Correlation between surface energy and uptake behavior of radiation-grafted methacrylic acid-*g*-LDPE

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Abstract An efficient and low-cost effluent adsorbent has been developed by grafting an ionizable monomer onto polyolefin surface and its efficacy was tested for dyes and metal ion uptake from aqueous medium. The grafted matrix was synthesized by optimizing various experimental parameters such as irradiation dose, dose rate, monomer concentration, inhibitor concentration, surfactant concentration, and backbone thickness. Grafting yield decreased with dose rate and thickness and increased with the concentration of methacrylic acid and inhibitor. Grafting kinetics studies indicated that grafting rate is comparatively much affected by dose rate that monomer concentration. Surface energy of the grafted surface was accessed from dynamic contact angle measurements. Uptake study of Basic Red 29, Methylene Blue showed high correlation with grafting yield and polar component of the surface energy; however, metal ion uptake was exceptionally high at ~ 25 grafting (%), highlighting anomalous behavior of MAA-*g*-LDPE with respect to surface energy and total ion uptake capacity.

Introduction

Water pollution due to the effluent discharged from dye, textile, metal finishing, and associated industries is an area of serious concern [1–3]. Such contamination leads to high level of toxic metal ions, high COD and BOD, and coloration of the wastewater stream which creates havoc with marine life and associated food chain [4]. Various chemical and physical strategies have been proposed to bring down the

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level of these pollutants to the permissible limit. However, as typical wastewater streams contain diverse group of pollutants in most of the cases, pollutant removal is very complex, multistep, and capital intensive process [5, 6]. Development of multifunctional adsorbents having high affinity toward variety of pollutants has been envisaged as an effective and economically viable solution to this problem [7].

Multifunctional polymer adsorbents can be developed by radiation-induced grafting, since a range of polymers (thermoplastics, elastomers; hydrophilic, hydrophobic) can be used as backbone in the radiation grafting process and both cationic and anionic groups can be incorporated in the matrix by selecting proper monomer and experimental conditions [8]. Polyelectrolyte- or ionizable-grafted polymer matrices demonstrate excellent dye and metal ion uptake behavior [9, 10]. They are low cost, multifunctional, efficient, reusable, and easy to fabricate. Low density polyethylene (LDPE) the most widely used thermoplastic is an excellent choice for the base matrix because of it low cost, easy process ability, and good weathering properties. There are several reports on photo-assisted grafting of methacrylic acid (MAA) onto LDPE; few reports on the high radiation-induced post-irradiation grafting of MAA onto LDPE are also available; however not much information is available on the simultaneous high energy radiation-induced grafting of MAA onto LDPE [11–13].

In contrast to acrylic acid-grafted LDPE (AA-*g*-LDPE), methacrylic acid-grafted LDPE (MAA-*g*-LDPE) is expected to yield different graft morphology both in terms of grafted chain density or chain length and surface energy. In a recent report, Yamada et al. [14] have compared photo-grafting of MAA and AA onto LDPE and HDPE and demonstrated noticeable difference between the functional characteristics of MAA- and AA-grafted polyethylene surfaces. Mainly due to difference in the grafting kinetics of AA and MAA and relatively less polar contribution from MAA, the metal ion and dye uptake efficacies of AA-*g*-LDPE and MAA-*g*-LDPE are expected to be very different. It is therefore worth investigating the radiation grafting kinetics of MAA onto LDPE and explores the use of MAA-*g*-LDPE matrix for removal of hazardous dyes and metal ions from effluents.

This study reports, synthesis of different MAA-*g*-LDPE matrices, kinetic studies of the grafting process, surface energy of the grafted matrices, and the efficacy of grafted matrices for the removal of metal ions and dyes from prepared aqueous solutions. Efforts have been made to understand the effluent uptake behavior of the matrices in light of variation in the surface energy and dye/ion uptake capacity with the changes in the grafting content.

Experimental

Materials

Commercial grade LDPE in granule form was procured from M/s IPCL, Ltd. Mumbai. LDPE sheets of thickness 0.3–3 mm were prepared by using press at 140 °C at 10 ton pressure. MAA monomer (purity >97 %) from M/s Central Drug House Limited, Mumbai was used as received. Mohr's salt {FeSO$_4$·(NH$_4$)$_2$SO$_4$·6H$_2$O} (MS), CuSO$_4$,

Basic Red 29 (BR29) dye, methylene blue (MB), and all other chemicals used were of Analar (Purity >99 %) grade. Double-distilled (DD) water was used for preparation of all solutions and diiodomethane (Mol. wt. 267.836; density = 3.325 g/cc) from Aldrich (Purity 99.9 %) and Millipore-Q water (conductivity 0.05 μS/cm) 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 2.6 kGy/h as measured by Fricke dosimetry were used for irradiation purpose with suitable lead attenuators.

Methods

Radiation grafting

Simultaneous radiation grafting method was used to graft MAA onto LDPE. Pre-weighed pieces of LDPE sheets were completely immersed in grafting solution of suitable concentration in stoppered glass bottles for an hour. The samples in glass bottles were then irradiated in gamma chamber for required irradiation doses at desired dose rates. The grafted samples were then soxhlet extracted for 8 h using DD water to remove any trapped homo-polymer poly(MAA) in the grafted matrix.

The grafted sample was vacuum dried at 50 °C and grafting yield was determined gravimetrically using following relation:

$$\text{Grafting } (\%) = \{(\text{Weight after grafting } - \text{ Initial weight})/\text{Initial weight}\} \times 100 \tag{1}$$

Grafting kinetics was followed by measuring grafting rate (R_g) using relation

$$R_g = \text{ Grafting } (\%)/\text{Time (h)} \tag{2}$$

Fourier-transform infrared spectroscopy (FTIR) studies

FTIR (JASCO 660) was used for confirmation of the grafting of MAA on LDPE. Spectra were obtained at 4 cm^{-1} resolution and averages of at least 16 scan in the standard wavenumber range 400–4,000 cm^{-1}.

Wet ability and surface energy analysis

The radiation-induced modification of surface was characterized by its wetting angle measurements. In this study, the Owens and Wendt method was used [15]. They assumed the total solid surface tension γ to be of the general form

$$1 + \cos\theta = 2\sqrt{\gamma_s^d}(\sqrt{\gamma_1^d}/\gamma_1) + 2\sqrt{\gamma_s^p}(\sqrt{\gamma_1^p}/\gamma_1) \tag{3}$$

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 needed to be measured by two different liquid 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 interfaced to image capture software (Windrop^{++}, GBX instruments).

Dye and metal ion uptake

MAA-g-LDPE sheets dipped in dye and copper sulfate solutions for 7 days with stirring. Absorbance of these solutions before and after absorption was determined by using UV–visible spectrophotometer (Thermo Electro Corporation, Evolution 300) at the λ_{max} of the respective metal ion or dyes. The concentration of metal ion/dye was calculated from a calibration curve obtained earlier from samples of known concentration.

Results and discussion

The surface properties of grafted matrix or dye uptake by it will depend upon the extent of incorporation of MAA (i.e., grafting yield) on to LDPE backbone. The extent of radiation grafting is a function of many experimental variables such as irradiation dose, dose rate, monomer concentration, composition of grafting solution, ambient condition, etc. Therefore, effect of various experimental parameters onto grafting yield was studied in detail in order to optimize the experimental parameter to obtain a desired extent of grafting.

Effect of irradiation dose and dose rate

The number of grafted chains and their length in mutual radiation grafting process are dependent on total irradiation dose and the dose rate [16]. While the total irradiation dose governs the total number of free radicals generated on the trunk polymer, dose rate determines the rate of initiation of grafting polymerization process. The effect of irradiation dose and dose rate was initially studied without MS. However, in the absence of MS, whole grafting solution (monomer concentration 10–30 %) turned into a solid mass at an irradiation dose as low as 2 kGy. For further studies, MS concentration of 0.04 M was arbitrarily chosen. As shown in Fig. 1, under experimental conditions grafting yield increased with irradiation dose in the dose range studied. The increase in grafting with irradiation dose was expected as increase in irradiation dose would proportionally increase the number of radical grafting sites on the trunk polymer and no further increase in grafting extent at later irradiation doses may be either due to monomer exhaustion or due to increased viscosity of the bulk of grafting mixture which restricts the monomer diffusion to propagating grafted chains. Figure 1 clearly indicates that
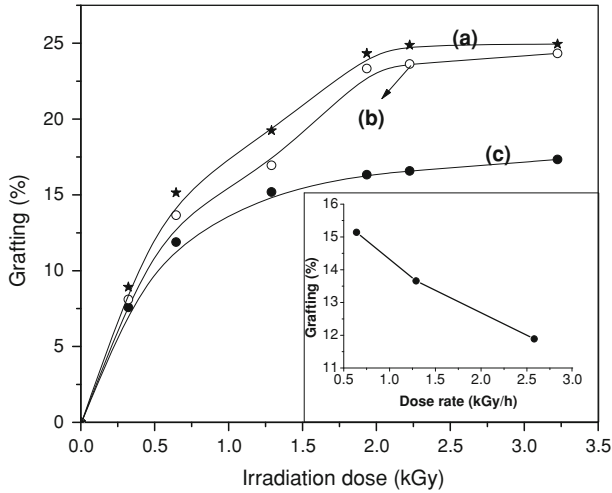
Fig. 1 Grafting yield as function of dose [MAA] = 30 % (v/v), [MS] = 0.04 M: (*a*) 0.64 kGy/h, (*b*) 1.29 kGy/h, (*c*) 2.58 kGy/h. *Inset* Effect of dose rate at total irradiation dose of 1.29 kGy

grafting extent is an inverse function of irradiation dose rate. The lower grafting yield at higher dose rates can be attributed to major energy deposition in the bulk of the solution during grafting. High dose rates produce higher radical density, which may favor recombination of radicals generated in close vicinity or faster generation of the homo-polymer in bulk and its subsequent gelation. The homo-polymerization reduces the grafting extents in two ways: (i) due to increased bulk viscosity the diffusion of monomer from bulk to the reactive site and growing chains at trunk polymer becomes difficult, (ii) due to the consumption of monomer in homo-polymer formation, less monomer would be available for grafting reaction. Since here grafting was carried out in presence of homo-polymerization inhibitor, there was no significant increase in the bulk viscosity therefore detrimental effect due to reason (i) can be ruled out.

Effect of monomer concentration

The concentration of monomer to be grafted can be an important variable in extent of grafting therefore grafting extent was studied at different monomer concentrations. The results of these studies are shown in Fig. 2. The grafting extent increased with 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. However, at monomer concentration >50 %, there was significant increase in homo-polymer formation as well. It was difficult to retrieve the grafted matrix from the sticky homo-polymer formed therefore, for further studies; concentration of monomer was fixed at 30 % (v/v) to achieve high grafting levels and low homo-polymer formation.
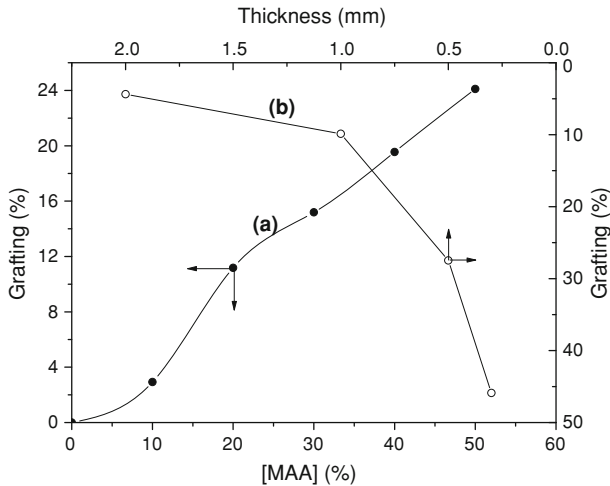
Fig. 2 Effect of (*a*) monomer concentration and (*b*) backbone thickness [MAA] = 30 % on grafting yield. Total irradiation dose = 1.29 kGy, dose rate = 2.58 kGy/h, [MS] = 0.04 M

Effect of backbone thickness on grafting extent

Figure 2 shows the effect of backbone thickness on the grafting extent of MAA on LDPE. From the figure, it can be concluded that grafting extent decreased with increase in thickness of LDPE backbone. Since LDPE does not swell in grafting solution (30 % MAA + 0.04 M MS solution in DD water), neither the radicals generated in bulk of LDPE are available for grafting nor monomer radicals generated in bulk of solution can penetrate into LDPE substrate and thus grafting is at surface only. At lower LDPE thickness, monomer radicals get higher surface area to graft upon, resulting in higher grafting degree. There have been contradictory reports on grafting extent dependence on thickness of the backbone. The effect of thickness on grafting has been reported to be independent [17], inversely dependent [18, 19] or on grafting temperature with thickness [20].

Radiation grafting in presence of homo-polymerization inhibitor and other additives

Simultaneous radiation grafting though has many advantages over pre-irradiation grafting [21] but it suffers from a serious disadvantage of homo-polymer formation during grafting, resulting in loss of monomer and requires extraction of homo-polymer from the grafted co-polymer. Homo-polymer formation around the grafted polymer also makes it difficult to retrieve the grafted sample particularly in the cases where the backbone is a thin sheet (as used in these studies) or fiber form. Addition of certain inorganic salts has been reported to suppress the production of undesirable homo-polymer during radiation-induced grafting or redox grafting, thus leaving more monomer available for grafting and hence enhancing the grafting extent and facilitating easy retrieval of grafted product [22]. This has been attributed
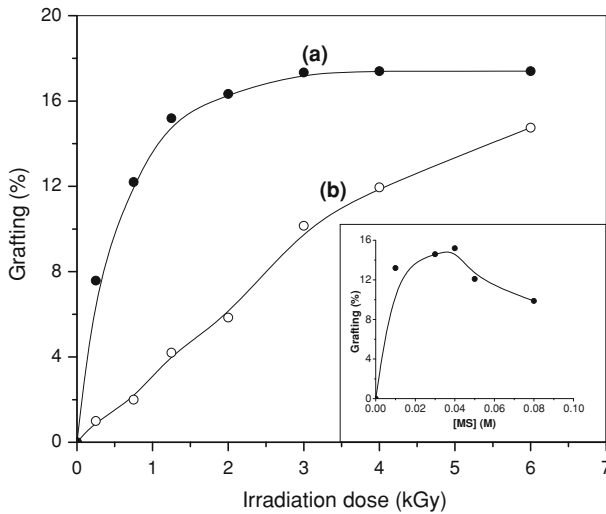
Fig. 3 Effect of presence of homo-polymerization inhibitors. Dose rate = 2.58 kGy/h, [MS] = 30 %: (*a*) MS = 0.04 M, (*b*) CuSO$_4$ = 0.04 M. *Inset* Effect of [MS] on grafting yield

mainly to scavenging of OH radical (generated due to radiolysis of water in the bulk of the mixture) by metal ions (Eq. 4) thereby reducing the homo-polymerization formation in the bulk.

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \tag{4}$$

In view of this fact reported earlier, grafting was carried out at different concentration of Copper sulfate and MS at known monomer concentration. Figure 3 shows the effect of copper sulfate and MS on grafting yield. It is clear that MS proved to be more suitable homo-polymerization inhibitor and enhanced grafting yield. It was just a co-incident that the grafting yield increased up to an optimum (0.04 M) MS (the concentration chosen arbitrarily for grafting studies) and decreased later at higher MS concentration. At MS concentration >0.04 M, no significant change in viscosity of the grafting solution before and after irradiation was observed indicating that the homo-polymerization as well as grafting were equally hindered. It seems the presence of MS in appropriate concentration decreases homo-polymerization reaction, which allows more monomer to be available for grafting and hence higher extent of grafting. Further grafting studies were carried out at 0.04 M MS concentration.

It has also been established that presence of inorganic acids enhances the grafting to a good extent and in combination with homo-polymerization inhibitors like MS can increase the grafting yield significantly [16, 23]. Therefore, efforts were made to investigate the grafting in presence of MS and acid in combination. However, it was observed that when taken in combination the monomer was not at all miscible in grafting solution and immediately formed a separate layer. Thus, grafting studies in presence of MS and acid could not be carried out.

Presence of surfactants has been reported to enhance grafting [24]. Therefore, grafting was investigated in presence of sodium lauryl sulfate (SLS). Figure 4 shows the effect of surfactant on grafting. The grafting yield decreased with increase in surfactant concentration. This observation suggests that the enhancement of grafting in presence of surfactant is system specific and many other parameters viz. emulsification of monomer in presence of surfactant and radiation chemistry of grafting solution may enhance or suppress grafting.

Effect of solvent on MAA grafting

Radiation grafting reactions can be performed in pure monomer or monomer dissolved in other solvents. The solvent may enhance or inhibit the extent of mutual grafting depending upon its interaction with the backbone and its own radiation chemistry. The solvents that swell or wet, the backbone polymer are generally known to assist grafting [8]. It has been reported that those monomer–solvent systems where the polymer formed is insoluble in the solvent, the monomer concentration at which maximum grafting is observed, is generally the monomer concentration at which the Trommsdorff peak appears for the monomer in that solvent [16] and enhanced grafting is observed in solvents in which the grafted polymer is soluble [25]. Since, LDPE does not swell in any solvent at room temperature solvent-assisted enhancement in grafting was not possible. Other possible route to enhance grafting was to carry out grafting in solvents in which both monomer MAA and its polymer were soluble. Thus, grafting carried out in methanol, water and their mixtures. Inset of Fig. 4 shows the effect of water content in methanol–water mixture on grafting. The grafting yield increased with the
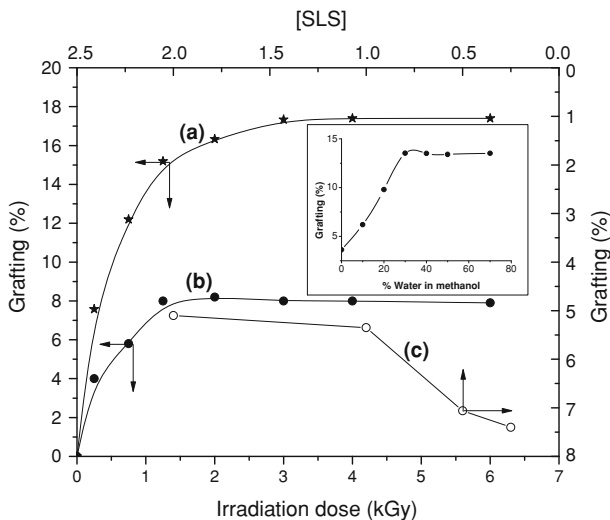

Fig. 4 Effect of SLS on grafting dose rate = 2.58 kGy/h, [MAA] = 30 % (*a*) [MS] = 0.04 M, (*b*) [SLS] = 0.25 %, (*c*) effect of SLS concentration on grafting yield. *Inset* Effect of methanol on grafting extent

increase in water content up to 30 % in mixture, and in pure water whole grafting solution turned into non-flowing solid mass. MAA is known to undergo very fast polymerization which finally results in formation of a crosslinked gel on irradiation in aqueous solution [17]. Also poly(MAA) is soluble in both, water and methanol. It seems as the water content in the mixture increases the rate of radiation-induced polymerization of MAA increases which contributes more to homo-polymer formation than to grafting extent at water concentration >30 % in mixture. The grafting yield for water–MAA could not be determined as the LDPE film was embedded in the gel and it could not be retrieved even after 48 h of soxhlet extraction.

Grafting kinetics

The above studies showed that the rate of grafting is a function of monomer concentration and of the dose rate, thus a simple equation relating these three parameters was deduced in form of equation

$$R_{\mathrm{g}} = K_{\mathrm{g}}[\mathrm{M}]^n D^m \qquad (5)$$

$$\text{or } \log R_{\mathrm{g}} = \log K_{\mathrm{g}} + n\log[\mathrm{M}] + m\log D \qquad (6)$$

where R_{g} is the rate of grafting {grafting (%)/h}, [M] is the monomer concentration (%), D is the radiation dose rate (kGy/h), and K_{g} is grafting constant. Values of parameters n and m were found by plotting logarithmically, initial rate of grafting for various MAA concentrations and dose rates. The exponent value for dependence of initial grafting rate on monomer concentration was found to be 0.74 and −0.83 for dose rate indicating that the grafting increased almost linearly with concentration while it decreased almost linearly with the dose rate. The exponent values for dose rate was comparable to that reported for other radiation grafting monomer–substrate system [26, 27] but the exponent value for concentration was significantly different than that reported by us for other monomer–substrate system [22]. The kinetic equation for grafting of MAA onto LDPE films in water as a solvent and MS as homo-polymerization inhibitor could be expressed as

$$R_{\mathrm{g}} = K_{\mathrm{g}}[\mathrm{M}]^{0.74} D^{-0.83} \qquad (7)$$

Characterization of grafted matrices

Hydrophilicity of MAA-grafted LDPE surfaces

Prior to surface analysis of grafted samples FTIR spectra of LDPE and MAA-*g*-LDPE were recorded to ascertain that grafting had taken place. The characteristic peaks of ethylene segments were observed at 2,915 and 2,846 cm^{-1} which were attributed to the symmetrical and asymmetrical stretching vibrations of methylene. The peaks observed at 1475, 1368, and 718 cm^{-1} were attributed to the deformation vibration of methylene, flexural vibration of methyl and inner rocking vibration of methylene, respectively. A sharp peak at 1,710 cm^{-1} for MAA-grafted LDPE film
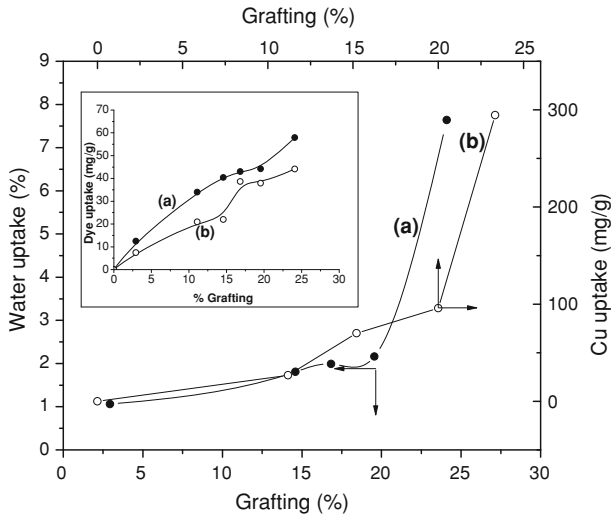
Fig. 5 (*a*) Water uptake of MAA-*g*-LDPE, (b) uptake of copper ion by MAA-*g*-LDPE. *Inset* Dye uptake of MAA-*g*-LDPE: uptake of (*a*) BR29 LDPE, (*b*) MB

was assigned to the carbonyl group of MAA and it confirmed that grafting of MAA on LDPE had taken place.

Surface and bulk hydrophilicity of the grafted substrates was estimated by contact angle and equilibrium water sorption measurements. Figure 5 shows water uptake of MAA-grafted LDPE sheet. Water uptake increased with increase in grafting yield, and an abrupt increase in the water uptake was observed at 25 % MAA grafting, highlighting sudden change in the polymer relaxation and water diffusion behavior. Solvent uptake of two samples which have same weight gain on processing but one only surface grafted and other surface grafted with simultaneous formation of interpenetrating networks can be different. In this study, as grafting solution did not swell LDPE backbone, formation of IPN was remote possibility. However, grafting assisted diffusion of monomer and water into the core of LDPE backbone cannot be ruled out as reported earlier for similar system [19]. The monomer diffused into the bulk would get grafted their and would further open up LDPE structure. To estimate the contribution from surface and bulk difference in the hydrophilicity, surface energy of the grafted matrix was investigated by contact angle measurements. The change in contact angle with time was recorded for these samples (Fig. 6). As expected, the contact angle for LDPE was highest and nearly did not change with time. Contact angle of grafted LDPE decreased appreciably during the time period which may be attributed to water affinity of grafted MAA chains. In order to quantify the change in hydrophobic character of LDPE on grafting, surface energy of the samples was estimated. Water and diiodomethane were used as test liquids for determination of surface energy of the samples. Table 1 gives the properties of the liquid used and the surface energy estimated for different samples. Variation in total surface energy and its polar and dispersive components with grafting yield has been plotted in Fig. 7. It is clear from the figure that polar
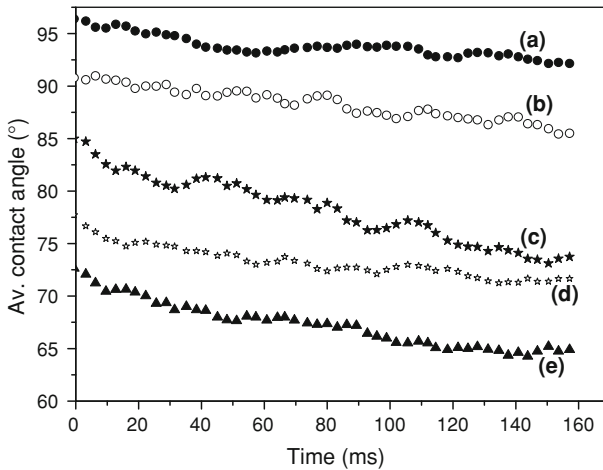
Fig. 6 The change in contact angle for samples grafted to extent: (*a*) 0 %, (*b*) 2.33 %, (*c*) 14.4 %, (*d*) 19.03 %, and (*e*) 23.03 %

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

Liquid	Surface tension (mN/m)		
	γ_1	γ_1^d	γ_1^p
Water	68.9	18.6	50.3
Diiodomethane	49.7	48.0	1.7

component and total surface energy increased with increase in grafting yield with no significant increase in the dispersive component (Table 2). This observation was similar to grafting of AA on polypropylene where significant increase in total surface energy due to increase in polar component was registered [9, 23, 28].

Dye and metal ion uptake by grafted LDPE

Dye uptake and metal ion uptake by different MAA-*g*-LDPE matrices have been shown in inset of Fig. 5. From these figures, it can be seen that dye and copper ion uptakes increased with the increase in degree of grafting. It was, however, interesting to see that uptake of both the dyes increased with increase in grafting yield, whereas Cu uptake showed an abrupt increase at ∼ 25 grafting (%), in sync with water uptake trend. As discussed in section above for grafted samples, there was a linear increase in polar component of surface energy with increase in grafting which may be attributed to grafted –COOH groups. The grafted –COOH group are primarily responsible for dye and metal ion uptake and therefore dye and ion uptake were expected (and observed) to increase with grafting yield. However, when normalized with respect to the grafting yield, the dye uptake decreased with the increase in grafting yield, whereas polar component of the surface energy and Cu^{2+} uptake increased. It has been documented that shorter grafted chains have higher
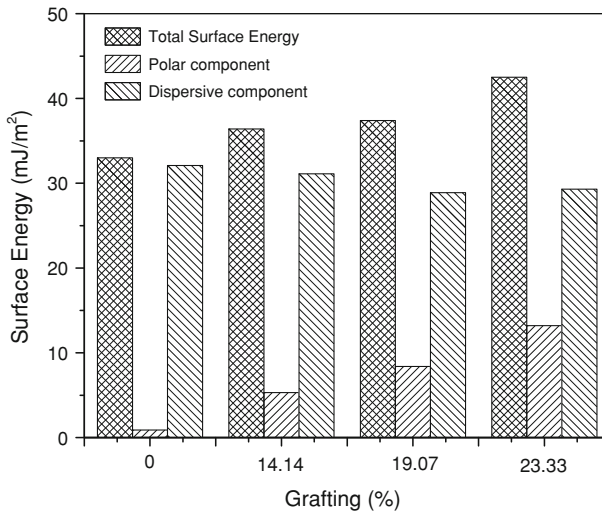
Fig. 7 The change in surface energy parameters with grafting yield

Table 2 Surface energy of the grafted samples

Sample	Surface energy (mJ/m²)		
	Total energy	Polar component	Dispersive component
Ungrafted LDPE	33.0	0.9	32.1
LDPE grafted (2.93 %)	37.2	1.1	36.1
LDPE grafted (14.14 %)	36.4	5.3	31.1
LDPE grafted (19.07 %)	37.4	8.4	28.9
LDPE grafted (23.33 %)	42.5	13.2	29.3

water retention capacity [14, 29]. Thus, both normalized dye and metal ion uptakes were expected to decrease with increase in grafting yield assuming the grafted chains length increases as grafting yield increases. This anomaly in Cu^{2+} ion and dye uptake behavior may be understood in light of stearic factors affecting penetrant diffusion and considering electrostatic interactions affecting the relaxation of grafted MAA segments (Fig. 8).

As uptake studies were carried out at near neutral pH and pK_a of MAA is ~ 4.83 [30], it can be fairly assumed that COOH group was completely de-protonated and grafted poly(MAA) chains in this state would repel each other to make condition conducive for ingress of water. When dye or Cu^{2+} ion molecule get bound to these grafted chains through electrostatic interaction the repulsion between the chains will be comparatively lowered and the chain configuration may change from fully extended state to closed state. Ionizable dye molecules are known to show electrostatic, hydrophobic, and hydrogen bonding with the host molecule [31]. Poly(MAA) shows strong hydrophobic interactions [32]. It seems the dye molecule in bound state further interacts with poly(MAA) chains through hydrophobic
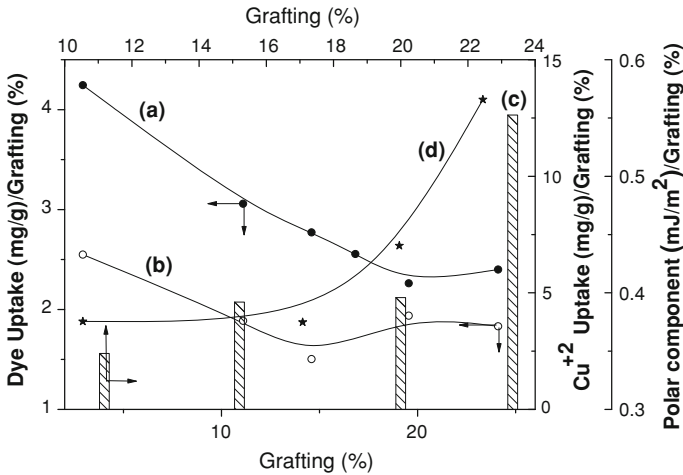
Fig. 8 The change in grafting yield normalized parameters with grafting yield: (*a*) BR29 uptake, (*b*) MB uptake, (*c*) polar component, (*d*) Cu^{+2} uptake

interaction which causes the chain to fold up and thus leaves less sites for further binding of dye molecules. This possibility was confirmed by non-release of dye molecules in presence of strong electrolyte line NaCl. As such hydrophobic interactions are not possible with Cu^{2+} ions; the initially bound ions would not hinder further binding of copper ions. The uptake of molecules would also depend on size of molecule. The diffusion of bulkier dye molecule will be comparatively difficult than Cu^{2+} ions. Further with increase in grafting yield, when the grafting chain density will be higher transport of bulkier dye molecule will be more difficult. Another factor that might affect the metal ion and dye uptake variation is the bulk modification of LDPE through progressive diffusion of monomer into LDPE bulk. Poly(MAA) present in the bulk will be more confined and will further reduce accessibility of dye molecules; such an effect, however, will pose relatively less stearic hindrance to small Cu ions, resulting in different uptake response of MAA-*g*-LDPE toward metal ions and dyes [3, 33, 34].

Conclusion

MAA can be grafted onto LDPE by simultaneous radiation grafting process under suitable experimental conditions. The grafting extent increases with dose and monomer content, whereas it decreases with the increase in dose rate and thickness of LDPE sheets. The grafting results in significant increase in surface energy of the LDPE matrix predominantly, due to increase in polar component of the surface energy. The extent of uptake of metal ion and dye is different than expected stoichiometrically. The different efficacy of dye and metal ions uptake can be explained due to different sizes, stearic hindrance, and different types of interactions with the grafting matrices.

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