# Surface and Bulk Properties of Glycidyl Methacrylate Modified Polypropylene: Experimental and Molecular Modeling Studies

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**ABSTRACT:** Modifications of polypropylene (PP) are often carried out to either functionalize them or meet specific property demands. This study considered the process of PP grafting with glycidyl methacrylate (GMA) as an intermediate step to achieve improvements in surface properties of this polymer. Abundant literature is available on this grafting process but little is known about the surface properties of the grafted PP. Present work considered both experimental and computational approaches to attain this goal. Experimentally, it was established that the melting temperature of modified PP changed with the addition of GMA, and at higher concentrations of GMA in the PP matrix, heterogeneous nucleation took place. Experimental results revealed a decrease in the surface energy (SE) as well. To discern the underlying reasons behind these changes, molecular dynamics simulations were undertaken. The computational results revealed that the changes in SE could be associated with the location of the functional group. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2983–2987, 2008

**Key words:** GMA-grafting; polypropylene; molecular dynamics

## INTRODUCTION

Because of good mechanical properties, excellent chemical resistance, ease of processability and relatively low cost, polyolefins, especially polypropylene (PP), have become one of the largest polymers in use today in a variety of applications.[1] However, due to its nonpolar nature, PP possesses poor adhesive properties limiting its application in laminates and composites.[2–4] Various chemical modification techniques have been employed for several decades to overcome this deficiency in PP. Melt-grafting of polar monomers is one of the many methods used to modify polyolefins.[5] PP is frequently grafted with such monomers as maleic anhydrate or carboxylic acid.[6–10] Glycidyl methacrylate (GMA) has been utilized as the grafting monomer for polyolefins because epoxy groups of GMA are able to react with —OH, COOH, and $NH_2$.[11–14] Being grafted on the fiber surface, GMA can also improve fiber wettability and adhesive properties, or GMA can be used as an ''anchor'' for the further polymer/fiber modifications.

In the work reported here, we considered grafting of PP with GMA and styrene monomers as an intermediate step for the improvement of PP adhesive properties. This technique was studied in details by Xie et al.[15] and Sun et al.[16] It was discerned that the presence of styrene decreased the degradation of PP during the melt-grafting process. This technique also led to the highest concentration of grafted GMA.

The primary focus of this study was to determine the optimal concentration and location of the functionalized group (i.e., GMA). Therefore, we examined the surface and bulk properties of the styrene-GMA modified PP experimentally. Additionally, we carried out molecular dynamics (MD) simulations to determine the underlying mechanisms. MD simulation is a powerful tool for studying microscopic properties of amorphous polymers, as well as for predicting the properties of polymeric materials. A number of studies have used this approach[17–24] to compute surface energy (SE), density profile, adhesion and compaction parameters for various polymers and their compatibility in blend systems. In the work reported here, the surface energies of PP containing different concentrations of GMA molecules and their location with respect to the surface were calculated.

## EXPERIMENTAL

### Materials

For this work, PP ($T_m$ = 160.7°C, $\rho$ = 0.91 g $cm^{-3}$, Melt flow index = 34) was obtained from Sunoco

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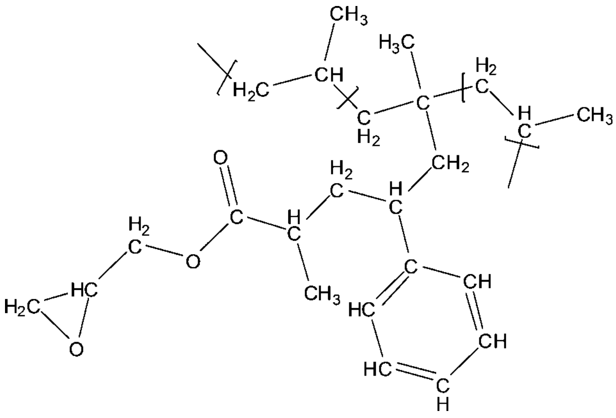

Figure 1 Structure of GMA-grafted polypropylene.

Chemicals. The rest of the chemicals required for melt-grafting, such as dicumyl peroxide (99%), GMA (97.5%), and styrene monomers (99.5%), were purchased from Sigma-Aldrich, USA.

### Sample preparation

Melt-grafting of PP with GMA was carried out by charging PP pellets, styrene, GMA and initiator into the twin-screw micro-compounder (ThermoHaake, USA). The reaction temperature was set and maintained constant at 175°C. The grafting was carried out for 11 min at the screw speed of 100 rpm. The styrene to GMA molar ratio was kept constant at 1 : 1 and the initiator at 0.6 or 1 wt %.[14] The concentration of GMA added ranged from 4 to 8 wt %, with 8 wt % being the maximum amount that could be loaded into the extruder.

After the designated reaction time, the polymer melt was extruded from the micro-compounder. Modified PP was then purified by dissolution in hot xylene. Unmodified and modified PP were precipitated by the addition of 400 mL of acetone. The precipitated polymer containing pure and grafted PP was filtered out leaving unreacted chemicals in the filtrate. The resulting ''cake'' was dried in the vacuum oven for 24 h at 80°C.

### Characterization

The amount of GMA reacted with the PP was determined by FTIR spectroscopy (Nikolet Nexus 470 FTIR).[16] For this purpose, the peak of carbonyl group appearing at 1730 $cm^{-1}$ and the peak of the PP at 2722 $cm^{-1}$ were taken as references. Calibrations for GMA were made using known concentrations of GMA.

The determination of total SE, its polar ($\gamma_p$) and disperse ($\gamma_d$) parts, was conducted via contact angle measurement using drop method. Two different liquids were used: water ($\gamma_d$ = 22.1 and $\gamma_p$ = 50.7 erg $cm^{-2}$) and ethylene glycol ($\gamma_d$ = 29 and $\gamma_p$ = 19 erg $cm^{-2}$). The final total surface energies were calculated by using a set of harmonic-mean equations.[25]

The DSC analysis was conducted on a Perkin–Elmer DSC 7 differential scanning calorimeter in nitrogen atmosphere. The samples were heated at a heating rate of 20°C $min^{-1}$ from 25 to 180°C. The samples were maintained at 180°C for 5 min and cooled down under the same conditions.

### Computational details

Simulation of polymers was carried out using a commercially-available MS modeling software from Accelrys, USA.[26] A series of MD runs and minimizations were performed with Discover module employing COMPASS forcefield.[27,28] The minimizations were conducted using ''Smart Minimizer,'' where the process of minimization starts with the steepest descent approach followed by conjugate graduate and Newton methods. Nonbonding interactions were calculated using the group-based method with the cut-off radius of 9.5 Å.

Polymer chains with 50 repeat units were generated using ''amorphous cell'' module with periodic boundary conditions. To construct the modified PP, the functionalized group was added to the center (25th repeat unit) of the PP chain as shown in Figure 1. Amorphous cells of PP and its grafted version, GMA-*g*-PP, were constructed at the experimental density of PP. The parameters of the resulting structures are shown in Table I. For each configuration, five amorphous cells were built.

These cells were then refined by running a ''basic refine'' protocol with MD run of 4000 fs at 298 K. To remove low or zero density areas, the cells were run through a temperature cycle—11 stages from temperature of 298 to 453 K and 11 stages from temperature of 453 to 298 K; keeping pressure at 1 atm (0.0001

**TABLE I**
**Properties of the Cells Studied**

| Concentration of GMA (wt %) | 0 | 0.8 | 1.3 | 1.7 | 2.2 | 3.3 | 4.4 |
|---|---|---|---|---|---|---|---|
| PP, number of molecules | 3 | 7 | 4 | 3 | 2 | 1 | 1 |
| GMA-*g*-PP, number of molecules | 0 | 1 | 1 | 1 | 1 | 1 | 2 |
| Average cell size (Å) | 23.13 | 32.09 | 27.32 | 25.63 | 23.34 | 20.39 | 23.60 |

**TABLE II**
**Grafting Efficiency and Surface Energies of GMA-Modified Polypropylene**

| GMA added (wt %) | GMA grafted (wt %) | Total surface energy (erg cm$^{-2}$) |
|---|---|---|
| 0 | 0.0 | 27.6 ± 0.4 |
| 4 | 0.45 | 25.0 ± 0.8 |
| 8 | 0.81 | 23.0 ± 0.4 |
| 6 | 1.31 | 23.2 ± 0.8 |
| 6[a] | 1.90 | 25.0 ± 0.6 |

[a] With 1 wt % of initiator.

GPa). Finally, all cells were minimized using ''smart minimizer'' to a convergence of 0.1 kcal mol$^{-1}$ Å$^{-1}$.

Ready bulk samples were relaxed for 50 ps via NVT (constant concentration, volume and temperature) MD simulation. Snapshots of the trajectory were taken every 0.025 ps during the last half of the run. The snapshot with the lowest potential energy was minimized to a convergence of 0.1 kcal mol$^{-1}$ Å$^{-1}$. The generated bulk samples were used to form film cells and to calculate the cell parameters.

To create the thin films, one edge ($z$ direction) of the minimized bulk samples was extended to 100 Å, so that the polymer chains no longer interact with its image along this direction. These newly-formed films were subjected to the energy minimization run followed by 50 ps of MD simulation at 298 K. The trajectory snaps were taken during last 25 ps and a cell with minimum potential energy was further minimized. In some cases however, the dynamics were conducted at 600 K to shake the cell out of unfavorable local minima. The resultant film cells were used for the calculations of surface energies and density profiles.

The surface energies were calculated as the difference of potential energies of the thin film ($E_{\text{film}}$) and its corresponding amorphous cell ($E_{\text{cell}}$) divided by surface area ($2A$) created upon formation of the thin film as given by the equation below:[18]

$$\gamma = \frac{E_{\text{film}} - E_{\text{cell}}}{2A} \quad (1)$$

## RESULTS AND DISCUSSION

### Experimental

The grafting process yielded a series of functionalized PP. The results are shown in Table II. Because of limitations of the present experimental apparatus, the highest concentration of GMA grafted onto PP was only 1.9 wt %. Nevertheless, the table depicts that there is a maximum concentration of GMA molecules that can be introduced onto PP chain without changing the initiator concentration. Similar observations were made by Xie et al.[15] The addition of the initiator resulted in an increase in grafting efficiency but at the expense of PP degradation by the initiator. The presence of GMA in PP matrix decreased SE of polymer wherein a minimum was obtained at about 0.8 wt %. These results might indicate the change in miscibility of the grafted and unmodified PP molecules.[29] To confirm this, the samples were analyzed by DSC.

The effect of grafting on crystallinity ($X_c$), crystallization ($T_c$) and melting ($T_m$) temperatures were determined by DSC. The results are shown in Table III. The DSC analysis of PP-*g*-GMA showed that the $T_c$ of modified polyolefin were higher than virgin PP. This indicates that grafted GMA molecules provided additional sites for PP during the crystallization process. The melting temperatures of the grafted PP were higher as well, with the exception of one sample containing 0.6 wt % of GMA. The melting temperature of this sample was observed to be 157.9°C, which is lower than the original PP polymer. Somewhat similar results were obtained by Liang et al.[30] and Pesetskii and Makarenko.[31] The former observed an increase in $T_m$ value. The results were elucidated by the heterogeneous nucleation effect of GMA. Pesetskii and Makarenko also observed a decrease in the $T_m$ of the samples explaining it by the difference in melt viscosities and grafting efficiency. However, the surface energies or the degree of grafting were not determined.

Taking into consideration the results obtained by Krump et al.[29] stating that the SE of well-miscible polymer blends tend to decrease, then the PP chains containing up to 0.6 wt % of GMA should possess good miscibility in an unmodified PP matrix. This sample had a lower SE and lower $T_m$ compared with ungrafted PP. However, the surface energies of the samples with a GMA content of 0.9 wt % and higher began to increase (see Table II). Also, the $T_m$ for these samples was higher than that of the virgin PP, that is, heterogeneous nucleation was observed.[30] These observations may imply limited miscibility of GMA-grafted molecules (above 0.9 wt %) with ungrafted PP.

It must be noted that the sample with 1.9 wt % was also an exception. The increase in the amount of initiator to 1 wt % led to a decrease in the viscosity of PP[15] and hence a decrease in melting temperature was observed.

**TABLE III**
**Melting ($T_m$), Crystallization Temperatures ($T_c$), and Crystallinity ($X_c$) of GMA-Grafted Polypropylene**

| GMA grafted (wt %) | $T_m$ (°C) | $T_c$ (°C) | $X_c$ (%) |
|---|---|---|---|
| 0 | 160.7 | 113.6 | 50 |
| 0.6 | 157.9 | 116.6 | 63 |
| 0.9 | 162.2 | 117.2 | 71 |
| 1.4 | 162.0 | 119.4 | 62 |
| 1.9 | 160.5 | 118.5 | 48 |

### Atomistic simulation

To reaffirm the changes in the bulk properties of PP-*g*-GMA and also to perceive the effect of high wt % of GMA grafted, we turned to computational methods. The modified PP chains were constructed based on the results observed by O'Rourke-Muisener et al.[32] They have concluded that the best architecture for the polymer having a polar functional group is when this group is placed at the center of the chain backbone. With this in mind, it is expected that the results from the computation will be slightly different from the experimental results because grafting occurred at random locations of the chain in addition to the slight variations in the structure of functional group. However, the phenomena observed experimentally should be also discerned computationally.

We began our analysis with the calculation of SE of the functionalized PP by using eq. (1) and comparisons with the results obtained experimentally. The data are presented in Figure 2. As can be seen from this figure, the values of SE obtained via MD simulation were quite close to experimental values. A small decrease in the SE values was observed at the GMA concentration of 1.7 wt %, which is a bit higher than one observed during the experiments. The values of SE at lower concentrations of the GMA (lesser than 1.3 wt %) were not possible to obtain as the cell sizes were relatively large to construct ''thin films'' and the correlation 1 was not applicable. However, MD simulations allowed us to project the SE values up to 4.4 wt % and higher. The MD simulation results show that the major changes in SE occurred up to GMA concentration of 3 wt %.

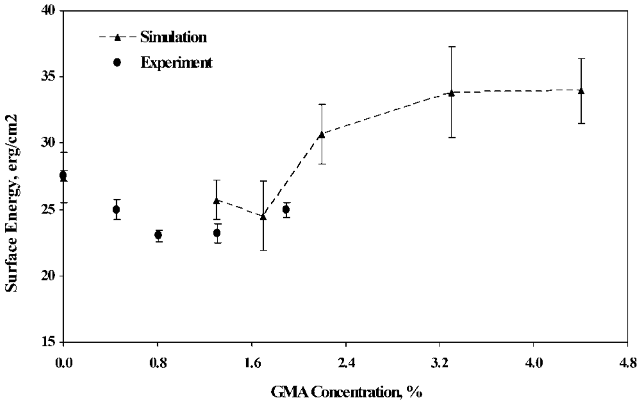

**Figure 2** The values of SE of modified PP. Comparison of the data obtained from the experiments and molecular dynamics simulations.

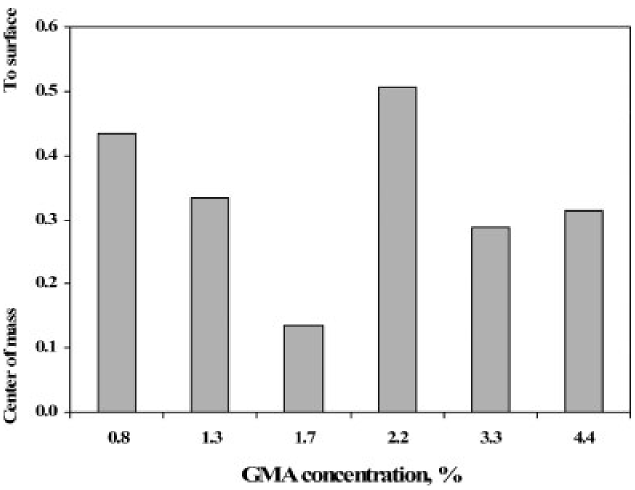

**Figure 3** Location of the functional group (epoxy) from the center of mass (c.m.): effect of the GMA concentration. The data represented are the average of five cells.

To determine if the changes in the SE values can be associated with the location of the functionalized group (epoxy), an analysis of the density profiles of the films along $z$ direction was conducted. Equation (2) was employed to obtain the position of interface and its thickness:[33]

$$\rho(z) = \frac{1}{2}\rho_{\text{bulk}}(z)\left[1 - \tan h\left(\frac{2(z-h)}{w}\right)\right] \tag{2}$$

where $\rho(z)$ is the density at position $z$, $\rho_{\text{bulk}}(z)$ is the bulk density, $h$ is the position from the interface, and $w$ is interfacial width.

Since the size of the cells was different, the ratio of distance of epoxy group from center of mass (c.m.) to the distance from the c.m. to the surface was calculated by:

$$R(z) = \frac{l(z)}{h+w} \tag{3}$$

where $l$ is the distance of epoxy group from c.m. along z direction. The results of the calculation are shown in Figure 3. This figure exhibits that the polar groups depleted from the surface. With an increase in its concentration, the high energy group drives away from the surface. At the concentration of 1.7 wt %, the location of the epoxy group was near at the center of mass. At this point, the SE was also observed to be the lowest. At 2.2 wt %, the epoxy group was found to be closer to the surface again. Perhaps it can be attributed to the rearrangement of this group to minimize its energy within PP due to its immiscibility with the rest polymer matrix, as it was observed during the experiments.

## CONCLUSIONS

The influence of the concentration of GMA molecules on the properties of PP polymer was investigated in this work. Experimental results indicated an initial decrease in SE. Thermal analysis showed that at low concentrations of GMA in the PP matrix melting temperature ($T_m$) was lower than that of unmodified PP. At a GMA concentration of about 0.9 wt % and higher, heterogeneous nucleation was observed as indicated by the values of $T_m$. MD simulation confirmed our experimental observations. The variation in SE could be attributed to the location of the functional group. The epoxy group was observed to be closer to the surface at lower concentrations of functional group, which suggests that further modifications of polymer/fibers could be more effective at the these concentrations.

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