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

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ABSTRACT

The graft copolymerization of methyl acrylate onto hydroxymethylated carbon black (HCB) using potassium diperiodatonickelate (DPN) as initiator has been studied. The effects of different reaction variables on grafting parameters, such as the water-to-dioxane ratio, the reaction time and temperature, the ratio of monomer-to-carbon black, initiator concentration, are investigated, and the graft conditions were optimized. The maximum graft efficiency and percentage of graft are 47.7% and 128.2%. The DPN-HCB pair is confirmed to be an efficient redox system for the graft copolymerization. A single electron transfer mechanism was proposed to explain the formation of radicals and the initiation. The graft copolymer is characterized by scanning electron microscope (SEM), fourier transform infrared spectroscopy (FTIR) and ultraviolet visible spectrophotometer. Through the SEM and UV spectrophotometer it is testified that the grafted HCB is much better than the carbon black in dispersive and consistent ability. The grafted HCB was blended into polyvinyl chloride (PVC) to improve the impact strength of PVC.

KEYWORDS

Potassium diperiodatonickelate(IV);
Carbon black;
Methyl acrylate;
Graft polymerization;
Redox system.

INTRODUCTION

Carbon black(CB) has so excellent properties, such as chemical and heat resistance, electric conductivity, so it is widely used as pigment for rubber, plastic and coating in industry. However, for lots of oxygenic groups on its surface, CB is difficult to scatter but form aggregates easily. In order to improve its dispersibility and expand the application of CB, the surface modification by graft polymers has been widely investigated[1-6].

There are some methods for the graft modification of CB, such as grafting monomer directly onto CB surface, firstly introducing active sites onto the CB surface then initiating polymerization, and so on. In the methods, the second can get higher graft efficiency by using transition-metals ions as initiator. Although Ce(IV)[5] is more efficient than other initiators in these studies, the high price and acid medium make its application limited. In recent years, we have obtained some achievements on polymerization initiated by supernormal valence transition-metals, such as diperiodatocuprate(III)[7], ditellurato cuprate(III) [8-9], diperiodatoargentate(III)[10], ditellu ratoargentate(III) [11-12] and diperiodatonickelate(IV) [13-16] (DPN). It has been demonstrated that DPN is an efficient initiator. However the graft of methyl acrylate onto CB using DPN as initiator has not been reported so far.

In this paper the graft copolymerization of methyl acrylate onto hydroxymethylated carbon black (HCB) with DPN as an initiator has been successfully carried out. The effects of different reaction variables on graft parameters, such as the water-to-dioxane ratio, the reaction time and temperature, the ratio of monomer to carbon black, initiator concentration, are investigated, and the experimental conditions are optimized. According to the experimental result, the maximum graft efficiency and graft percentage are respectively 47.7% and 128.2% when the monomer-to-carbon black ratio is 5.58 at 45°C for 1 hour with [DPN] $=1.79 \times 10^{-2}$ mol/L and the total volume was 15 ml, which is higher than other methods in a shorter time. The DPN-HCB pair is confirmed to be an efficient redox system for the graft copolymerization. The grafted HCB is blended into polyvinyl chloride(PVC) to improve the impact strength of PVC. A single electron transfer mechanism is proposed to explain the formation of radicals and the initiation. The graft copolymer is characterized by scanning electron microscope (SEM), fourier transform infrared spectroscopy (FTIR) and ultraviolet visible spectrophotometer.

EXPERIMENTAL

Materials

The methyl acrylate, obtained from huadong reagent factory (Tianjin), is distilled under reduced pressure. The carbon black, from Tianjin jinqiu reagent factory, was used after being introduced of hydroxylmethyl groups onto the surface. The DPN was synthesized and measured according to the method of the literature[17-18]. The other reagents were analytical reagent and used without any further purification.

Graft copolymerization

The carbon black, methyl acrylate and aqueous, dioxane mix solution were added into a flask, with constant stirring under nitrogen for a few minutes. And then DPN was added in. After a period of time the reaction was terminated. The reaction mixture washed by water was filtered, dried to a constant weight under vacuum then was extracted by acetone in a soxhlet extractor for 48 hours to remove the homopolymer of methyl acrylate. The final graft copolymer was then dried to a constant weight again under vacuum at 50 °C.

The graft copolymerization was performed on the conditions of different water-to-dioxane ratio, reaction time and temperature, ratio of monomer-to-carbon black, initiator concentration.

Measurements

The FTIR spectra of the CB and HCB-g-PMA were recorded on an FTS-40 spectrometer (BIO RAD Co. U.S.A.) using potassium bromide pellets technique. Transmission electron microscope (JEM-100CXII) and scanning electron microscope (AMKAY-1000B) were used to observe the morphologies of CB and HCB-g-PMA. The mechanical properties of the blends were measured using XCJ-40 notch impact strength tester at 25 °C. The Vicat softening point was measured using Vicat softening point tester at a heating rate of 2°C/min. The dispersivity of the HCB-g-PMA and the pure CB in water was testified by Ultraviolet Visible spectrophotometer WFZ 800-D3A (Ruili Analytic Apparatus Co., Beijing) at 430nm.

RESULTS AND DISCUSSION

The graft parameters, such as graft efficiency (GE), percentage of graft (PG) and total conversion percentage (TC); the index of dispersive stability (D) are defined and calculated as follows:

GE% = (weight of PMMA grafted/ total weight of PMMA) × 100%

PG% = (weigh of PMMA grafted/ weight of carbon black) × 100%

TC % = (total weight of PMMA/ weight of MMA charged) × 100%

D% =(100-T)/100×100 %; T was the ratio of light transmission

Effect of the water-to-dioxane ratio

When the other reaction conditions are invariable, the graft parameters at various ratio of water-to-dioxane are shown in figure 1. It shows that PG%, TC% and GE% increase initially with increasing water-to-dioxane ratio, then decline after the point of ratio=1.5. The free radicals produced by DPN increase markedly because of the solubility of DPN in the mixed solution augments with increasing water-to-dioxane ratio. As a result the graft parameters increase gradually. But when the ratio is too high, the HCB aggregates easily in the mixed solution which reduces the probability of free radicals encountering the monomer, so the graft parameters declines.

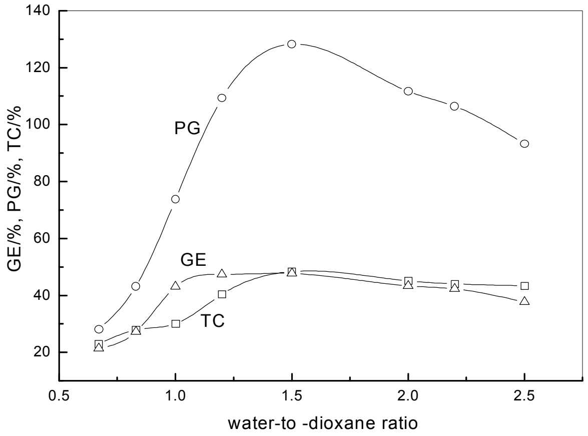


Figure 1: Effect of water-to-dioxane ratio on graft parameters: Time=60min, Temperature=45 °C, W(MA)/W(HCB)=5.58, [DPN]=1.79×10^{-2} mol/L

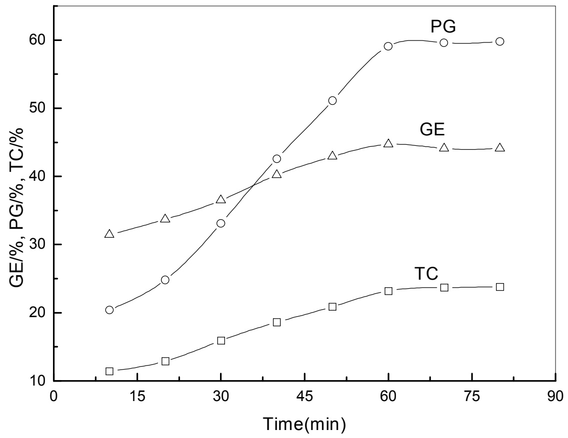


Figure 2: Effect of time on graft parameters: V(water)/V(dioxane) =1.5, Temperature=45 °C, W(MA)/W(HCB)=5.58, [DPN]=1.79×10^{-2}mol/L

Effect of time

Figure 2 illustrates the influence of reaction time on graft parameters when all the other variables are unchanged. TC%, PG% and GE% increase steadily with the reaction time prolongs. After 60 mins the tendency of increase turns into stabilization, for the chain propagation reaction is preponderant at the initial reaction stage, whereas the chain transfer reaction is dominant after 60 mins. In addition the reactants decrease gradually with the reaction time prolongs. So the increase trend of the TC%, PG% and GE% reaches a plateau after 60 mins.

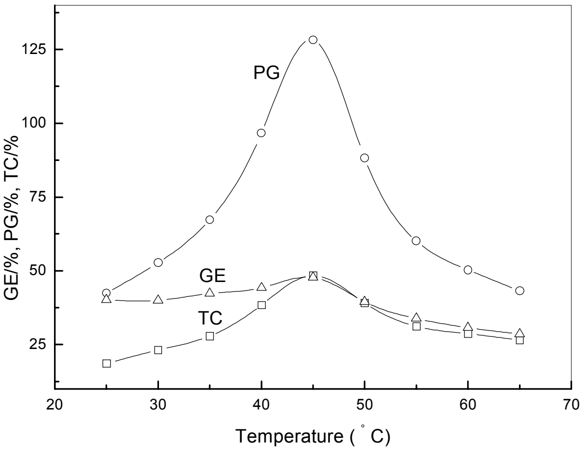


Figure 3: Effect of temperature on graft parameters: V(water)/V(dioxane) =1.5, Time=60min, W(MA)/W(HCB)=5.58, [DPN]=1.79×10^{-2}mol/L

Effect of temperature

The effects of the temperature on the graft parameters are shown in figure 3 when the other reaction conditions are invariable. The graft parameters show increase tendency at first, and reach the peak value at 45 °C, then decrease rapidly. It can be explained that lower temperature is of benefit to the chain initiation reaction and the chain propagation reaction. When it exceeds 45 °C the extortionate temperature make DPN oxidize radicals more easily to confine the chain propagation reaction and the chain termination reaction as well as the chain transfer reaction speeds up to be dominant?? resulting in the graft parameters decrease fleetly. The optimum temperature in this study is 45 °C.

Effect of monomer-to-HCB ratio

The effects of monomer-to-HCB(weight) ratio on graft parameters are depicted in figure 4. It shows that the graft parameters increase initially with the MA-to-HCB ratio increasing, then TC% and PG% decrease when the MA-to-HCB ratio beyond 5.58, while GE% changes little. The increasing ratio redounds to the encounter of the monomer with the free radicals as well as the possibility of graft polymerization resulting in the increase of the graft parameters. However, DPN not only reacts with reductant producing radicals to initiate graft polymerization but also reacts with radicals to terminate polymerization. In addition, the more increscent ratio is the more chance of chain transfer reaction happens. As a result TC% and PG % decrease continuously though the total weight of PMA is relatively increasing according to the MA charged. The higher MA-to-HCB ratio influences GE% little.

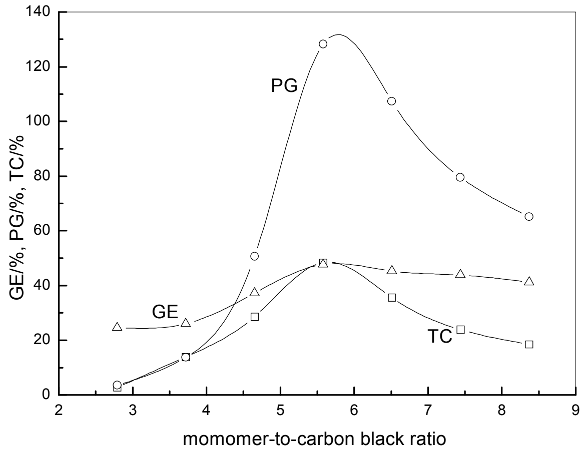


Figure 4: Effect of monomer-to-carbon black ratio on graft parameters: V(water)/V(dioxane) =1.5, Time=60min, Temperature=45°C, [DPN]= 1.79×10^{-2}mol/L

Effect of DPN concentration

The influence of DPN concentration on the graft parameters is shown in figure 5. The TC% and PG% both show the tendency of increase firstly with the accretion of DPN concentration, then decline rapidly after the peak value at the point of [DPN] =1.79×10^{-2} mol/L, while GE% changes little all the time. It is because DPN attacks on the characteristic group (–OH) of HCB backbone directly that free radicals are engendered with the increasing DPN concentration to initiate the polymerization of MA onto HCB more easily. As a result, the TC% and PG% augment initially. However, the excess of DPN will accelerate the reaction of DPN with radicals, the coupling chain termination reaction as well as the chain transfer reaction to monomer and radicals. Accordingly TC% and PG% decrease when DPN concentration is higher. The DPN concentration affects the GE% little.

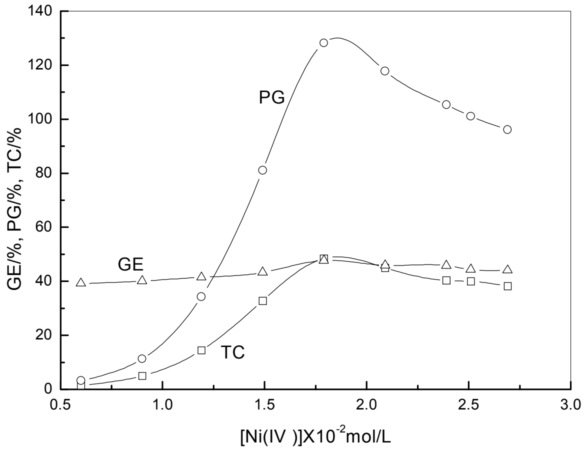


Figure 5: Effect of DPN concentration on graft parameters: V(water)/V(dioxane) =1.5, Time= 60 min, Temperature=45°C, W(MA)/W(HCB)=5.58

Test of the dispersivity of HCB-g-PMA and pure

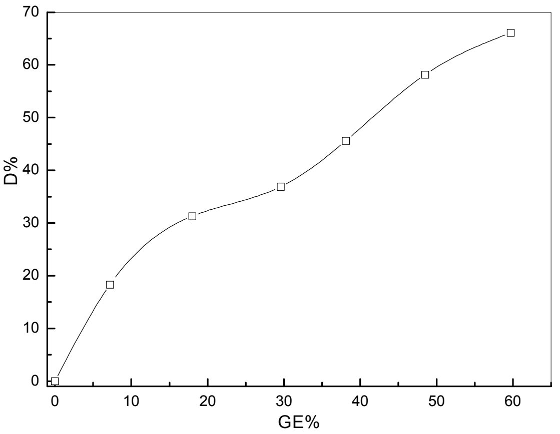


Figure 6: The dispersivity of the HCB-g-PMA and pure CB in water(25 °C)

CB in water

In this paper, the dispersivity of the HCB-g-PMA and pure CB in water is determined by the ultraviolet visible spectrophotometer at 430nm. The result is shown in figure 6, from which we can see that D% presents an obvious tendency of increase with the accretion of GE%. It is due to the hydrophilic ability of PMA which make HCB-g-PMA dispersed in water more eximious than pure CB. Accordingly we can draw a conclusion that the dispersivity of HCB-g-PMA is evidently improved comparing with the pure CB.

Impact strength of PVC, PVC-HCB, PVC-grafted HCB

As is shown in TABLE 1, the impact strength of PVC blended with pure CB decreases obviously. And the impact strength of PVC blended with HCB-g-PMA is improved markedly, showing itself with a trend of increasing initially and then falling-off. This may be due to the consistent ability of PMA with PVC. When being exposed to impulsive force, flaws come into being inside the blends to abate the impact energy, finally improving the impact strength of the materials. In addition, the best weight-ratio of HCB-g-PMA to PVC is obtained to be 0.16, when the impact strength reaches 6.31 KJ/m^2.

TABLE 1: Impact strength of PVC, PVC-HCB, PVC-grafted HCB(25 °C).

$W_{Pure\ CB}/W_{PVC}$	Impact strength (KJ/m^2)	$W_{Grafted\text{-}HCB}/W_{PVC}$ (PG%=15.2)	Impact strength (KJ/m^2)
0	4.20	0	4.20
0.08	4.10	0.08	5.21
0.12	4.00	0.12	6.20
0.16	3.80	0.16	6.31
0.2	3.70	0.2	6.10
0.22	3.57	0.22	5.87
0.25	3.48	0.25	5.78
0.27	3.41	0.27	5.70

Proof of graft copolymerization

FTIR spectroscopy

The proof of graft copolymerization is obtained from the Fourier transform infrared spectroscopy (FTIR) of HCB and HCB-g-PMA after exhaustive soxhlet extraction with acetone. As is shown in figure 7, the characteristic absorption band at 3400cm^{-1} is the hydroxyl absorption peak(-OH) of ungrafted HCB(A). In the spectrum of HCB-g-PMA(B), the absorption bands at 2952.45 cm^{-1} and 1439.76 cm^{-1} are due to C-H(atr) and C-H(def) of $-CH_2-$. And the absorption peak 1163.19 cm^{-1}, belongs to C-O(str). The sharp peak at 1734.55cm^{-1} corresponds to >C=O. The absorption bands at 3426.35cm^{-1} are the absorption peak of residuary ungrafted-OH. Basing on all the foresaid the presence of PMA segment in the graft copolymer is indicated adequately.

SEM

As is shown in figure 8, the ruptured surface of PVC(A), PVC/Ungrafted HCB(B) and PVC/HCB-g-PMA(C) are studied by SEM. It can be seen that the pure PVC presented a typical brittleness ruptured surface, while PVC/Ungrafted HCB indicates many grains. That may be due to the HCB congregating in PVC. The ruptured surface of PVC/ HCB-g-PMA presents a flexility rupture. The hazy boundary and much less grains proves that the PMA spread around well in the blends, and the dispersibility of CB is improved biggishly.

The initiation mechanism of graft reaction

The FTIR spectrum above has characterized the structure of graft copolymer, illustrated that MA has been successfully grafted onto the HCB surface, veri-

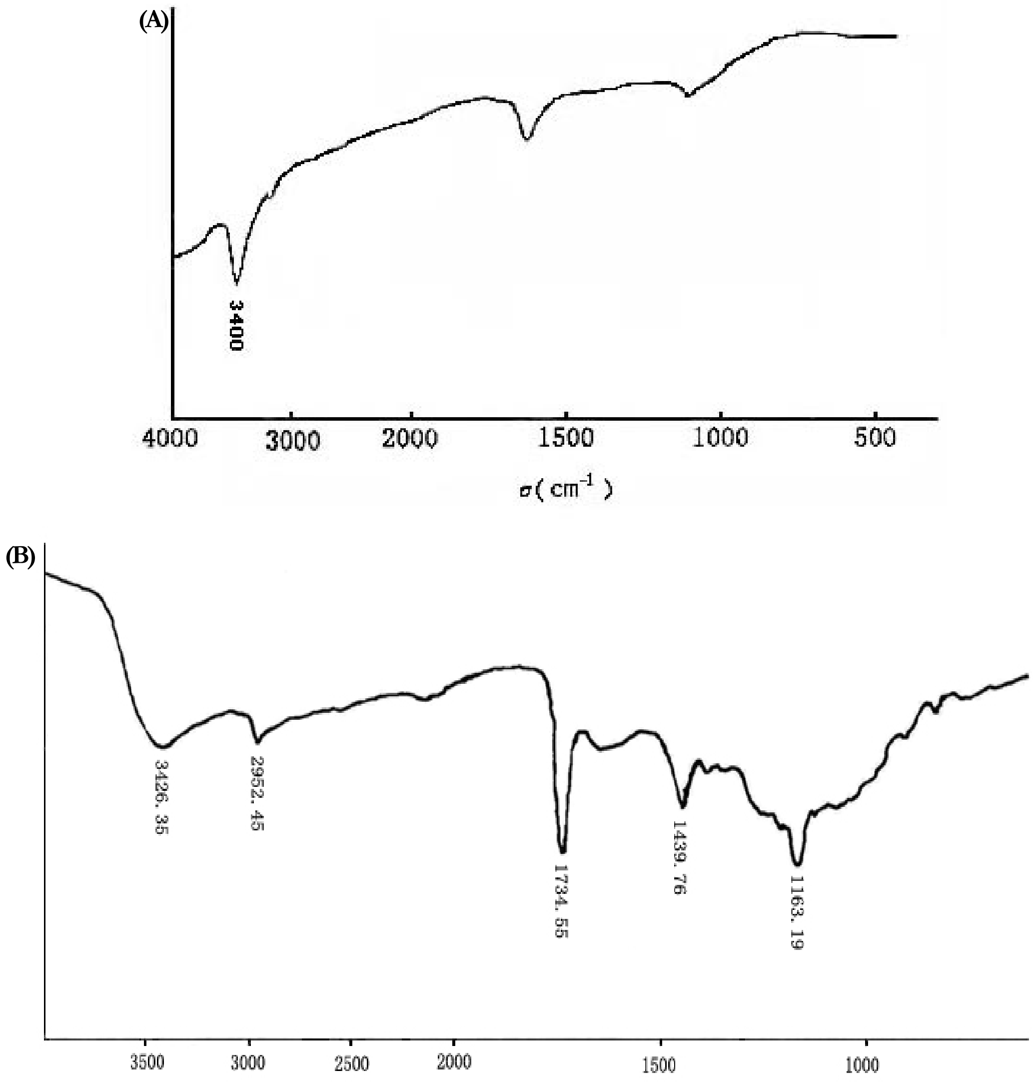
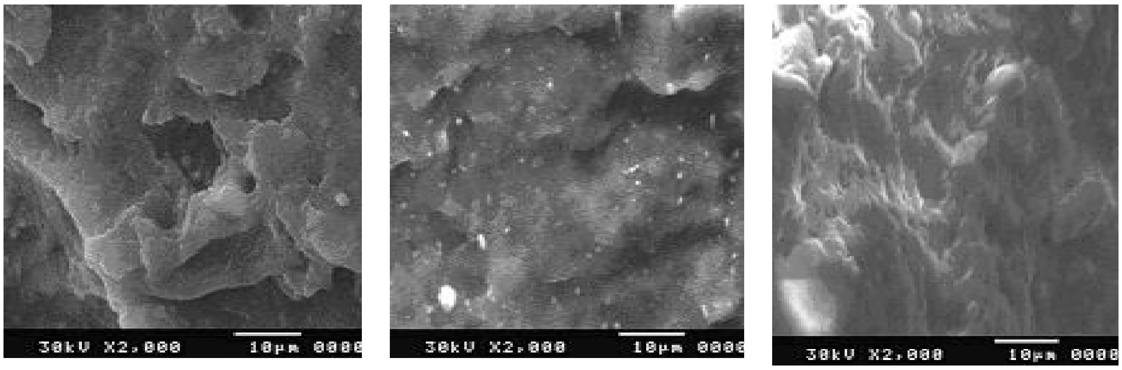


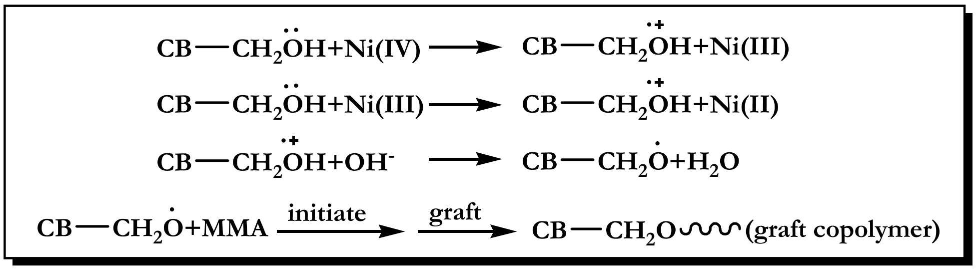
Figure 7: FTIR spectroscopy of ungrafted HCB(A) and HCB-g-PMA (B)



(A) (B) (C)

Figure 8: SEM of PVC(A), PVC/Ungrafted HCB(B) and PVC/HCB-g-PMA(C)

fying again that Ni(IV) can successfully initiate the graft copolymerization of vinyl monomers onto macromolecular. A possible two-step, single electron transfer mechanism[13-16] is proposed to explain the formation of radicals and the initiation as follows:



$$CB-CH_2\ddot{O}H+Ni(IV)\longrightarrow CB-CH_2\overset{\cdot+}{O}H+Ni(III)$$

$$CB-CH_2\ddot{O}H+Ni(III)\longrightarrow CB-CH_2\overset{\cdot+}{O}H+Ni(II)$$

$$CB-CH_2\overset{\cdot+}{O}H+OH^-\longrightarrow CB-CH_2\dot{O}+H_2O$$

$$CB-CH_2\dot{O}+MMA\xrightarrow{initiate}\xrightarrow{graft}CB-CH_2O\sim\sim(\text{graft copolymer})$$

CONCLUSION

In this paper, graft copolymerization of MA onto CB is carried out with results satisfying which is using DPN as an initiator in alkaline medium. The optimal reaction conditions are V(water)/V(dioxane) =1.5, Time=60min, Temperature=45 °C, W(MA)/W(HCB)=5.58, [DPN]=1.79×10^{-2}mol/L. The proof of graft copolymerization was confirmed by IR analysis. Based on the SEM, UV/VIS spectrophotometer results and impact strength test of PVC/HCB-g-PMA, it was validated that the dispersivity and consistent ability of grafted HCB are improved obviously.

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