

Graft-Modified HCPE with Methyl Methacrylate by the Mechanochemistry Reaction. II. Physical-Mechanical Properties and Processability

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ABSTRACT: In this article, the physical-mechanical properties and processability of graft-modified highly chlorinated polyethylene (HCPE; chlorine contents: $\geq 60\%$) with methyl methacrylate (MMA) by mechanochemistry reaction were studied. The results showed that the HCPE-g-MMA system is superior to unmodified HCPE in physical-mechanical properties, particularly in processability. In addition, the HCPE-g-MMA system, with about 62% chlorine content, was the same as PVC in its physical-mechanical properties. The HCPE-g-MMA system, with about 65.5% chlorine con-

tent, is the same as chlorinated poly(vinyl chloride) (CPVC) in its physical-mechanical properties, except that the Vicat softening temperature and processability of HCPE-g-MMA system are superior to PVC and CPVC. Compared with PVC and CPVC, the HCPE-g-MMA system proves better due to its lack of a toxic monomer. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 282–287, 2004

Key words: properties; processability; HCPE-g-MMA; physical-mechanical properties

INTRODUCTION

HCPE, with chlorine content of over 60%, has excellent physical-chemical properties. Many patents on HCPE for corrosion-resistant paints have been issued in recent years.^{1–9} However, to our knowledge, until now no application of HCPE as a structural material has been reported. Compared with other Cl-containing synthetic materials HCPE has many advantages in addition to its good mechanical properties. Its physical-chemical characteristics are controllable over a wide range by changing its chlorine content, and it is safe because it contains no vinyl chloride monomer, which is a known carcinogen. Therefore, HCPE has been explored for use as a medical material.¹⁰ The results of this study show that if HCPE is modified with MMA, its properties are improved significantly mainly in tensile strength, Vicat softening temperature, and thermal stability, and especially in processability. Although the physical-chemical properties of the material can be enhanced with an increase of the chlorine content of HCPE, it has some drawbacks as well. For example, the processability of the material decreases as a result, and the chlorination and reaction times are delayed considerably.

The mechanochemistry reaction is an old, but simple and effective method for synthesizing the graft copolymer.¹¹ According to the reaction mechanism,^{12,13} most copolymers formed in this process have a block structure and only a few have a graft structure. Regardless of which form they take, they can contribute to improving the properties of the materials.

For many years we have made special efforts, and conducted a number of experiments, on the syntheses and mechanochemistry modifications of HCPE. As a result, Vicat softening temperature of HCPE has been improved significantly by grafting maleic anhydride and styrene¹⁴ besides the results of this study. Both kinds of graft-modified HCPE have improved physical-mechanical properties.^{14,15}

A study on the properties of the HCPE-g-MMA system by mechanochemistry, with chlorine contents between 45 to 56% wt, has been reported in a previous article.¹⁵ This article focused on systems with chlorine contents of over 60% wt. The physical-mechanical properties and processability of graft-modified HCPE with MMA, as influenced by chlorine contents of HCPE, monomer parts, and processing conditions are the subject of this article. At the same time, MMA graft-modified HCPE is compared with PVC and CPVC in physical-mechanical properties. The results show that MMA graft-modified HCPE with different chlorine contents is similar in properties to PVC and

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TABLE I
Characteristics of Polymers Used in This Study

Resin notation	Source	Characteristics
PVC	Qilu Petro-chem. Company (China)	XS-700; number-average molecular weight of 4.3722×10^4 , polymerized by aqueous suspension
CPVC	Linqu Chemical Factory (Shandong, China)	XS-700 PVC chlorinated by aqueous suspension; chlorine contents. 65.2%
HCPE	Huan Hai Rubble and Plastics Chemical Factory (Qingdao, China)	HDPE (MI: 0.5, density: 0.955) chlorinated by solid-phase method; chlorine content of HCPE: $\geq 60\%$

CPVC and, because of having no vinyl chloride monomer, MMA graft-modified HCPE should have a wide variety of applications.

EXPERIMENTAL

Material

Commercial grades of resins, with the physicochemical properties listed in Table I, were used as received.

HCPE-g-MMA system preparation

A general procedure for the preparation of the HCPE-g-MMA system is illustrated by the following example: 20 g of MMA and 100 g of HCPE with 61.7% of chlorine contents were mixed thoroughly at room temperature before being masticated. The mixture was then added into a two-roll mill and masticated for 15 min. After that, the sample was drawn from the machine. The temperature of the two-roll mill was kept below 40°C by adding cool water, but the temperature between the two rolls was higher than 40°C due to the shearing stress. The two-roll mill had a diameter of 160 × 320 mm, and rotary speed was 24.4 rpm for the front roller and 32 rpm for the back roller.

Measurements

Tensile strength was tested with a tensile testing machine at 25°C and at a tensile rate of 10 mm/min. Impact strength was tested with a simple supported beam (impact test machine) at 25°C. The size of notch test specimens was 120 × 15 × 10 mm. Vicat softening temperature was measured by a Vicat needle tester. Brinell hardness was tested by a Brinell durometer.

The measurement specimens were prepared as follows: Modified HCPE with MMA 100 parts, epoxy cotton seed oil 2 parts, and calcium stearate 5 parts were well mixed. The mixed blend was poured into a two-roll mill. It was then compression molded in a thermostatic laboratory press: 160 kg/cm² for 10 min at 150°C. The mold provided a pattern of standard test specimens, and cooling under pressure was applied

for 10 min. Following this, the specimens were pulled out from the patterns and made into a dumbbell shape according to the requirement of measurements.

All viscosity data (η_a) with Figures 4–6 were measured by a capillary rheometer (SHIMADZU CFT-500, capillary tube L/D10/1, the measurement temperature: room temperature).

Thermogravimetric analyzer: SHIMADZU TGA-50; room temperature to 100°C at a speed of 5°C/min and 100 to 200°C at a speed of 2°C/min.

RESULTS AND DISCUSSION

Physical-mechanical properties

The influence of chlorine contents on the properties

According to measures indicated in the Experimental section, we made HCPE modified with MMA. As a result of MMA being introduced to HCPE, the physical-mechanical properties of the material varied dramatically, depending on the chlorine contents of HCPE and amount of monomer MMA added to the system.

Figures 1–3 show the influence of chlorine contents on tensile strength at break, Vicat softening tempera-

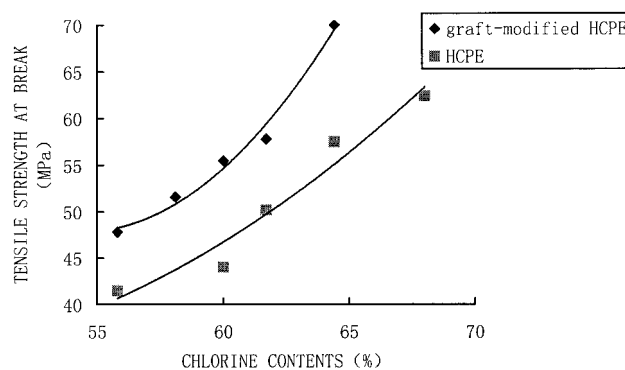


Figure 1 The relationship between chlorine contents and tensile strength at break. The formation of graft-modified HCPE with MMA is HCPE 100; MMA 20; reactive time: 15 min (i.e., mastication time; the flowing is the same).

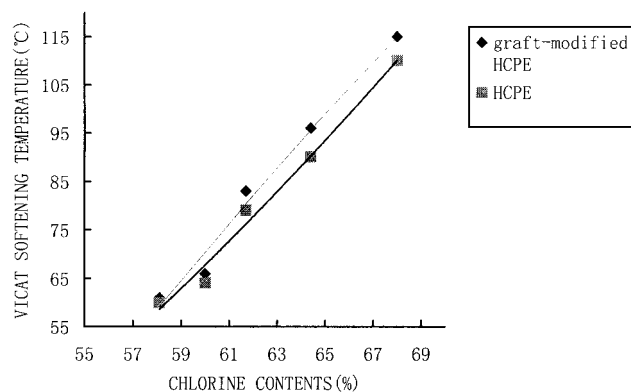


Figure 2 The relationship between chlorine contents and Vicat softening temperature. The formulation of graft-modified HCPE with MMA is HCPE 100; MMA 20; reactive time: 15 min.

ture, and Brinell hardness of the material. The results show that tensile strength of the HCPE-g-MMA system is higher than HCPE's, corresponding to their chlorine contents. In addition, as the chlorine contents increase, the difference between them becomes larger up to a margin of 10 MPa. This can be explained by grafting yield relating closely to the chlorine contents of HCPE in the mechanochemical reaction.¹⁶ The higher the chlorine contents of HCPE, the higher the grafting yield of MMA, which will result in the increase difference. Furthermore, the chlorine contents of HCPE have similar effects on Vicat softening temperature and Brinell hardness of graft-modified HCPE with MMA.

The influence of amount of MMA on the properties

The properties of the HCPE-g-MMA system relating to the amount of MMA added into the system are displayed in Table II. The results show that MMA

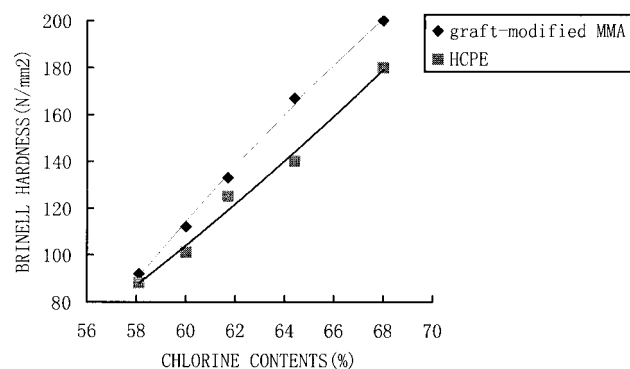


Figure 3 The relationship between chlorine contents and Brinell hardness. The formulation of graft-modified HCPE with MMA is HCPE 100; MMA 20; reactive time: 15 min.

TABLE II
The Influence of Amount of MMA on Properties of the Material^a

Amount of MMA parts	Tensile strength at break MPa	Vicat softening point °C
0	57.3	90
10	67.6	92
15	72.4	94
20	74.4	96
25	73.6	95

^a Reactive time: 15 min; chlorine contents: 64.8%.

amount added into the system influences the tensile strength at break and Vicat softening temperature. The influence of the grafting yield of MMA on HCPE has been explained in another article by the author.¹⁶ GD reaches its maximum value with about MMA of 20 parts and the best physical-mechanical properties of the material are obtained when 20 parts MMA is added.

Processability

Processability of the HCPE-g-MMA system is much better than the original HCPE's, due to the MMA grafted onto HCPE, resulting in polymers having good fluidity. Comparison of their apparent viscosities supports this statement.

The influence of shearing rate on apparent viscosity

Figure 4 demonstrates the relationships of the apparent viscosity (η_a) of the HCPE-g-MMA system and HCPE to shearing rate ($\dot{\gamma}_\omega$). The flows of polymer melts are mostly non-Newtonian fluid, and η_a varies

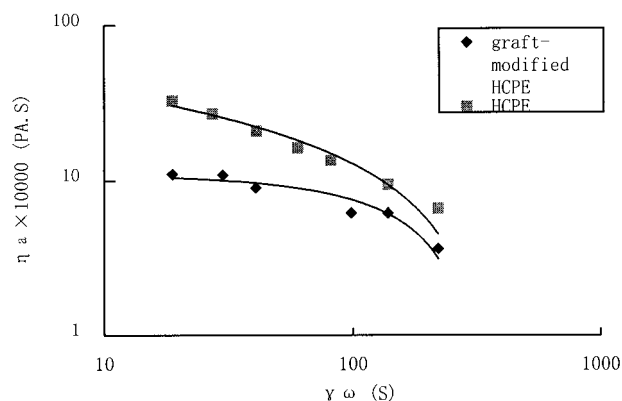


Figure 4 The relationship between shearing rate and apparent viscosity. The formulation of graft-modified HCPE with MMA is HCPE 100, MMA 20; reactive time 15 min; the chlorine contents of two samples: 62.7%.

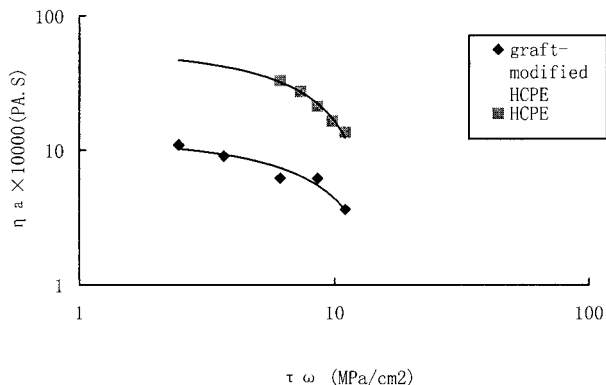


Figure 5 The relationship between shearing stress and apparent viscosity. The formulation of graft-modified HCPE with MMA is HCPE 100, MMA 20; reactive time; 15 min; the chlorine contents of two samples: 62.7%.

with γ_{ω} . In Figure 4, it can be seen that both polymer melt flows are non-Newtonian, and that the HCPE-g-MMA system has lower η_a than the HCPE. It shows that the processability of the HCPE-g-MMA system is superior to HCPE's. As the γ_{ω} increases, the η_a of HCPE displays a more rapid drop than that of the HCPE-g-MMA system, indicating that the rigidity of the HCPE-g-MMA system is higher than HCPE's. This is the result of the physical-mechanical properties of HCPE-g-MMA discussed previously.

The influence of shear stress on apparent viscosity

Figure 5 illustrates the influence of shear stress (τ_{ω}) on η_a of the two polymers. Such an influence can be attributed to the non-Newtonian behavior of the polymer. Furthermore, it varies with the flexibility of polymer, the flexible polymer having higher sensitivity than the rigid polymers with shear stress, with the viscosity descending more rapidly. It is confirmed once more that the rigidity of the HCPE-g-MMA system is higher than HCPE. It is also found from Figure 5 that the HCPE-g-MMA system has a lower η_a over HCPE.

The influence of working temperature on apparent viscosity

Figure 6 is drawn according to $\ln \eta = \ln A + \Delta E_{\eta}/RT$. Figure 6 shows the impact of the processing temperature on the relative apparent viscosities η_a of the two polymers. According to the Arrhenius formula, the activation energy of the flow process was 5.4 kcal/mol for the HCPE-g-MMA system and 4.5 kcal/mol for HCPE. The activation energies of the flow process for the two polymers are slightly different from each other. This is because the GD of MMA on the sample is only about 3%. Regardless, it still indicates the same

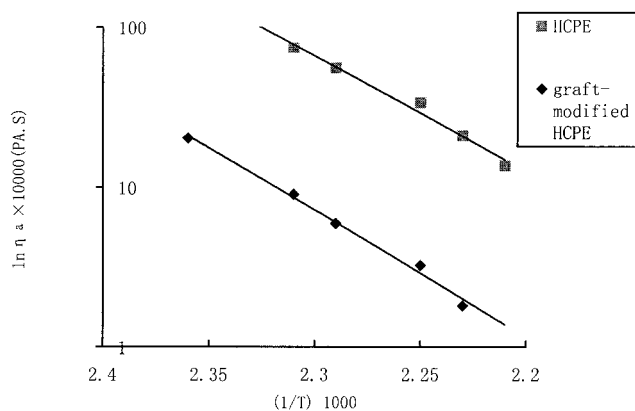


Figure 6 The relationship between working temperature and apparent viscosity. The formulation of graft-modified HCPE with MMA is HCPE 100, MMA 20; reactive time: 15 min; the chlorine of two samples: 62.7%.

conclusion that the rigidity of HCPE-g-MMA is stronger than HCPE's.

According to the above experimental results, it is concluded that the apparent viscosity of HCPE-g-MMA is lower than that of HCPE at each temperature: at the same conditions, modified HCPE should process more easily.

Thermal stability

TG analyses of the HCPE-g-MMA system (the upper curve in Fig. 7) and HCPE (the lower curve in Fig. 7) show that the thermal decomposition temperature of modified HCPE is 150°C, which is higher than the 115°C for HCPE. The improvement of thermal stability of the polymer is due to the introduction of acrylate monomers. Acrylate monomers, blended with PE and are chlorinated, can increase the thermal stability of a

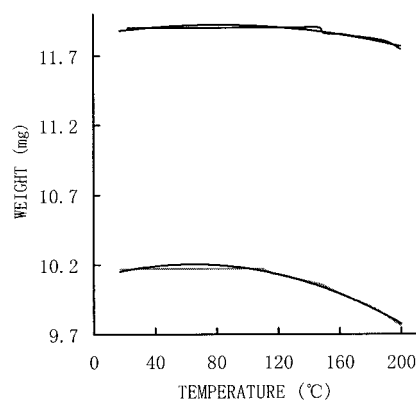


Figure 7 The comparison of TG curves. The formulation of graft-modified HCPE with MMA is HCPE 100, MMA 20; reactive time: 15 min; the chlorine of two samples: 62.7%.

TABLE III
Modified HCPE Comparing with PVC in Physical-Mechanical Properties

Specimens	PVC	HCPE	Graft-modified HCPE
Chlorine contents, %		62.0	62.0
Impact strength, kJ/m ²	1.33–1.43	2.00	2.73
Tensile strength at break, MPa	39–58	50.3	59.3
Extensibility at break, %	2.0–4.0	2	4
Brinell hardness, N/mm ²	100–128	122	134
Vicat softening temperature, °C	72–82	80	83

^a The formulation of graft-modified HCPE with MMA is HCPE 100 MMA 20: reactive time: 15 min.

polymer system, which will have a lighter color.¹⁷ Our experimental results verified this point of view.

Comparison with PVC and CPVC

Comparison with PVC

HCPE with a chloride content of 62% wt is similar to PVC in physical-mechanical properties. The HCPE-g-MMA systems with this kind of HCPE have a slight advantage in physical-mechanical properties compared with PVC (Table III). However, the experimental results of the capillary rheometer show that the processability of the HCPE-g-MMA system is better than both HCPE's and PVC's. For example, the HCPE-g-MMA system can be extruded at 160°C and a load of 100 kg, whereas PVC (average degree of polymerization: 700) and HCPE with chloride contents of 62% wt can be extruded only at 170°C and a load of 280 kg, and 160°C and a load of 250 kg, respectively.

Comparison with CPVC

HCPE with a chlorine content of about 67% wt has mechanical properties similar to CPVC. Graft-modified HCPE with MMA has physical-mechanical properties better than CPVC, except for the Vicat softening temperature (Table IV). CPVC processing must be carried out at 190°C, but the two processes including

TABLE IV
The Comparison of Modified HCPE and CPVC in Physical-Mechanical Properties

Specimens	CPVC	Modified HCPE
Chlorine content, %	65.2	67.5
Impact strength, kJ/m ²	1.20	1.39
Tensile strength at break, MPa	70	72
Brinell-hardness, N/mm ²	130	190
Vicat softening temperature, °C	125	115

^a The formulation of graft-modified HCPE with MMA is HCPE 100 MMA 20: reactive time: 15 min.

HCPE modification and processing can be carried out together at a colder temperature or even at room temperature.

In addition, as mentioned in the introduction, HCPE and graft-modified HCPE with MMA have an advantage over PVC and CPVC in their lack of a carcinogenic VC monomer.

Raising the Vicat softening point

Influence of grafted MMA

From Table II it can be concluded that, although the Vicat softening temperature of the material is enhanced by adding MMA grafted onto HCPE, Vicat softening temperature of HCPE modified with MMA is still too low to be used as a heat-resistant structural material. Some attempts have been made to raise softening temperature and are discussed briefly below:

Influence of increase in the chlorine contents of HCPE

The experimental results displayed above show the increase of the Vicat softening temperature of material with increase of chlorine content of HCPE. The Vicat softening temperature of the HCPE-g-MMA system, with 62% chlorine content HCPE, was 83°C and, with 68% chlorine content HCPE, was 115°C. However, the change of Vicat softening temperature is confined to a small range with the increase of chlorine content. In addition, a crosslinking reaction accompanies the necessarily longer chlorination reaction time for obtaining high chlorine contents HCPE. Crosslinking would deteriorate material processability. Therefore, increasing the chlorine content is not the best way to achieve this result.

Graft-copolymerization of two or more kinds of monomers

In the mechanochemistry reaction, 20 parts of MMA were added to 100 parts of HCPE, with chlorine con-

tent of 65.7%, with the Vicat softening temperature of the sample being only 98°C. At the same conditions, 100 parts of HCPE react with 10 portions of styrene (St) and 10 portions of MMA by the mechanochemistry reaction and the Vicat softening temperature of the sample was 112°C. So, it is possible to raise the Vicat softening temperature by using a second monomer with rigid groups. For example, the Vicat softening temperature of graft-modified HCPE with maleic anhydride (MA) and St was 125°C (chlorine content was about 67%; MA/St molar ratio was 1.5).¹⁴

CONCLUSIONS

1. Compared with HCPE, tensile strength of the HCPE-g-MMA system had an increase of 10–15 MPa, and the Vicat softening temperature was raised about 5°C. As a result, both the processability of this material and the thermal stability were improved. The addition of MMA was 10–20 parts for 100 parts of HCPE.
2. The physical-mechanical properties of modified HCPE vary with chlorine contents of HCPE and the amount of MMA added to the system. MMA at about 20 parts added to the system provided material with excellent properties.
3. The physical-mechanical properties of modified HCPE with chlorine content of 62% were equal to

PVC; and modified HCPE with a chlorine content of 65.5% was equal to CPVC, except for the Vicat softening temperature. The processability of these modified HCPE's was better than PVC and CPVC.

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