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Graft Copolymerization Of Methyl Acrylate Onto PET Initiated By Potassium Diperiodatonickelate (IV)

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ABSTRACT

A novel system, potassium diperiodatonickelate(IV) (DPN)–poly (ethylene terephthalate) (PET), was employed to initiate the graft copolymerization of methyl acrylate (MA) onto PET in alkali medium. The effects of reaction conditions, such as initiator concentration, ratio of MA to PET, temperature and time, were investigated. Graft copolymers with high grafting parameters were obtained (E%>80%), indicating that DPN-PET system is an efficient initiator for the graft copolymerization. The structures and the thermal stability of PET and PET–g–PMA were characterized by scanning electron microscope (SEM), infrared spectroscopy (IR) and thermogravimetric analysis (TGA). A mechanism is proposed to explain the generation of radicals and the initiation of graft copolymerzation. The SEM photographs show that the graft copolymer greatly improved the compatibility of the PET /PMMA blends. The moisture regain (MR) of PET–g–PMA is found to increase compare with PET.

KEYWORDS

Potassium diperiodatonickelate (IV);
Transfer initiated;
Poly (ethylene terephthalate);
Methyl methacrylate;
Graft copolymerization

INTRODUCTION

There is a widespread use of synthetic fibers in the textile industry today. PET have a prominent place among these synthetic fibers. However, in spite of many superior properties of PET fibers, some of their poor features such as low MR, difficulty of dyeing, and poor antistatic properties limit their usage. One of the most common ways reported to, to give new properties or improve poor features of PET, is grafting various monomers onto them by graft copolymerization. It is generally thought that, as a result of graft copolymerization, the properties of PET backbone are not affected and the fibers acquire new properties, depending upon the monomer grafted. The graft copolymerization can be chemically initiated using initiators such as benzoyl peroxide[1-2], hydrogen peroxide[3] and ceric ion[4-6]. In addition, supernormal valence transition-metals have received considerable attention and the feasibility of their applications to radical polymerization appeals to more and more attention of researchers. Noticeably, some achievements on the polymerization and graft copolymerization of vinyl monomer initiated by supernormal valence transition-metals have obtained by our group since 1990s[7-10].

In this paper, DPN-PET system was used to initiate the grafting copolymerization of MA onto PET backbone. The effects of reaction conditions, such as the initiator concentration, the ratio of MA to PET, temperature and time, were investigated, and the grafting conditions were optimized. At the same time, the structures and properties of PET and PET-g-PMA were characterized by SEM, IR and TGA. The SEM photographs show that the graft copolymer greatly improved the compatibility of the PET /PMMA blends. The moisture regain (MR) of PET–g–PMA is found to increase compare with PET.

EXPERIMENTAL

Materials

PET was washed with acetone to remove any adhering impurity before use, then dried under vacuum at 60°C. MA, from Tianjin Huadong chemical reagent station, was washed successively with aqueous sodium hydroxide solution, distilled water, and then distilled under reduced pressure. DPN was synthesized and measured according to the reported procedure[9]. The other solvents were all of analytical reagent and used without any further purification.

Graft copolymerization and treatment of copolymer

Required amounts of PET, MA and water were added in the reaction tube. Eliminating oxygen was performed by injecting pure nitrogen into it and the reaction system was maintained at certain temperature in a thermostatic reservoir. Then appropriate amounts of DPN were added under a stream of dry N_2 gas. After a given time, the reaction was terminated by adding hydrochloric acid. The formed polymer was filtered, washed well with water and then dried under vacuum at 60°C to constant weight. The homopolymer of MA (PMA) was removed from the crude graft copolymer by Soxhlet extraction with acetone for 48 hours. The titled copolymer was then obtained after drying to a constant weight under vacuum at 60°C.

Definition of the grafting parameters

The grafting parameters were defined and calculated in the following manner:

C% = (total weight of PMA/ weight of MA charged) × 100%
E%= (weight of PMA grafted/ total weight of PMA) ×100%
P %= (weight of PMA grafted/ weight of PET) ×100%

Measurements

AMKAY-1000B was used to observe the morphologies of PET and PET–g–PMA. The FTIR spectra of PET and PET-g-PMA were recorded on an FTS–40 spectrometer (BIO RAD Co. U.S.A.) using potassium bromide pellets technique. TGA curves of PET and PET–g–PMA were carried out on a Shimadzu apparatus (DGC-40 DTA-TG) at a heating rate of 10°C /min in a static air atmosphere.

RESULTS AND DISCUSSION

Effect of different factors on grafting parameters

1. MA-to-PET Ratio

The effect of MA-to-PET (weight) ratio on graft copolymerization is depicted in figure 1. It is observed from this figure that the grafting parameters increase initially with the increasing MA-to-PET ratio, this may be ascribed to the surface-activity and self-emulsifying properties of PET and MA-to-PET, which assists in the proximity of monomer to the growing chains and active sites on the PET. However, beyond MA/PET (weight) =6.37, grafting parameters decline. This may be explained as follows: with the total volume fixed, an increase in ratio MA-to-PET means the higher DPN concentration in the water

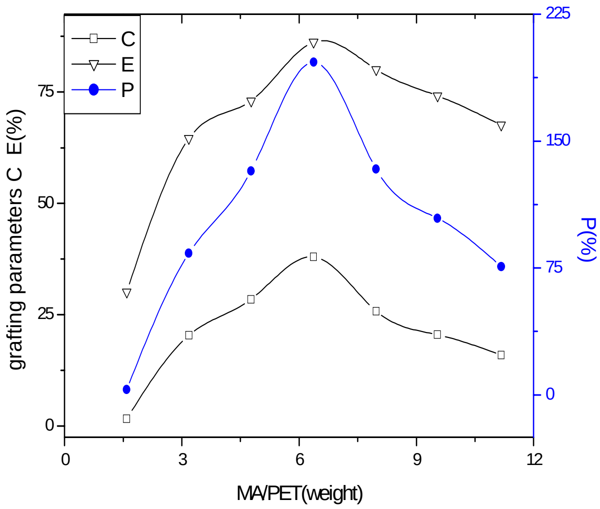


Figure 1: Effect of MA/PET on grafting parameters. T=35 °C, [DPN] =3.48×10-3, t= 1h

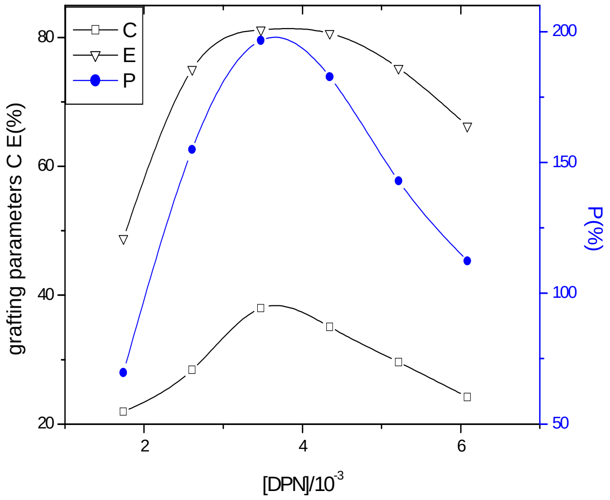


Figure 2 Effect of [DPN] on grafting parameters T=35 °C, MA/PET =6.37, t= 1h

phase, thus the chain transfer reaction of radicals to MA is accelerated. Moreover, when the MA-to-PET ratio is higher, the obvious adsorption of monomers onto PET largely impeding the approach of between DPN and PET, which is necessary for initiation. Therefore, homopolymerization rate enhances and E% declines correspondingly.

2. DPN Concentration

As shown in figure 2, when the total volume, the ratio of MA/ PET as well as reaction temperature and time are kept invariably, by changing the DPN concentrations, C%, E% and P% increase significantly first, reach a maximum value, and then decrease. The initial increasing trend may be due to the fact that in this concentration range, DPN attacks grafting sites of PET backbone directly, and creates a great deal of macroradicals which will initiate the grafting in the presence of MA, leading to the increase of graft parameters. However, a further increase of the DPN concentration accelerates the reaction of DPN and radical, which terminates the chain propagation reaction, hence decreasing C% and P%. Meanwhile, at higher DPN concentration, the chance of chain transfer to monomer is enhanced, resulting in the decline of E%.

3. Temperature

Keeping the other variables constant, the grafting reactions are carried out at different temperatures between 25°C and 50°C. In figure 3, grafting parameters increase in the beginning up to 35°C and then decrease to some extent with further increasing of temperature. The improvement in grafting parameters can explained by the higher decomposing rate of initiator, producing more PET macroradicals (which attracts more DPN) as well as the quickened diffusion and mobility of the MA from the aqueous phase to the backbone with the increase of temperature. The decline of grafting parameters at high temperature can be ascribed to both the enhanced radical termination reaction through oxidation by DPN and the increased chance of chain transfer reaction.

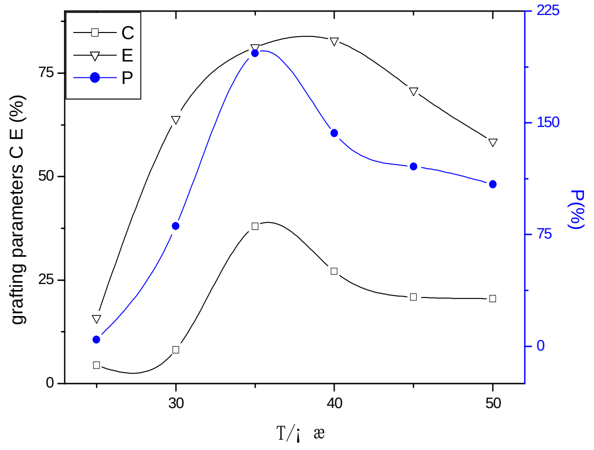


Figure 3: Effect of temperature on grafting parameters. [DPN]=3.48×10-3, MA/PET =6.37, t=1h

4. Time

As shown in figure 4, it can be seen that E% keep unchanged in a range of 0.5h to 3.5h, however, both C% and P% increase steadily with the reaction time prolonged up to 2h, and then maintain a plateau, which is in consistent with the general rule of radical polymerization initiated by supernormal valence transition- metals.

Characterization of graft copolymer

1. Scanning electron microscopy

The SEM of PET(a), PET-g-PMA(b), PET/PMMA(c) and PET/PET-g-PMA/PMMA(d) are shown in figure 5. It was found that the PET(a) shape

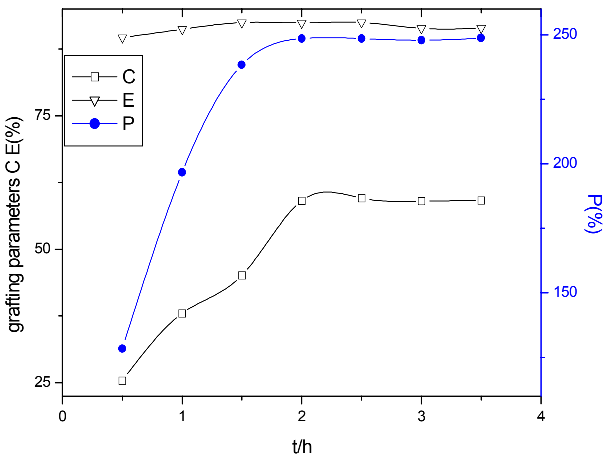
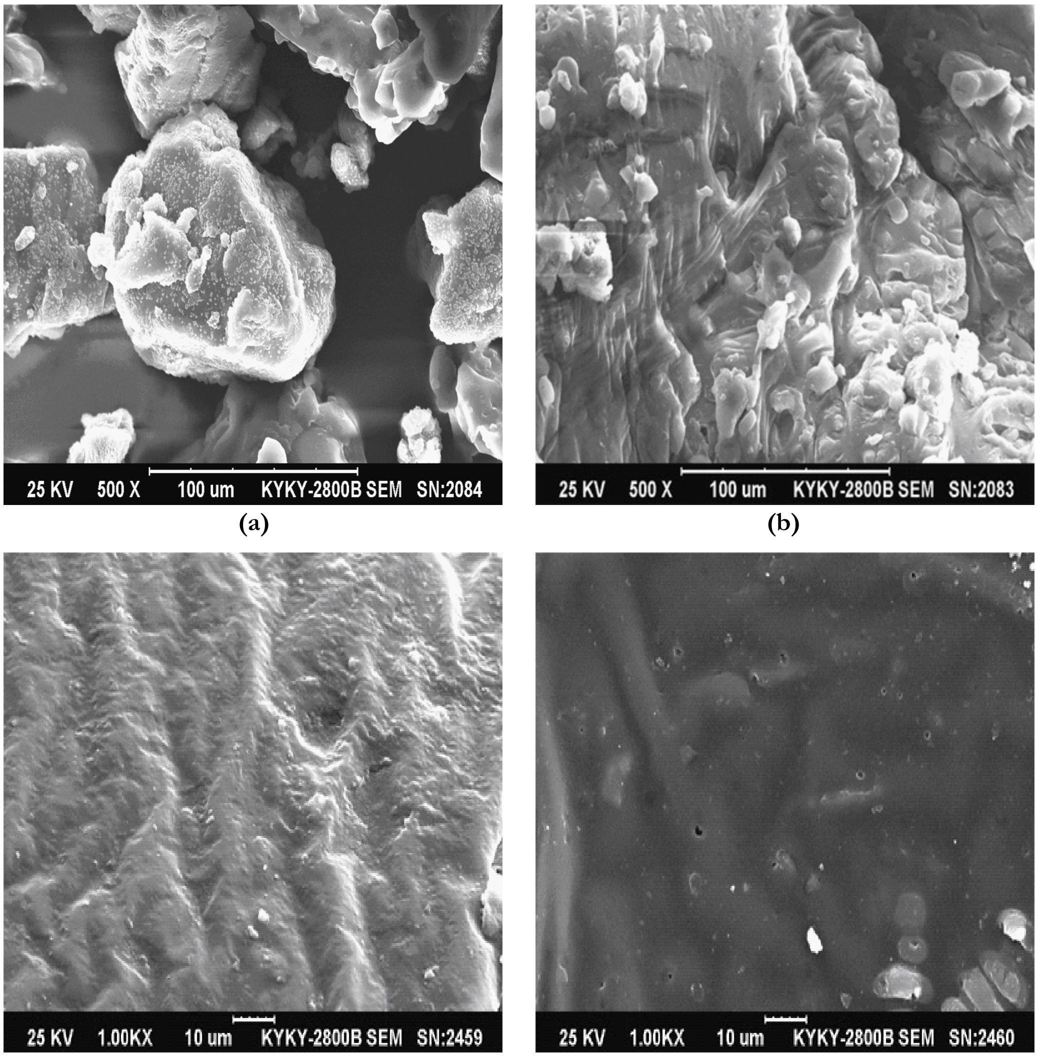


Figure 4: Effect of time on grafting parameters [DPN]=3.48×10^{-3}, MA/PET =6.37, T=35 °C



(a) (b)

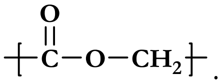
(c) (d)

Figure 5: (a) SEM of PET (b) PET-g-PMA (c) PET/PMMA and (d) PET /PET-g-PMA/PMMA blends

is grain, whereas the PET-g-PMA almost turns into an entirety, which may be due to the incorporation of PMA with the PET backbone , this not doubt that the graft reaction brings these alterations . The surface of PET/PET-g-PMA/PMMA(d) is smoother than PET/PMA(c)'s. This indicates that the graft copolymer greatly improved the compatibility of the PET/PMMA blends.

2. IR spectroscopy

In the FTIR spectra of PET-g-PMA (Figure 6), some characteristic absorptions such as 1734cm^{-1}, 1164 cm^{-1} and 826 cm^{-1} assigned to PMA and 1600 cm^{-1}, 1500 cm^{-1} for PET, respectively, have been recorded, indicating the successful grafting of MA onto PET. Additionally, the absorption intensity of phenyl moiety in the IR measurement of PET-g-PMA becomes weaken, implying another evidence that PMA has been grafted onto PET under the above-mentioned reaction condition. Furthermore, the character absorption of –CH$_2$ at 2960cm^{-1} for PET-g-PMA become weaken, which illuminates that the grafting reaction maybe occurred at the segment of



$\left[\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2\right]$.

3. Thermogravimetric analysis

The thermograms from TGA are shown in figure 7. In the TG curve of PET-g-PMA, an inflextion

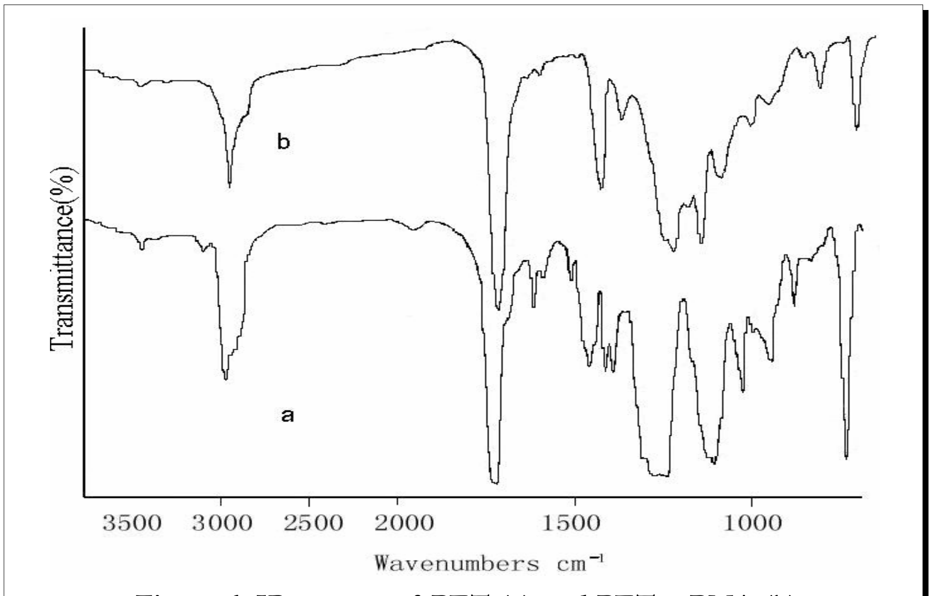


Figure 6: IR spectra of PET (a) and PET-g-PMA (b)

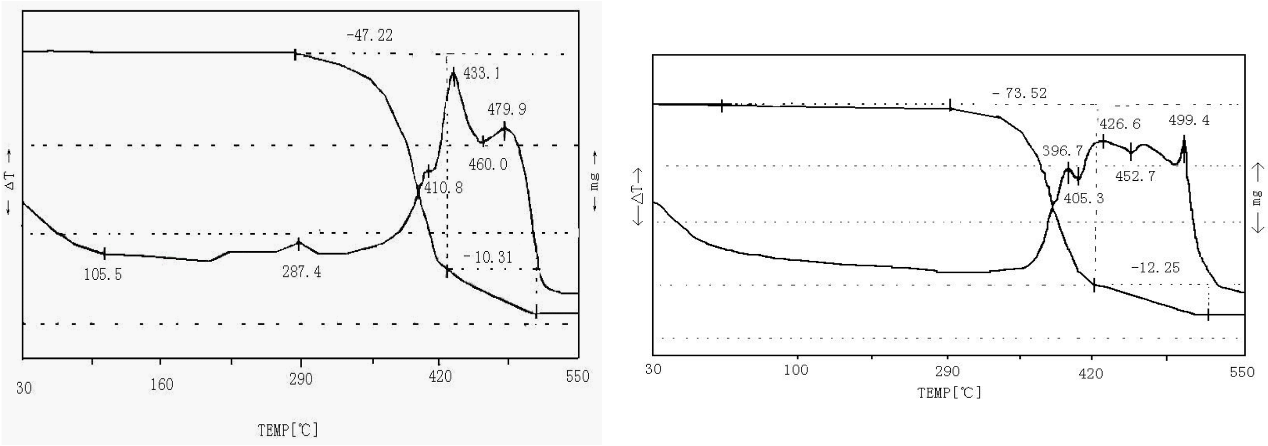


Figure7: Thermal analysis for PET (a) and PET-g-PMA (b)

due to absorbed moisture lies between 45 °C -330 °C. No such inflextions are observed in the TG curve of PET. This reveals that graft copolymer can increase the moisture absorption. Furthermore, PET-PMA has an additional decompose peak at 433.1 °C, this may be that the grafted PMA destroy the structure of PET in some degree.

4. Determination of moisture regain

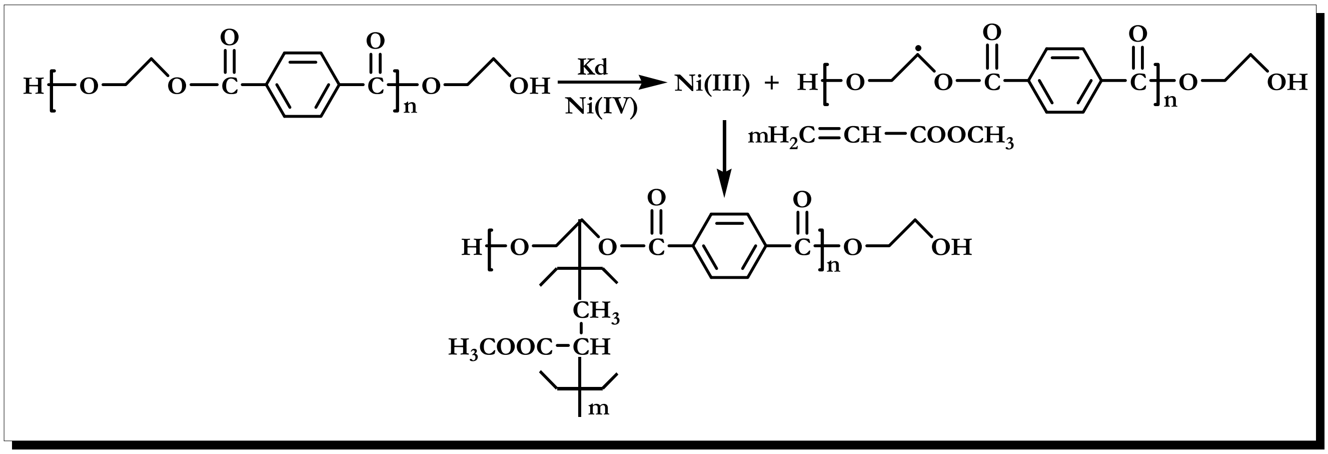
In the MR measurement, PET and PET-g-PMA were immerged in 36% H_2SO_4 solution and followed by placing them into desiccator for 48h and then drying to a constant weight under 110 °C. The MR was defined and calculated as follow:

MR = the added weight after moisture absorption / the weight of PET before moisture absorption

The percentage of MR for PET-g-PMA is found to increase with the increasing of E%, the moisture content of the PET, however, is very low under normal conditions of temperature and humidity because of its high hydrophobicity. Grafting with MA not only brings about the opening of the structure to a certain extent but also increases hydrophilicity of the fiber due to the introduction of the polar groups (an ester group) into the PET matrix. This obvious change in the hydrophobicity for PET can be attributed to the enhancement of the MR with increasing the percentage of E%.

The initiation mechanism of grafting reaction

An initiation mechanism of transfer graft based on IR spectra and literature[10] was proposed as follows:



CONCLUSIONS

In this study, graft copolymers with high graft parameters have been successfully synthesized, using DPN-PET system as an efficient initiator for graft copolymerization. The optimal conditions have been evaluated and listed as follows: temperature (35 °C), concentration of [DPN] (3.48×10^{-3}), weight ratio of MA/PET (6.37:1) and reaction time (2h). The structure of the titled copolymer has been testified by a series of charactering techniques including SEM, IR and TGA. Meanwhile, DPN–PET system is expected to be a considerable foreground in its practical application due to the facile preparation of DPN from $CuSO_4 \cdot 5H_2O$ and the mild reaction conditions for the graft polymerization. Further work is now in progress.

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