

# Solvothermal preparation of maleic anhydride grafted onto acrylonitrile–butadiene–styrene terpolymer (ABS)

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## Abstract

The grafting copolymerization of maleic anhydride (MAH) onto acrylonitrile–butadiene–styrene terpolymer (ABS) was carried out through solvothermal process. Infrared (IR) spectra and <sup>1</sup>H NMR spectra confirmed that maleic anhydride was successfully grafted onto the ABS backbone. The influences, such as MAH concentration, the initiator's content, reaction temperature and time, comonomer, ABS concentration and different solvents, on the grafting copolymerization were also studied. Results indicated that the preparation of MAH grafted onto ABS through solvothermal method can be carried out in both good solvent and poor solvent, which is much different from the traditional solution grafting method, and high grafting degree can be obtained in good solvent.

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*Keywords:* Solvothermal preparation; ABS; Grafting copolymerization

## 1. Introduction

Grafting copolymers of maleic anhydride with synthetic and natural polymer have been widely studied in recent years. The introduction of polar constituents onto hydrophobic polymers is known to result in a considerable improvement in physical chemical properties. Several studies have appeared dealing with grafting vinyl monomers onto polymers such as styrene–butadiene block copolymers [1], styrene–isoprene copolymers [2], styrene–(ethylene-*co*-butadiene)–styrene tri-block copolymers [3], poly-*cis*-butadiene rubber (PcBR) [4], and acrylonitrile–butadiene–styrene (ABS) terpolymer [5,6], and many ways were developed to prepare grafting copolymer, such as high energy (gamma ray, electron beam) [7,8], plasma treatment [9], ultraviolet light (UV) [10,11], chemical initiators (including grafting polymerization in solution and in melt) [12–17] and oxidation of polymers. However, the most common method to prepare grafting copolymer is initiated by chemical initiators. Due to the special chain structure and physical properties, acrylonitrile–butadiene–styrene (ABS)

terpolymer was widely modified by grafting vinyl monomers [9,10,12–14], and we also have done some works on it [16,17]. However, the grafting degree (GD) obtained by the traditional methods is usually low, and how to get high grafting degree (GD) is pursue of many researchers.

In the past years, as one of the most effective methods, solvothermal method has been widely used to prepare inorganic materials, and many kinds of new materials have been prepared [18]. In this process, the solvents are sealed in vessel (bomb, autoclave, etc.), and can be brought to temperatures well above their boiling points by the increase of autogenous pressures resulting from heating. The critical point for water lies at 374 °C and 22.09 MPa. Exceeding this temperature and pressure, water is said to be supercritical. Supercritical fluids exhibit characteristics of both a liquid and a gas: the interfaces of solids and supercritical fluids lack surface tension, yet supercritical fluids exhibit high viscosities and easily dissolve chemical compounds that would otherwise exhibit very low solubility under ambient conditions. Some solvothermal processes indeed involve supercritical solvents. Most, however, simply take advantage of the increased solubility and reactivity of metal salts and complexes at elevated temperatures and pressures without bringing the solvent to its critical point. In any event, solvothermal process allows many materials to be prepared at temperatures substantially below those required by traditional solid-state reactions [19].

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Due to the increased solubility and reactivity of compounds and complexes at elevated temperatures and pressures, the solvothermal method has been widely used to prepare inorganic nanomaterials [20] and polymer-inorganic nanocomposites [21,22]. In this paper, the solvothermal method was first successfully used to prepare the ABS-g-MAH copolymers, and the effects of reacting time, temperature, MAH concentration, the initiator's content, ABS concentration, comonomer and different solvents were also studied. Different from the traditional solution grafting method, the grafting copolymerization can be carried in both good solvents and poor solvents, and high grafting degree can be obtained in good solvent. Furthermore, the solvents and monomers are sealed in autoclave, and it can also avoid the evaporation of solvents and monomers, which is favorable for the environment and high grafting yield.

## 2. Experimental

### 2.1. Materials

ABS was purchased from Taiwan Qimei Co., Ltd (Taiwan, China) (number-average molecular weight = 49,000, weight-average molecular weight = 134,000, the polydispersity index = 2.72; 2.7 wt% additives, 22.4 wt% acrylonitrile, 13.5 wt% butadiene, and 61.4 wt% styrene, as determined by elemental analysis and solvent separation). Benzoyl peroxide (BPO) (Shanghai Lingfeng Chemical Solvent Factory, Shanghai, China) was purified by dissolution in chloroform at room temperature and precipitation in cool methanol. MAH (Shanghai Chemical Solvent Factory) were used without further purification.

### 2.2. Synthesis of the grafted copolymers

The grafting reactions were performed in a sealed vessel with different solvents under various processing conditions (the detailed reactive conditions were showed in Figs. 4–10). In a typical process, an appropriate amount of ABS, MAH, initiator and 1,2-dichloroethane (as a solvent), were introduced into a sealed vessel simultaneously. Then the sealed vessel was put into constant temperature oven after purged by nitrogen. After the grafting reaction was taken at a certain time, the obtained products were taken away from the sealed vessel and precipitated in ethanol, and then the solid residue was washed several times with ethanol to remove any uncreative MAH. The purified polymer was collected and dried to a constant weight in a vacuum oven at 80 °C.

### 2.3. Characterization

The samples were cast into films (0.010–0.015 mm thickness) with chloroform as a solvent. IR spectroscopy information on ABS and grafted ABS was obtained on a Perkin Elmer Paragon 1000 Fourier transform infrared (FT-

IR) spectrophotometer (USA). No significant changes were observed in the FT-IR spectrum of the grafted ABS after further purification, and this indicated that the procedure was effective.

<sup>1</sup>H NMR spectra were recorded on a Varian Mercury Plus-400 MHz spectrometer at 400 MHz, CDCl<sub>3</sub> was used as solvent and tetramethylsilane (TMS) as internal standard.

### 2.4. Determination of the GD of MAH

The grafting degree (GD) of grafted copolymer (wt%) was estimated from the following equation: GD = weight of MAH in ABS-g-MAH/weight of ABS-g-MAH × 100%. The GD of MAH was calculated from FT-IR spectrum. Fig. 1 shows the FT-IR spectra of pure ABS (ABS) and modified ABS (ABS-g-MAH). Peaks located at 1780 and 2237 cm<sup>-1</sup> are assigned to units of carbonyl (C=O) and acrylonitrile (AN) in grafted copolymer respectively [23,24]. The intensity ratios (C1) of the absorbance peak of C=O at 1780 cm<sup>-1</sup> and a reference peak of AN at 2237 cm<sup>-1</sup>, were calculated. Calibration curve for FT-IR analysis (Fig. 2) was established using a series of quantitatively prepared mixtures of ABS and MAH in various compositions. Good correlation ( $R=2.764$ ) among the data was achieved and the linear relationship was used as the calibration curve. GD can be calculated as

$$GD(\text{wt}\%) = 2.764 C1_{\text{Samples}}$$

where  $C1_{\text{Samples}}$  is the C1 of ABS-g-MAH samples.

## 3. Results and discussion

### 3.1. Characterization of grafting

The reaction was carried out by solvothermal process at 120 °C, which is a well-above the boiling point of

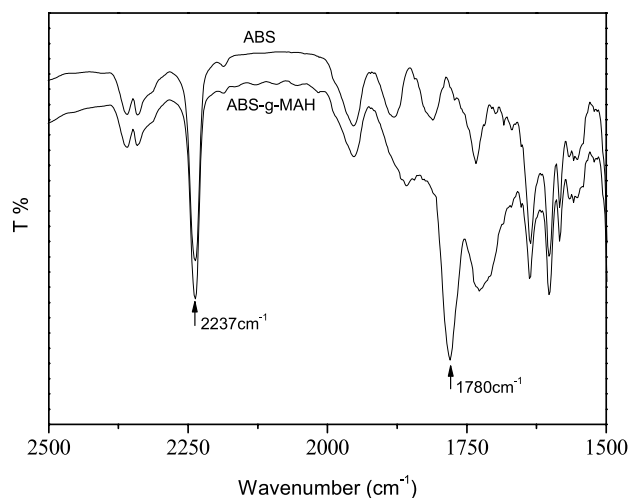


Fig. 1. FT-IR spectra of ABS and ABS-g-MAH.

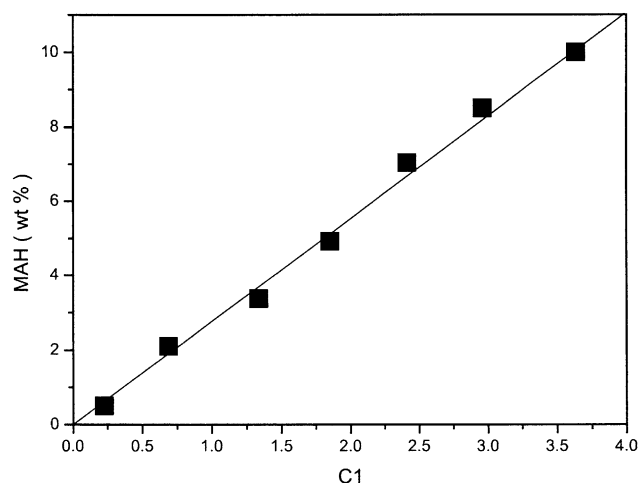


Fig. 2. Calibration curve for FT-IR analysis.

1,2-dichloroethane (bp 83 °C), so the autogenous pressure in autoclave far exceeds the ambient pressure. Furthermore, the high temperature and the autogenous pressures result from heating increased solubility and reactivity of MAH and ABS, and that is favorable to the grafting reaction at low temperature than in the ambient pressure. Otherwise, the reaction is confined in the sealed autoclave, and it can also avoid the evaporation of MAH and solvent, and more favorable to the reaction. The new absorbance peak at  $1780\text{ cm}^{-1}$  (C=O stretching from anhydride) in FT-IR spectrum (Fig. 1) indicated that MAH has been grafted onto ABS, which also mean that the solvothermal process was an effective method to the grafting copolymerization of MAH onto ABS.

In order to further confirm that MAH was grafted on the backbones of ABS, the  $^1\text{H}$  NMR spectra of pure ABS and ABS-g-MAH are shown in Fig. 3. Compared the  $^1\text{H}$  NMR spectra of pure ABS and ABS-g-MAH, a new peak at 3.736 ppm, which could be assigned to the hydrogen proton on the anhydride ring [2], was observed in ABS-g-MAH besides the expected signals for the block copolymer. From the results of FT-IR and  $^1\text{H}$  NMR spectra, we can conclude that MAH was successfully grafted on the backbones of ABS.

### 3.2. Effect of initiator concentration

The effect of initiator concentrations on the GD of MAH was investigated through IR absorbance ratio. Fig. 4 gives the GD of MAH as a function of the initiator concentration. As can be seen, the GD is about 1.7 wt% when the amount of BPO is 0.1 g/100 ml and the GD is up to 5 wt% when the amount of BPO is 0.5 g/100 ml. Compared with the GD of ABS-g-MAH obtained through melt process or normal solution method [12,16,23], the GD is much higher. It is meaning that the grafting reaction was easy to carry out in the solvothermal conditions. In addition, we can also found that the GD of the ABS-g-MAH copolymer increased with

the increasing of the initiator concentration, which might be because the number of free radicals, formed by the decomposition of the initiator, increased along with increasing of the initiator concentration, and further increased the grafting yield.

### 3.3. Effect of MAH concentration

Fig. 5 shows that the GD initially increased with the increasing of MAH concentration, and reached a maximum at 2 g/100 ml, and then decreased with the further increasing of the MAH concentration. This is because the extent of grafting is governed by the monomer number diffusing throughout the reaction medium and reaching the polymer backbone, and monomer acted as a trap for radicals, otherwise it would have undergone chain scission or cross-linking. But a higher monomer concentration could result in the homopolymerization of MAH and lead to the low GD.

### 3.4. Effect of ABS concentration

The effect of ABS concentration on the grafting polymerization is shown in Fig. 6. From which we can see that the highest grafting degree was up to 4.18 wt% when ABS is 12 g/100 ml. It is well known that the grafting polymerization was depended on the number of active sites available, and the grafting degree increased with the increasing of the grafting site as a double bond in ABS, so the GD increased with the increasing of ABS concentration and up to the highest grafting degree when ABS is 12 g/100 ml. However, if ABS concentration was much higher, the viscosity of reaction medium was remarkably increased, and the diffusion and mobility of MAH and BPO onto ABS backbone became difficult, and further leading to the decreasing of grafting degree.

### 3.5. Effect of reaction time

The grafting reaction time also has great effects on the grafting degree of MAH, and different reaction time in range of 1–10 h was investigated. Fig. 7 shows the relationship between the reaction time and the grafting degree of MAH. It can be seen that GD is very low and slightly increased with the prolong of reaction time when the reaction time is less than 3 h, then the grafting degree rapidly increased with an increasing reaction time up to 4 h and thereafter slightly decreased. This could be explained that the grafting reaction is carried out in a sealed vessel, and the reaction solution contained solid polymer is cold in the beginning of the reaction, and a period time is necessarily needed for the dissolution of polymer and for the reaction system up to the reaction temperature, so the grafting copolymerization was difficult to happen, and only low GD was obtained. When the reaction time is up to 4 h, the optimal reaction conditions for the grafting reaction were obtained, and as a

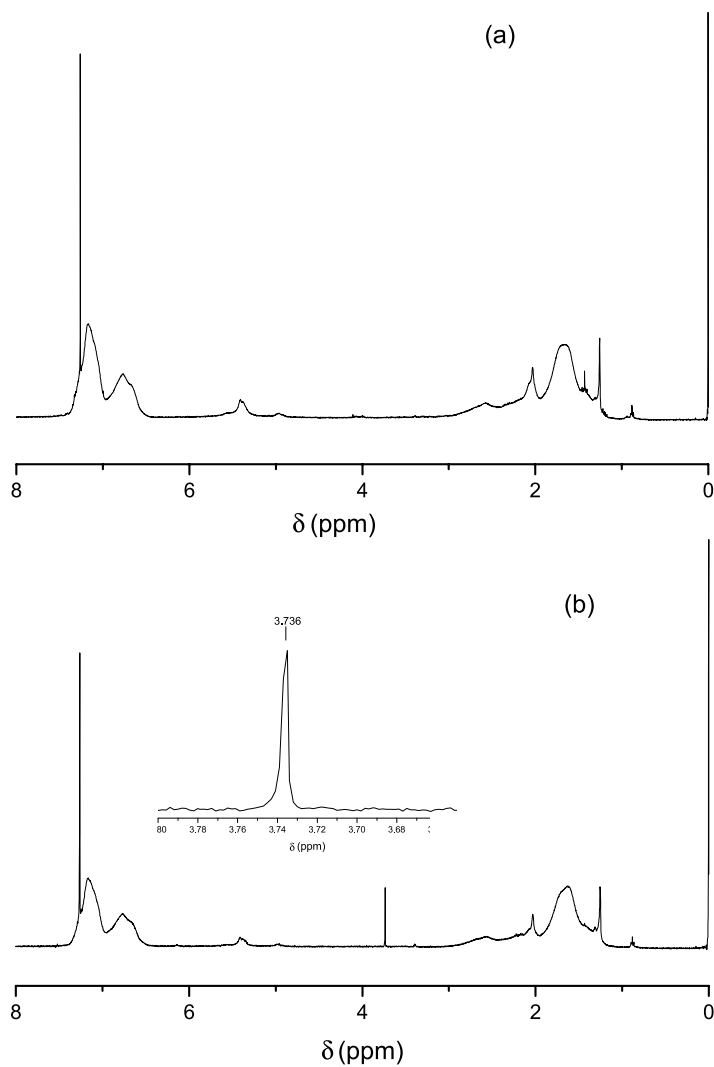


Fig. 3. <sup>1</sup>H NMR spectra of pure ABS (a) and ABS-g-MAH (b).

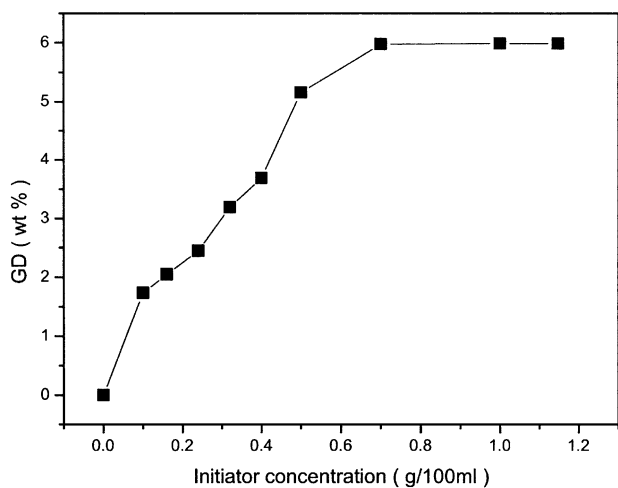


Fig. 4. Effect of the initiator concentration on the GD. Amount of ABS = 5 g; amount of MAH = 0.4 g; amount of 1,2-dichloroethane = 50 ml; the reactive temperature = 120 °C; the reactive time = 5 h.

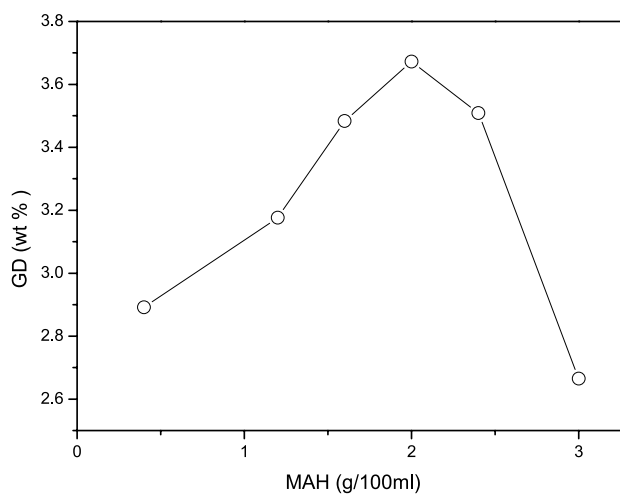


Fig. 5. Effect of the monomer concentration on the GD. Amount of ABS = 5 g; amount of 1,2-dichloroethane = 50 ml; BPO = 0.1 g; the reactive temperature = 120 °C; the reactive time = 5 h.

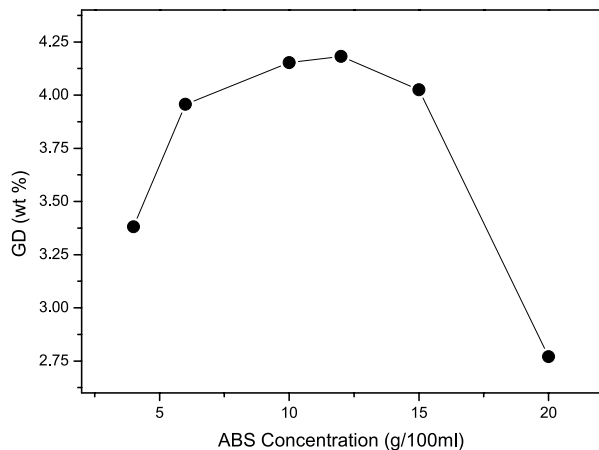


Fig. 6. Effect of ABS concentrations on the grafting polymerization. Polymerization time: 5 h; polymerization temperature: 120 °C; BPO: 0.2 g; MAH: 1 g; 1,2-dichloroethane: 50 ml.

result the GD was greatly increased and highest GD was obtained. While the further prolong of the reaction time has not any useful for increasing the GD because of the radical reaction [25,26].

### 3.6. Effect of reaction temperature

The grafting copolymerization was carried out at different temperatures ranging from 100 to 200 °C. Fig. 8 shows the effect of temperature on the GD. It was found that the GD increased with the increasing of temperature for whole range of temperatures used. This is because the number of radicals, their mobility and the sealed vessel's pressure increased and the solution viscosity decreased with the increasing of the temperatures, which was favorable for the grafting copolymerization and resulted in the increasing of the GD.

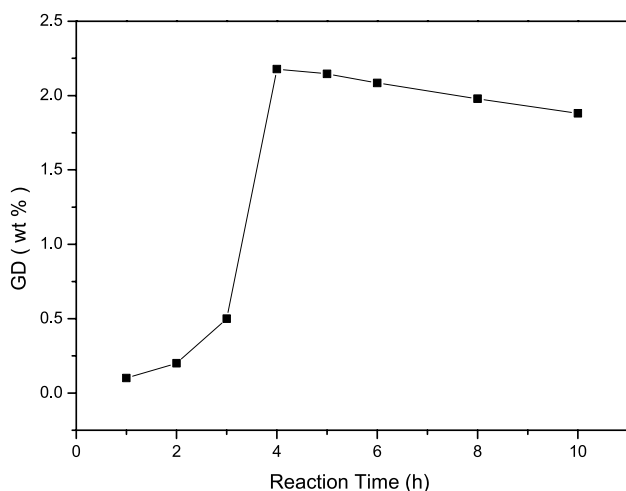


Fig. 7. Effect of reaction time on the grafting degree. ABS: 5 g; MAH: 0.4 g; BPO: 0.1 g; solvent: 50 ml of 1,2-dichloroethane; reaction temperature: 120 °C.

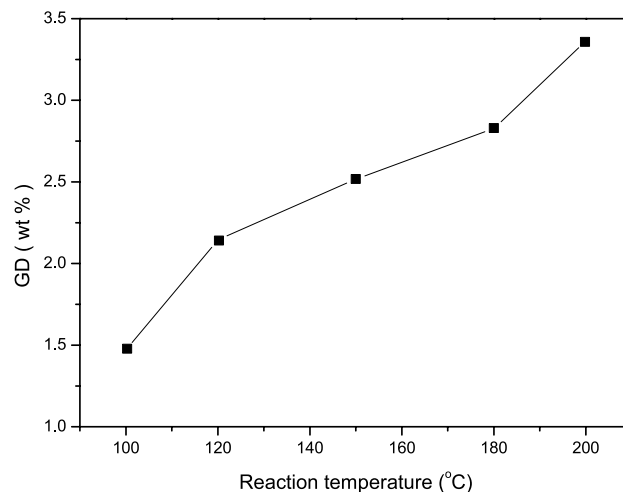


Fig. 8. Effect of the reaction temperature on the GD. Amount of ABS=5 g; amount of MAH=0.4 g; amount of BPO=0.1 g; amount of 1,2-dichloroethane=50 ml; the reaction time=5 h.

### 3.7. Effect of the comonomer

To minimize side reactions, it is important to trap radicals on the ABS backbone as rapidly as possible. Some monomers are more effective in trapping such radicals because of their relatively high solubility in the ABS melt or the inherent reactivity of the monomers.

Some studies on enhancing grafting efficiency have involved the use of mixed monomer systems; in particular, the synergistic effects of comonomers may lead to more efficient grafting processes. This strategy involves choosing a monomer combination in which the comonomer is effective in trapping the radicals formed on the ABS backbone and the resultant propagating radicals are highly reactive toward the desired sites [27]. As a comonomer, styrene can effectively improve the grafting reaction of MAH with ABS [16]. Fig. 9 gives the influences of binary system of styrene and MAH with various compositions on the grafting of MAH onto ABS. The GD initially increased with the increasing of styrene content, and reached a maximum (GD=7.9 wt%) at a comonomer composition of 0.42 (styrene/MAH molar ratio). Then, it decreased with further increasing of styrene content. This result showed that a synergistic effect on the grafting process of a styrene and MAH binary mixtures onto ABS occurred, and the styrene content in the binary monomer mixtures had a considerable influence on the GD in the grafting process.

### 3.8. Effect of solvent

The grafting polymerization was carried out in a solution; therefore, how to select optimal solvent is very important for this grafting polymerization. In order to study the influence of solvent on the grafting polymerization, good solvent like 1,2-dichloroethane and poor solvents like ethanol and acetone for ABS were chosen. The results show

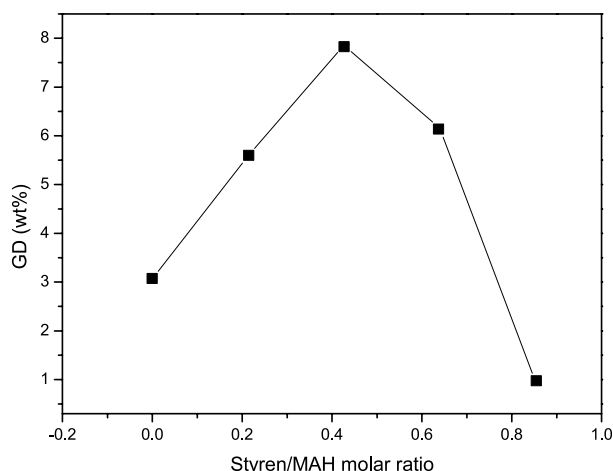


Fig. 9. Effect of the styrene/MAH comonomer composition on the GD onto ABS. ABS: 5 g; BPO: 0.1 g; solvent: 50 ml of 1,2-dichloroethane; reaction temperature: 120 °C; the amount of MAH is 0.6 g.

that the grafting polymerization can proceed in the all solvents and the grafting degree was highest (about 8.4 wt%) with 1,2-dichloroethane as a solvent (Fig. 10) because 1,2-dichloroethane is a kind of good solvent for ABS, while ethanol and acetone are not. Though the GD obtained in the poor solvents like ethanol and acetone is low than that of in 1,2-dichloroethane, the grafting polymerization still happened, while it is difficult to happen in the poor solvent in atmospheric pressure according to the traditional solution method. This is because the elevated temperatures and autogenous pressures resulting from heating in sealed autoclave are favorable to increase the solubility and reactivity of polymers, so the grafting polymerization still happened when poor solvents were used.

#### 4. Conclusions

The ABS-g-MAH copolymer was successfully synthesized by solvothermal method, and high grafting degree is obtained. The effects of various reaction conditions on the

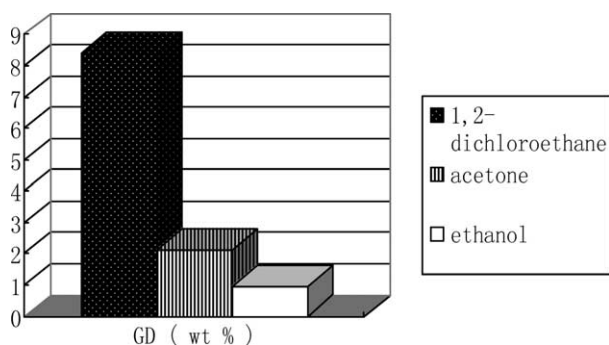


Fig. 10. Effect of solvents on the grafting polymerization. ABS: 5 g; MAH: 0.6 g; styrene: 0.27 g; BPO: 0.2 g; solvent: 50 ml; reaction temperature: 150 °C; reaction time: 5 h.

grafting degree were also investigated. The important results are summarized as follows:

1. In the grafting polymerization of MAH onto ABS, the grafting degree increased with the increasing of initiator content and reaction time, and reached to a maximum, and then leveled off.
2. The grafting degree was initially increased with the increasing of MAH content, ABS concentration and styrene/MAH molar ratio, and reached to a maximum, and then decreased with a further increasing of MAH content.
3. The grafting degree increased with the increasing of reaction temperature.
4. The grafting copolymerization can proceed not only in good solvent but also in poor solvents, which is much different from the traditional solution grafting copolymerization due to the special characteristic of solvothermal method.

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