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Synthesis and Characterization of CPE-g-GMA Graft Copolymers Obtained by Suspension Copolymerization

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Graft of glycidyl methacrylate (GMA) onto solid-state chlorinated polyethylene (CPE) has been performed by suspension copolymerization in a complex dispersion medium which was a compound with H₂O, ethyl acetate (EA) and tert-butyl alcohol (TBA). Benzoyl peroxide (BPO) was used as the free radical initiator. The graft level (graft degree and graft efficiency) was calculated gravimetrically, and the graft copolymer was characterized by infrared (IR) spectroscopy, thermogravimetric analysis (TGA) and contact angle study. The effects of reaction conditions on graft level, including chemical parameters (the concentration of monomer, initiator, and interfacial agent) and processing parameters (reaction time and temperature), have been investigated in detail. The experimental results showed that GMA could be grafted onto the chain of CPE with comparative higher graft degree, which could reach 37% with graft efficiency above 80%.

Keywords: CPE, GMA, swelling suspension, graft copolymerization

1 Introduction

Elastomers have been used in a wide range of fields, particularly in the building industry and automotive industry, under several conditions of temperature, frequency and deformation. In order to acquiring more commercial applications, elastomers are seldom used commercially in a pure state. Multi-component mechanical blending technology and chemical modification are familiar methods for obtaining improvement of elastomers.

As a type of speciality elastomer, chlorinated polyethylene (CPE) generated much interest in modification and application, which exhibits not only high flexibility, good weatherability, flame retardancy and also resists deterioration by oils, solvents, oxygen, ozone and heat. These excellent capabilities should be primarily attributed to the chlorine atoms added to the polyethylene backbone. CPE containing 35–39 wt% of chlorine content is a type of random chlorinated polymer which has weak polarity (1). However, due to its low melting temperature, low tensile strength and poor compatibility with synthetic polar polymers, CPE is limited in its application in several technologically fields, such as preparing polymer alloys with

certain polar polymers. In order to extend the application of CPE or obtain polymers for special purpose, CPE needs to be modified by physical or chemical methods. Especially in the field of polymers blending, quite a few researches have been reported (2–7). Grafting copolymerization is the most useful method of chemical modification. When CPE is grafted with certain monomers, the chemical and physical properties of copolymer will change compared with the original CPE. The grafting monomers onto CPE has been performed by several methods.

Considerable effort has been expended over the past several years to synthesizing and characterizing CPE graft copolymers. For instance, He et al. (1) synthesized amphiphilic macromolecules, CPE-g-AA and CPE-g-AM, by chemically initiated oil-swelling suspension graft copolymerization, which was executed by grafting acrylic acid (AA) and acrylamide (AM) onto solid-state CPE. Zhao et al. (8) synthesized a graft copolymer, highly chlorinated polyethylene-graft-methyl methacrylate (HCPE-g-MMA), which was prepared by the mechanochemistry reaction. The mechanochemistry method was accomplished on a two-roll mill, which was used as a chemical reactor for chemical modification of host polymers or the synthesis of new polymers. A novel approach, so-called *in situ* chlorinating graft copolymerization (ISCGC) was used to synthesize CPE-g-HEA and CPE-g-MMA. In this original synthesis method, chlorination and monomer grafting took place simultaneously (9,10). A typical chemical modifications

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basing on CPE is the preparation of chlorosulfonated polyethylene in a tank reactor using chlorinated polyethylene and a gaseous mixture of chlorine, dioxide sulfur and nitrogen initiated by ultraviolet light (11). In addition, graft copolymerization of CPE or other polyolefin could also react in organic solvent (12–15) or in water (16).

Glycidyl methacrylate (GMA) is a kind of vinyl ester monomer with correspondingly higher activity. In recent years, GMA has been utilized as the grafting monomer of polyolefins that can be functionalized as in-situ compatibilizers for preparing polymer alloys, such as polyolefins/polyamides, polyester, etc. Because epoxy groups in GMA are able to react with -OH, -COOH and -NH₂, much attention has been devoted to grafting GMA onto polyolefin in recent years. For example, Pan et al. (17) grafted GMA monomer onto polypropylene at certain reaction temperature which was below the melting point of PP, so that PP was modified in the solid phase, and the solid-phase grafting of GMA onto powdered PP was conducted on a Haake Rheomix. Ethylene-propylene copolymer (EP) was functionalized with GMA by means of a radical initiated melt grafting reaction, and FTIR and ESCA were used to characterize the formation of EP-g-GMA copolymers (18). Usually, the graft degree of GMA on polyethylene is just below 10%, and not higher than 20% on polypropylene (19), and there are no new reports with regard to obtaining higher graft level of GMA on various polyolefins. Grafting GMA onto CPE has rarely been explored, and that, by the above-mentioned synthesis technologies, it is difficult to obtain graft copolymers of a higher graft degree and efficiency. In this investigation, the suspension copolymerization method, which avoids solvent waste in dissolving and high operation temperature in melt process, was introduced into the synthesis of the graft copolymer, CPE-g-GMA. The effects of various factors such as monomer, initiator, component ratios of the complex dispersion system, reaction time, and reaction temperature on the graft level were studied in detail.

2 Experimental

2.1 Materials

Chlorinated polyethylene (CPE, 135A, Cl–35%) powder used in this work was supplied by Weifang Yaxing Chemical Co. Ltd., Shandong, China, and dried in an oven at 50°C before use. Glycidyl methacrylate (GMA) was purchased from J&K Chemical Ltd., and used without further purification. Benzoyl peroxide (BPO, chemical factory of Hubei University, Hubei, China.) was purified by dissolving in chloroform and reprecipitating with methanol. Ethyl acetate (EA), tert-butyl alcohol (TBA) and acetone were provided by Tianjin Kermel Chemical Reagent Development Center, China, all were analytical reagents.

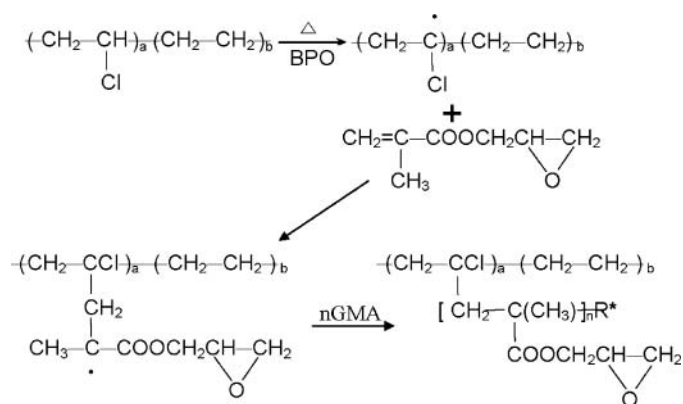
2.2 Preparation and Purification of CPE-g-GMA

The graft reactions were performed in a four-necked, round-bottom flask of 250 mL capacity, fitted with mechanical stirrer, a N₂ gas inlet, a thermometer and a reflux condenser. The reaction temperature was controlled by a constant-temperature water bath. Firstly, 2.0 g CPE, 5.0 mL EA as sweller, a certain amount of initiator BPO, and monomer GMA were added into the flask in proper order. The vessel was flushed with purified N₂ for several minutes to displace the air in it and the reaction was proceeded under the N₂ atmosphere. After CPE was swelled by the liquid mixture for about 30 min, it can be swelled sufficiently. A known volume of TBA dissolved within 50 mL distilled water was added slowly by a drop funnel, and at the same time, the mixture was stirred rapidly to make the system homogeneous. Then, the reaction temperature was raised and kept at 80°C for several hours to the end. The solution was filtered, and then the crude products were washed with hot water and dried in vacuum. After the weight was recorded, the crude products were extracted with acetone by means of a Soxhlet extractor for 48 h to remove residual GMA, and possible homopolymer PGMA.

The process of grafting GMA onto CPE backbone is depicted in Scheme 1.

To evaluate the graft degree (GD) and the graft efficiency (GE) of GMA, the leftover products, pure graft copolymers, were dried in vacuum at 60°C and weighed. The GD and GE were calculated by the following equations (20):

$$\begin{aligned} \text{GD} &= \frac{\text{wt of grafted GMA polymer}}{\text{wt of CPE}} \times 100\% \\ &= \frac{\text{dry wt of grafted product} - \text{dry wt of CPE}}{\text{dry wt of CPE}} \times 100\% \\ \text{GE} &= \frac{\text{wt of grafted GMA polymer}}{\text{wt of GMA polymer}} \times 100\% \\ &= \frac{\text{dry wt of grafted product} - \text{dry wt of CPE}}{\text{dry wt of crude product} - \text{dry wt of CPE}} \times 100\% \end{aligned}$$



Sch. 1. Synthesis of CPE-g-GMA copolymer *R stands for hydrogen atom or CPE chain.

2.3 The Blending and Segregation of Homopolymer and CPE

The monomer homopolymer PGMA was prepared under the same reaction conditions as the previous graft copolymerization, and then cooled to room temperature to blend with a required amount of CPE. After filtering, PGMA was separated by the same extractive purified method to check the efficiency of the extraction agent.

2.4 Characterization

The pure CPE, PGMA/CPE mixture, and graft copolymer CPE-g-GMA samples were pressed into thin translucent films between aluminum sheets in a press vulcanizer at 140°C under 20 MPa pressure. FTIR spectra of these films were scanned on a Perkin–Elmer Spectrum One spectrometer.

Thermogravimetric analysis of CPE-g-GMA of different GDs was performed with a Shimadzu TGA-60 at a heating rate of 10°C/min under nitrogen atmosphere, and the quantity of specimens was about 10 mg.

Contact angles (θ) of water on the plain CPE and CPE-g-GMA samples were measured at 20°C by using a Kruss K12 dynamic surface energy analyzer. The products of different GDs were pressed into sheets in a press vulcanizer at 140°C under 10MPa pressure, and then the sheets were cut into strip samples.

3 Results and Discussion

3.1 Effect of the Reaction Medium

Basing on previous research (1), EA was adopted as the sweller for CPE expanding. GMA is an oil-soluble monomer, which would make solid-phase viscous resulting in a reaction system unhomogeneous without any interfacial agent. So we chose various additives to ameliorate the dispersive state. Finally, we selected tert-butyl alcohol (TBA) to improve the dispersion. TBA has a higher solubility parameter (δ) than CPE and GMA, which is about $11.8(\text{cal}/\text{mL})^{0.5}$, while CPE-8.9, GMA-8.5, EA-9.1. If there are only EA and GMA for swelling CPE, the δ of their mixture is too close with CPE, which could explain why oil-phase cannot disperse without TBA. It was found that a complex suspension medium, which was compounded with water and TBA of proper concentration, could make oil-phase be homogeneous. Solid-phase substrate began to disperse into grains and the grainy reaction units became smaller gradually as the dosage of TBA increased.

The effect of volume percentage of TBA in H₂O (fixing amount of H₂O, 50 mL) on graft level was studied in the range 0–8%, as shown in Figure 1. A continuous increase in the GD and GE were observed on increasing the percentage

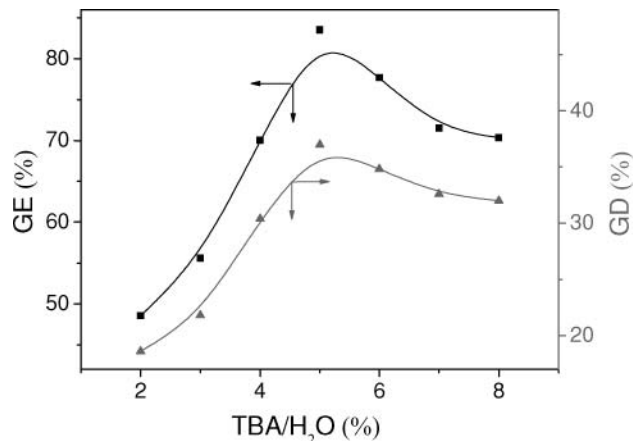


Fig. 1. Effect of the volume ratio TBA/H₂O on GE and GD volume ratio: H₂O/EA = 50/5; mass ratio: CPE/GMA/BPO = 2/1.08/0.05; reaction time: 8 h; temperature: 80°C.

of TBA from 0 to 5%. On a further increase of TBA, the GD and GE dropped.

3.2 Effect of the Monomer Concentration

The effect of monomer concentration (mass ratio with CPE) on the GE and GD is illustrated in Figure 2.

It is evident that GD increases initially with an increase of monomer amount up to 54 wt% (1mL) and then increases slowly. This could be explained by the fact that, initially, the number of monomer molecules reaching the free-radical sites on the polymer backbone governs the grafting extent. However, at higher monomer concentration, the number of free-radical sites available on the CPE backbone becomes a limiting factor and homopolymerization of the monomer becomes greater (17). On the other hand, when the monomer concentration increases, the homopolymerization rate shows a quicker rise than the grafting rate. In

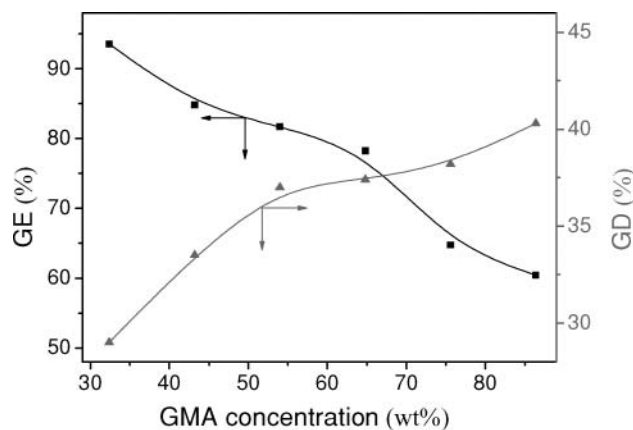


Fig. 2. Effect of the monomer concentration (GMA/CPE) on GE and GD volume ratio: H₂O/EA/TBA = 50/5/2.5; mass ratio: CPE /BPO = 2/0.05; reaction time: 8 h; temperature: 80°C.

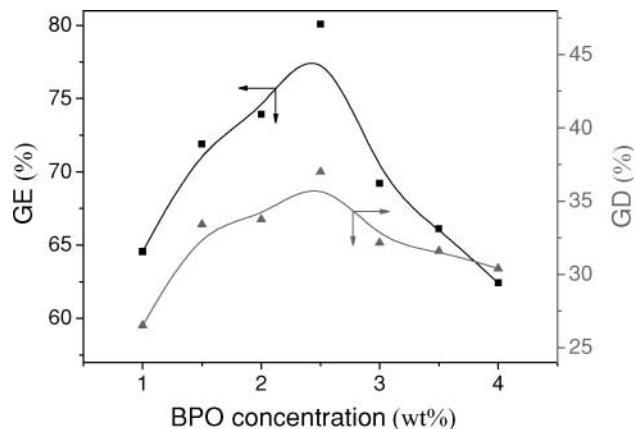


Fig. 3. Effect of the initiator concentration (BPO/CPE) on GE and GD volume ratio: $H_2O/EA/TBA = 50/5/2.5$; mass ratio: CPE/GMA = 2/1.08; reaction time: 8 h; temperature: $80^\circ C$.

other words, the greater the amount of GMA, the larger is the homopolymerization rate. Increasing the concentration of monomer is especially helpful in terms of forming PGMA. Therefore, GE decreases continually, so 54 wt% GMA is an economical concentration in this reaction system.

3.3 Effect of the Initiator Concentration

The concentration of initiator is a significant parameter in most graft copolymerization studies. The effect of BPO concentration was studied in the range 1~4 wt% (Fig. 3). GE and GD increase with an increasing concentration of BPO from 1~2.5 wt%. This trend can be explained by the fact that the amount of free radicals generates an increase on increasing the concentration of BPO, resulting in the increase in graft level. On a further increase of BPO concentration, the graft level dropped. A further increase in the initiator concentration results in serious homopolymerization of the monomer due to the enhanced mutual termination reaction of radicals. As the initiator concentration reaches a higher level, there would be a tendency for the chain transfer to the monomer, which would be more pronounced and facilitate the homopolymerization of GMA.

3.4 Effect of Reaction Temperature

In this reaction system, liquid phase is mixed by H_2O , EA, TBA and a little of GMA. The boiling point of the mixture (volume ratio: $H_2O/EA/TBA/GMA = 50/5/2.5/1$) was measured, which is about $80^\circ C$. So we investigated effect of reaction temperature on GE & GD in the range 55– $80^\circ C$, as shown in Figure 4.

With increasing temperature, the graft level increases uneventfully in a given period of time due to an increased decomposition rate of the initiator. Therefore, the amount of free radicals, as well as their mobility also increases,

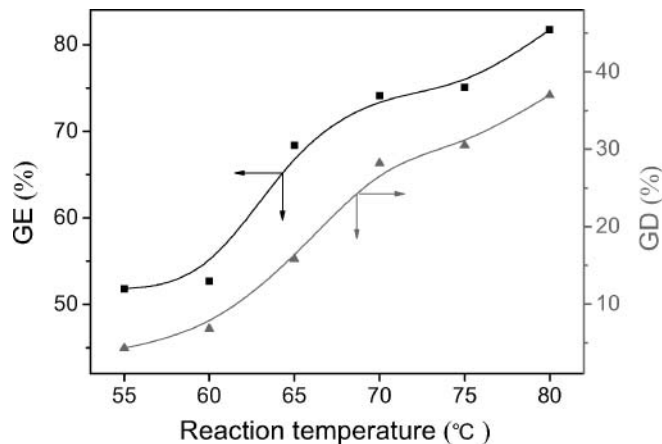


Fig. 4. Effect of the Reaction Temperature on GE and GD volume ratio: $H_2O/EA/TBA = 50/5/2.5$; mass ratio: CPE/GMA/BPO = 2/1.08/0.05; reaction time: 8 h.

which results in a higher level of grafting. There is not a reduced trend in GE and GD as the temperature increases at 55– $80^\circ C$, so $80^\circ C$ is a proper reaction temperature.

3.5 Effect of Reaction Time

The half-lifetime of BPO is about 4.3 h at $80^\circ C$. Therefore, more than 70% of the initiator decomposes in about 8 h. This primarily determines the reaction time. Figure 5 illustrates the effect of reaction time on the graft level. It is evident that the graft level increases initially and reaches a plateau in 7~8 h. With an increase in reaction time, the free radicals will have more time for reaction and therefore, result in a higher level of grafting. After some time, most of the initiator and monomer are used. Thus, no further rise in the graft level was observed with increasing reaction time, therefore, 8 h is a reasonable reaction time for this copolymerization.

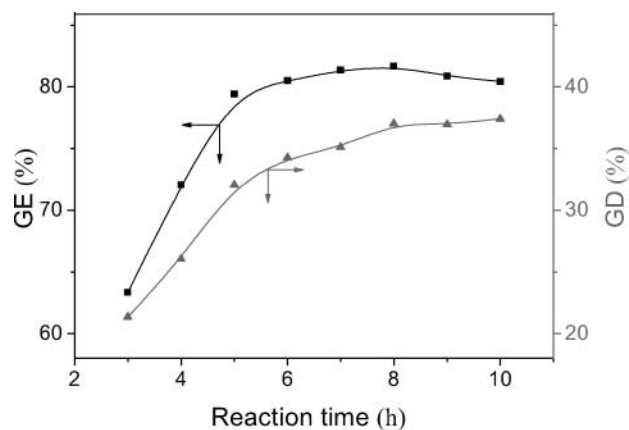


Fig. 5. Effect of the Reaction Time on GE and GD volume ratio: $H_2O/EA/TBA = 50/5/2.5$; mass ratio: CPE/GMA/BPO = 2/1.08/0.05; reaction temperature: $80^\circ C$.

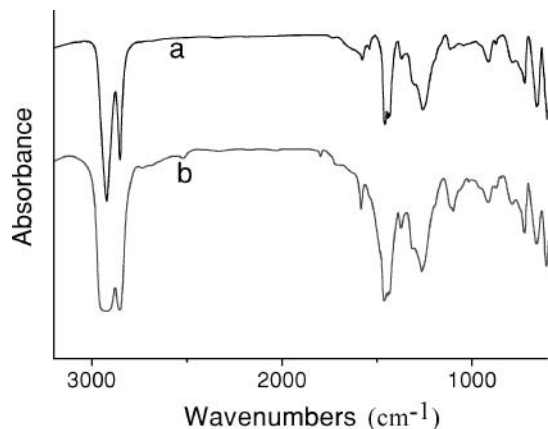


Fig. 6. IR spectrum of pure CPE (a) and the blends CPE/PGMA after extracting (b).

3.6 Characterization

3.6.1. Infrared Spectra

In the synthesis of graft polymers, the products were not only graft copolymers CPE-g-GMA, but also residual GMA and homo-PGMA. It is necessary to separate them from graft copolymers when studying the structure of graft copolymers. For discussing whether acetone is an effectual extractor, IR spectra of the blends CPE/PGMA which had been extracted for 48 h was recorded. The result showed that the curve of the blends CPE/PGMA was nearly the same as pure CPE, as shown in Figure 6, which could prove that acetone is an appropriate extractor.

The curve c in Figure 7 is the IR spectrum of CPE-g-GMA. Compared with the curve a, it is clearly seen that new absorptions at 1729 and 908 cm^{-1} , are attributed to contributions of carbonyl and epoxy groups of GMA, respectively (21). This result verifies that GMA has been grafted onto the CPE chains.

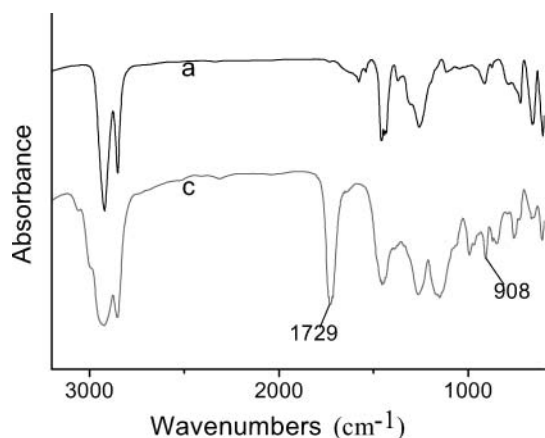


Fig. 7. IR spectrum of pure CPE (a) and graft copolymer CPE-g-GMA (b).

Table 1. TGA Data for CPE and different CPE-g-GMAs

No.	GD (%)	IDT ^a	T _{d1} ^b (°C)	T _{90%} ^c (°C)
1	0	206.25	293.54	633.06
2	11.75	204.5	294.12	543.5
3	25.75	203.23	297.84	510.43
4	37	201.81	314.31	505.66

^a IDT initial decomposition temperature.

^b T_{d1} decomposition temperature of first step.

^c T_{90%} temperature when the weight loss is 90%.

3.6.2. Thermogravimetric analysis

The TGA data for pure CPE and graft copolymers of different GDs are given in Table 1, and the TGA curves are shown in Figure 8. The result shows that there is a considerable change in the thermal behavior of CPE upon monomer concentration. From the figure, it is evident that the thermal degradation of the samples involved two different steps. In the curve of CPE, there is a decrease of about 33% weight loss in the first step at around 230–410°C, which results from the removal of HCl. It corresponds to the chlorine content (35 wt%) in CPE macromolecules (22). The initial decomposition temperature (IDT) of poly(GMA) is 188°C (23), so the IDT of CPE-g-GMA is a little lower than that of CPE. In the curves of CPE-g-GMA, weight loss of the first decomposition step is about 50% occurred in the range 225–400°C, and the higher GD, the more weight loss, which is due to the loss of HCl, volatilization of CO₂ in GMA branches and low-molecular weight species caused by the rupture of ester groups (23). The second decomposition step should be caused from rupture of weak linkages in backbone, and thereby volatilization of low-molecular weight species, like lower hydrocarbon.

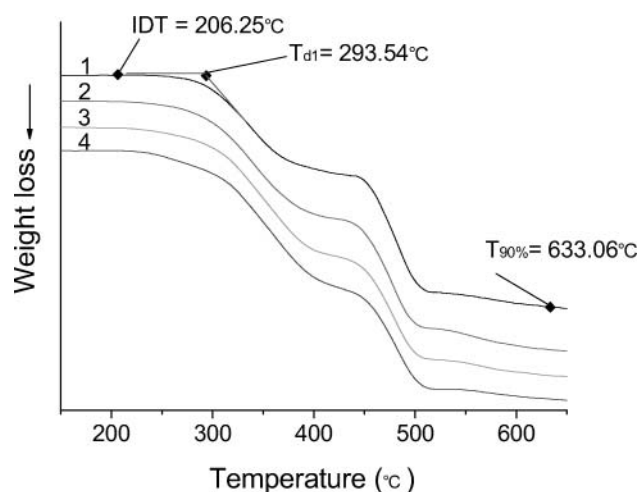


Fig. 8. TGA curves of (1) pure CPE and CPE-g-GMA of different GDs, (2) 11.75%, (3) 25.75% and (4) 37%.

Table 2. Contact angles against water of CPE-g-GMA

No.	GD (%)	Contact angle
1	0	93.6
2	11.75	83.1
3	20.2	80.7
4	25.15	77.3
5	31.2	76.1
6	34.55	75.3

3.6.3. Contact angles study

Contact angles against water of the plain CPE and CPE-g-GMA samples are reported in Table 2. It is observed that with an increasing percentage of grafted GMA, contact angles increased monotonically. This result suggests that the surface polarity of grafted copolymer is augmented by an increase of the content of GMA in CPE-g-GMA samples.

4 Conclusions

This article describes an effective method to synthesize certain graft copolymers of higher graft degree. Glycidyl methacrylate has been successfully grafted onto chlorinated polyethylene using the suspension copolymerization technique. In previous studies and in the present one, it has been shown that this graft copolymerization process is an easy and environmentally friendly method to graft monomers onto polymer chains, with convenient product disposal and using few organic solvents. The effects of various reaction parameters have been investigated and quantified. The optimum reaction conditions to obtain maximum grafting were evaluated: $H_2O/EA/TBA = 50/5/2.5$ (volume ratio); $CPE/GMA/BPO = 2/1.08/0.05$ (mass ratio); temperature $80^\circ C$ and time 8 h. When the graft efficiency of glycidyl methacrylate is in an acceptable range (above 80%), a copolymer with maximum graft degree, 37 wt%, has been obtained.

Acknowledgments

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