3$ and CH_2 groups in FTIR spectrum of PP as shown in Figure 1. The grafting of acrylic acid was established by well resolved absorption peak at 1760 cm^{-1} which increased with extent of grafting (indicated by arrow in Figure 1)

The grafted PP films were characterized for their water uptake. The figures given in brackets on grafting profiles (to be described later in Figure 4) are the water uptake capacities at that grafting yield. The water uptake by grafted sheets was quite significant however there was a decrease in the water uptake capacity at higher grafting yield. The decrease in water uptake at higher grafting yield can be attributed to crosslinking of the grafted chains at higher radiation doses.

2.4. Wettability and surface energy analysis

The radiation-induced modification of surface was characterized by its wetting angle measurements. In this work, the Owens and Wendt method was used to determine the total surface energy and its resolution into polar and dispersive components [15], wherein the total solid surface tension γ was assumed to be of the general form as shown in Equation (2):

$$1 + \cos \theta = 2\sqrt{\gamma_s^d} \frac{\sqrt{\gamma_l^d}}{\gamma_l} + 2\sqrt{\gamma_s^p} \frac{\sqrt{\gamma_l^p}}{\gamma_l} \quad (2)$$

In this equation, the subscripts s and l refer to the solid and liquid surface tension respectively; the superscripts d and p coincide with dispersive and polar components of total surface tension, where sum of these two values are equal to the total surface tension. The $\sqrt{\gamma_s^d}$ and $\sqrt{\gamma_s^p}$ are needed to be resolved. Therefore two independent contact angles were measured by two different liquids (water and diiodomethane) whose surface tension components are known.

The measurement of contact angles of the sample was carried out by sessile drop technique using image analysis software. A liquid droplet (1.5–2.5 μl) was allowed to fall on the samples to be studied from a software-controlled syringe. An image sequence was taken through a CCD camera of goniometer from GBX instruments, France which was connected to a PC computer and inter-

faced to image capture software (Windrop++, GBX instruments).

3. Results and discussion

Radiation grafting is a function of many experimental variables such as dose, dose rate, ambient condition, monomer concentration, composition of grafting solution and properties of backbone material. Therefore, effect of various experimental parameters onto grafting yield was studied.

Initially grafting of acrylic acid (AA) on polypropylene (PP) was tried by irradiating PP film in presence of 15–100% AA [v/v] in aqueous medium. It was found that even at lowest concentration of 15% acrylic acid studied, the grafting solution turned to a soft, non-flowing gel at a dose of 2 kGy. The gel formation prevailed over the entire dose rate range 1.25–5 $\text{kGy}\cdot\text{h}^{-1}$. Acrylic acid undergoes very fast homopolymerization and finally results in the formation of a crosslinked gel on irradiation in aqueous solution [16]. During homopolymer formation, some grafting would have taken place but it could not be determined as the PP film embedded in the gel got damaged during removal from the gel. In order to arrest the homopolymerization and enhance grafting yield, some established efficient homopolymer inhibitors in form of inorganic salts were tried. It has been reported that addition of certain metal salts to the reaction mixture suppresses the formation of homopolymer, thus leaving the monomer radicals free to take part in the grafting thereby reducing the homopolymer formation, increasing grafting and facilitating the retrieval of the resulting grafted copolymer [17, 18].

3.1. Radiation grafting in presence of homopolymerization inhibitor

Addition of certain inorganic salts suppresses the production of undesirable homopolymer during radiation induced grafting or redox grafting, thus leaving more monomer available for grafting and hence enhancing the grafting yield and facilitating easy retrieval of grafted product [19]. This has been attributed mainly to scavenging of OH radical (generated due to radiolysis of water in the bulk of the mixture) by metal ions (Equation (3)) thereby reducing the homopolymer formation in the bulk.

Figure 2. Effect of homopolymer inhibitor salts on grafting yield: salt concentration = 4% and acrylic acid concentration = 20% in aqueous solution at a dose rate of 5 kGy·h⁻¹
a) FeSO₄·(NH₄)₂SO₄·6H₂O b) CuSO₄ c) Cu₂SO₄

In view of the works reported earlier, our grafting was carried out initially in the presence of Ferrous ammonium sulphate {FeSO₄·(NH₄)₂SO₄·6H₂O}, cupric sulphate (CuSO₄) and cuprous sulphate (Cu₂SO₄). Figure 2 shows effect of presence of these salts as a function of irradiation dose. It is clear from the results that Mohr's salt {FeSO₄·(NH₄)₂SO₄·6H₂O} is most effective in increasing the grafting. Therefore, further studies were carried out at different concentrations of Mohr's salt. Figure 3 shows the result of these studies. It was seen that grafting yield was maximum at salt concentration of 4%, at higher concentration

Figure 3. Effect of FeSO₄·(NH₄)₂SO₄·6H₂O on grafting yield in 20% AA solution at a dose rate of 5 kGy·h⁻¹ a) 0.5% b) 2% c) 4% d) 5%

the grafting decreased. At Mohr's salt concentration > 4 grafting yield was low and there was no significant change in the viscosity of the grafting solution before and after irradiation indicating that the homopolymerization as well as grafting was severely hindered. It seems that the presence of Mohr's salt in appropriate concentration decreases homopolymerization reaction, which allows more monomer to be available for grafting and hence higher extent of grafting. Further grafting studies were carried out at 4% Mohr's salt concentration.

3.2. Effect of dose rate on grafting

Figure 4 shows the grafting yield as a function of radiation dose when the grafting was carried out in 20% AA + 4% FeSO₄·(NH₄)₂SO₄·6H₂O aqueous solution at different dose rates. The number of grafted chains and chain lengths produced in mutual grafting method is a function of total radiation dose and the dose rate [20]. While the total dose is a measure of total number of free radicals generated on the trunk polymer, dose rate determines the rate of initiation of polymerization. As expected, and shown in Figure 4, grafting yield increased with radiation dose. However, it was interesting to observe that the grafting yield increased with dose rate also, unlike other grafting systems reported [21, 22] where grafting has been reported to decrease with the dose rate. Lower grafting yields at higher dose rates have been attrib-

Figure 4. Effect of dose rate on grafting yield when grafting was carried out in 20% AA solution containing 4% FeSO₄·(NH₄)₂SO₄·6H₂O a) 5 kGy·h⁻¹ b) 2.5 kGy·h⁻¹ c) 1.25 kGy·h⁻¹. Digits in brackets: water uptake%.

uted earlier to energy deposition taking place predominantly in bulk of the solution, favoring homopolymerization of the monomer. The homopolymerization suppresses the grafting yields in two ways (i) the increased bulk viscosity restricts the diffusion of monomer from bulk to the reactive site thereby making the growing of chains at trunk polymer difficult (ii) due to the consumption of monomer in homopolymer formation, less monomer would be available for grafting reaction. Since here grafting was carried out in presence of homopolymerization inhibitor, there was no significant increase in the bulk viscosity therefore detrimental effect due to reason (i) above was not observed. Also, due to decrease in homopolymer formation more monomer was available to be grafted.

3.3. Effect of monomer concentration

The concentration of monomer to be grafted can be an important variable in extent of grafting. Therefore grafting was studied at three different concentrations. The results of these studies are shown in Figure 5. The grafting yield showed an increase when the concentration was increased from 10 to 20% of monomer. However there was no significant difference between 20 and 30% monomer concentration. Higher grafting yields are expected with increase in monomer concentration as, at any instant radicals generated on the backbone are able to interact with more monomer molecules. How-

ever, beyond certain monomer concentration, it seems that homopolymerization due to radicals generated in the bulk becomes predominant process and hence there is no significant increase in the grafting. Therefore, for further studies, concentration of monomer was fixed at 20% [v/v] to achieve high grafting levels and low homopolymer formation.

3.4. Effect of acid on grafting

Presence of additive like inorganic acid has been reported to enhance grafting by two ways [23, 24]. The presence of acid converts the radiolytically generated e_{aq}^- into H, radical, which abstracts other H atoms from the backbone to generate more grafting sites on the polymer backbone as shown in Equations (4) and (5):

It has been postulated that the presence of acid improves the partition coefficient of the monomer between the polymer film and the bulk leading to an increase in local monomer concentration around the grafted growing chain thus increasing the grafting yield. Initially the grafting was studied in presence of acids without any Mohr's salt. This resulted in formation of soft cross-linked gel at a very low dose of 0.6 kGy and the grafted film could not be retrieved. This indicated that the polymerization of AA in aqueous solution was much faster in presence of acid. Further effect of acid on grafting was studied in presence of 4% Mohr's salt. Figure 6 shows the effect of presence of different acids on grafting yield. The grafting studies were tried in presence of HNO_3 also, however in presence of HNO_3 the grafting solution turned to crosslinked soft mass within few minutes of irradiation and grafting yield could not be determined. It is clear from Figure 6 that H_2SO_4 was most effective in improving the grafting yield, therefore further studies were carried out in presence of H_2SO_4 . As shown in Figure 7, grafting increased with H_2SO_4 concentration in the concentration range studied. Therefore for further studies H_2SO_4 concentration of $0.5 \text{ mol}\cdot\text{dm}^{-3}$ was fixed. In order to investigate the reason for increase in grafting yield in presence of acid, the uptake of grafting solution by backbone PP in presence of different acids was studied. It was

Figure 5. Effect of monomer concentration on grafting yield in 4% Mohr's salt solution a) 10% AA b) 20% AA c) 30% AA; $5 \text{ kGy}\cdot\text{h}^{-1}$

Figure 6. Effect of different acids on grafting yield in 20% AA solution in presence of 4% $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ at a dose rate of $5 \text{ kGy} \cdot \text{h}^{-1}$ a) $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$ b) $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ HClO}_4$ c) $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl}$

Figure 7. Effect of H_2SO_4 on grafting yield in 20% AA solution in presence of 4% $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ at a dose rate of $5 \text{ kGy} \cdot \text{h}^{-1}$ a) $0.01 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$ b) $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$ c) $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$

seen that the backbone PP film did not swell in presence of acid even up to $2 \text{ mol} \cdot \text{dm}^{-3}$ concentration of acid. This clearly indicated that as reported for other grafting systems [21, 22] where grafting enhancement was attributed to swelling of backbone in presence of solvent, enhancement in grafting in this study could not be any way assigned to swelling of PP due to grafting solution. Also, no swelling was observed for PP in 20% AA solution, 20% AA + 4% $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ solution and 20% AA + 4% $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ + $0.5 \text{ mol} \cdot \text{dm}^{-3}$ solution.

3.5. Effect of ambience on grafting in presence and absence of acid

In order to study the effect of ambient on the grafting, grafting was carried out in 20% AA + 4% Mohr's salt solutions under three different ambient conditions (N_2 purged, aerated and O_2 saturated), at a dose rate of $3.2 \text{ kGy} \cdot \text{h}^{-1}$. Results of this study, shown in Figure 8, indicate that effect of ambience on grafting yield was not significant. However when the grafting was carried out in presence of $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$ (all other conditions remaining the same) there was drastic effect of

Figure 8. Effect of ambience on grafting yield in 20% AA + 4% Mohr's salt solution. Dose rate = $3.2 \text{ kGy} \cdot \text{h}^{-1}$ a) de-aerated, b) aerated c) O_2 saturated. Inset: grafting yield at lower doses a) de-aerated b) aerated c) O_2 saturated.

Figure 9. Effect of ambience on grafting yield in 20% AA + 4% Mohr's salt + $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$. Dose rate = $3.2 \text{ kGy} \cdot \text{h}^{-1}$ a) de-aerated b) aerated c) O_2 saturated.

ambience as shown in Figure 9. We may suppose that in presence of acid all available e_{aq}^- are converted to H radical in accordance with Equation (6a). Under aerated/oxygenated condition the H radicals efficiently react with available O_2 to form $HO_2^\bullet$ (Equation (6b)) whereas in absence of acid e_{aq}^- reacts with O_2 to form superoxide anion ($O_2^{\bullet-}$) (Equation (6c)). $HO_2^\bullet$ radical is known to undergo abstraction reaction with organic molecules (Equation (6d)) [25]. Thus $HO_2^\bullet$ through H abstraction reaction with backbone may generate grafting sites on backbone thereby contributing to increase in grafting yield. On the other hand the superoxide anion (Equation (6e)) is known to undergo very slow abstraction reaction and hence may not contribute significantly to increase in grafting yield.

3.6. Surface wettability studies of grafted surfaces

From the studies discussed above two important observations were made (i) The presence of Mohr's salt does not allow the viscosity of the bulk solution to increase and (ii) changes in the composition of grafting solutions had little effect on swelling of PP. Thus it would be worth investigating whether the availability of more monomer during grafting process was the sole reason for grafting enhancement, or did the affinity of PP increased for grafting solution as the grafting process progressed. To address this question affinity of PP for grafting solution was investigated by contact angle measurement. PP irradiated under different conditions namely in water, in 4% $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, in 0.5 mol·dm⁻³ H_2SO_4 , in 4% $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ + 0.5 mol·dm⁻³ H_2SO_4 and grafted to different extent with AA were examined for their wettability against the grafting solution (20% AA +

4% $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ + 0.5 mol·dm⁻³ H_2SO_4 in aqueous medium). Figure 10 shows the photographs recorded immediately after drops of solution were allowed to fall on PP. Figure 11 shows the change in contact angle with time. It is clearly visible from the photographs that contact angle decreases as the extent of grafting increase in the range 0–26.2% (Figures 10a–10c). Even at grafting yield as low as 0.99% of AA there was significant decrease in contact angle from 72 to 52°. Poly(acrylic acid) is insoluble in its monomer acrylic acid [23] but is soluble in water. It seems the covalently grafted and growing poly(acrylic acid) chains are more easily able to interact with the acrylic acid around when they are in extended, opened up state in grafting mixture due to their affinity for water and contribute to grafting enhancement. Similar increase in grafting yield in presence of suitable common solvent for polymer and monomer has been reported for other systems by us earlier [24, 26]. It is well known that irradiation of polymers under aerated conditions leads to generation of several functional groups on the surface which alter the surface energy and hence the wettability [27]. In order to probe any enhancement

Figure 10. Initial contact angle of different PP surfaces for grafting solution (20% AA + 4% $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ + 0.5 mol·dm⁻³ H_2SO_4) a) un-grafted PP b) PP grafted to an extent of 0.99% c) PP grafted to an extent of 26.2% d) PP irradiated in aqueous medium e) PP irradiated in 4% Mohr's salt f) PP irradiated in 0.5 mol·dm⁻³ H_2SO_4

Figure 11. Change in contact angle with time against the grafting solution (20% AA + 4% $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ + $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{H}_2\text{SO}_4$) for PP grafted to different extents a) un-grafted PP b) PP grafted to an extent of 0.99% c) PP grafted to an extent of 8% d) PP grafted to an extent of 16.6% e) PP grafted to an extent of 26.2%

of grafting due to irradiation in water, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, H_2SO_4 or $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} + \text{H}_2\text{SO}_4$ the PP was irradiated in these separately for same dose as for grafting. The PP irradiated under different conditions (total dose = 0.8 kGy) was studied for its contact angle analysis against the grafting solution. Fig-

Figure 12. Change in contact angle with time against the grafting solution (20% AA + 4% $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ + $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{H}_2\text{SO}_4$) for PP initially irradiated (total dose = 0.8 kGy) under different conditions a) un-grafted PP b) $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{H}_2\text{SO}_4$ c) 4% $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ + $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{H}_2\text{SO}_4$ d) 4% $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ e) water

ures 11 and 12 show the results of these studies. Comparing Figures 10a–10e and Figure 12 it is clear that irradiation in presence of water and other additives enhance the affinity for grafting solution to different extents. However in presence of acid alone or in combination with Mohr's salt there is no enhanced affinity for the grafting solution i.e. presence of sulphuric acid in the medium does not as such contribute to affinity of PP for grafting solution. Though the presence of acid may enhance grafting in accordance with Equation (4) or some way in which presence of AA in protonated state favours grafting in comparison to it being in deprotonated state. In order to substantiate our explanation given above the grafting of pre-grafted and pre-treated PP was studied at very low doses. Figure 13 shows results of these studies. As is clear from the figure the pre-treatment prior to grafting contributed significantly to grafting enhancement. However at present it is difficult to explain the grafting enhancement even for PP initially irradiated in sulphuric acid, as these membranes did not show any decrease in contact angle i.e. enhance affinity for grafting solution.

The increase in polar component of the similar polymer surfaces on plasma or conventional grafting of suitable monomers has been reported earlier [28, 29]. Efforts were made to estimate the change in the surface energy and resolve different components of surface energy of PP on grafting and also after irradiating PP under different conditions.

Figure 13. Grafting of PP treated initially under different conditions a) untreated b) grafted to an extent of 0.99% c) irradiated in water d) irradiated in $0.5 \text{ mol} \cdot \text{dm}^{-3} \text{H}_2\text{SO}_4$ e) irradiated in 4% Mohr's salt. Dose rate = $3.2 \text{ kGy} \cdot \text{h}^{-1}$.

Table 1. The properties of liquids used for surface energy determination at 20°C

Liquid	Surface tension [mN/m]		
	γ_l	γ_l^d	γ_l^p
Water	68.9	18.6	50.3
Diiodomethane	49.7	48.0	1.7

Water and diiodomethane were used as test liquids for determination of surface energy of the samples. Tables 1 and 2 give the properties of the liquid used and the surface energy estimated for different samples. It is clear from the values in Table 2 that the grafting of AA enhances the total energy with substantial increase in the polar component. Slight increase in the polar component was also seen for the PP samples initially irradiated in different solutions. It is clear from these surface energy estimation and the results of Figure 13 that grafting enhancement under certain conditions is due to *in-situ* increase in the polar component of surface energy during irradiation. The increase of the polar component contributes to the enhanced affinity for the grafting solutions, which is reflected in decrease in the contact angle and enhanced grafting.

3.7. Performance of grafted PP membranes under actual battery conditions

The developed AA grafted PP sheet was tested for its performance under actual battery conditions related to the battery separator membrane presently used by Indian battery industry. For testing the grafted samples, the samples grafted to different extent were put in one Ni/2Cd electrode cells and soaked with KOH electrolyte. All the cells were subject to C/5 charging and 1C rate discharging. Those samples, which enabled the cells to pass 60 minutes of discharging, were considered to be working satisfactorily. Samples grafted to different extents were tested. Figures 14 and 15 show the results of some of the samples. It was seen that

Figure 14. Performance of grafted membranes during charging a) PP grafted to an extent of 20% b) presently being used commercial membrane c) PP grafted to an extent of 10%

Figure 15. Performance of grafted membranes during discharging (a) PP grafted to an extent of 20% b) presently being used commercial membrane c) PP grafted to an extent of 10%

samples grafted to extent of 10% did not give satisfactory results. The samples grafted to extent >20% only gave satisfactory results. The sample grafted to an extent of 21% was also used for a fuel cell consisting of 17 Ni and 16 Cd electrodes. The performance was comparable with the cell assembled

Table 2. Surface energy of samples

Sample	Surface energy [mJ/m ²]		
	Total energy	Polar component	Dispersive component
Ungrafted PP	33.7	2.8	30.9
PP grafted to an extent of 0.99%	48.9	15.0	33.9
PP grafted to an extent of 26.2%	45.9	14.1	31.8
PP irradiated in 4% Mohr's salt solution	29.1	4.7	24.4
PP irradiated in water	33.5	3.3	30.2
PP irradiated in 0.5 mol·dm ⁻³ H ₂ SO ₄	34.2	7.0	27.2

using battery separator presently used by the industry. The actual testing results indicated that grafting not only converts the hydrophobic PP into battery active hydrophilic state but also helps to retain the hydrophilic state over longer storage period, which is a necessity for Ni-Cd batteries.

4. Conclusions

AA grafted PP micrometer thick, micro-porous membrane has been successfully prepared by mutual radiation grafting technique. The grafting yield was found to be a function of experimental variables like dose, dose rate, ambience of grafting and the composition of grafting solution. The presence of acid in the grafting solution was found to enhance the grafting yield by many folds. The contact angle analysis of grafted product established that initial grafting enhances the wettability of the PP membrane and thus helps in grafting at latter stages. The prior radiation treatment of PP under suitable conditions also contributed to enhanced grafting. The membrane having grafting yield of 20% was found to perform comparably with the separator presently being employed by the industry with an added advantage of retaining the hydrophilic state over longer storage period.

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