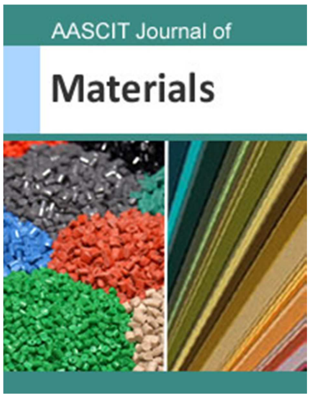
**AASCIT Journal of Materials**
2015; 1(3): 51-56



**Keywords**
Polyvinyl Chloride,
Blending Modification,
Toughening,
Cold Resistance

Received: July 22, 2015
Revised: August 5, 2015
Accepted: August 5, 2015

# Advance in Toughening and Cold Resistance Modification of PVC by Blending Method

**Changtong Song, Xuejia Ding***

Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, Beijing, China

## Email address
dingxj2011@126.com (Xuejia Ding)

## Citation
Changtong Song, Xuejia Ding. Advance in Toughening and Cold Resistance Modification of PVC by Blending Method. *AASCIT Journal of Materials.* Vol. 1, No. 3, 2015, pp. 51-56.

## Abstract
The research work on the toughening modification of PVC by blending method in recent years is described; some kinds of blending toughening mechanisms are introduced; the study on transparent and cold resistant modification of PVC by blending method was briefly summarized; The compatibility and toughening effect of some blending systems are discussed.

## 1. Introduction

Polyvinyl chloride (PVC) is one of the most widely used thermoplastic elastomer in the world. It has excellent flame retardant properties, chemical resistance, abrasion resistance and transparency. In addition, It also has good comprehensive mechanical properties, electrical insulation, etc.. So it is widely used in many applications, such as automobile, daily chemical, construction, home, medical treatment and so on.

However, PVC also has its own defects in its performance, Its thermal stability, toughness, processing, impact strength and cold resistance are less than satisfactory. When PVC is excited by light, heat and oxygen, it will produce free radicals due to structural defects (such as vinyl activity), remove HCl triggered a chain reaction, resulting in discoloration of PVC products. At low temperatures, PVC will quickly become hard and brittle, brittle crack, which limits the application of PVC in many fields, especially in the field of medical devices. In order to obtain better mechanical properties to a wider application in the field of medical apparatus and instruments, it is necessary to be toughened[1-2] and improved cold resistance. This paper gives a brief introduction to the domestic and foreign work on the toughening and cold resistance modification of PVC by blending method in recent years.

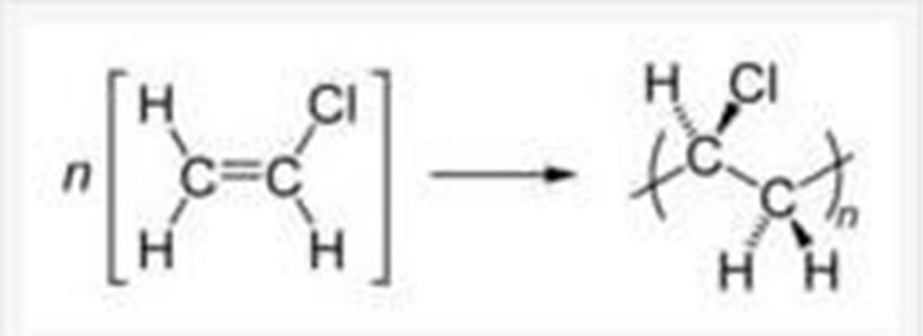


***Figure 1.*** *PVC synthesis and structure.*

## 2. PVC Toughening Modification Technology

PVC toughening modification can be divided into chemical modification and physical modification.

### 2.1. Chemical Modification

Chemical modification is a hot spot in recent years[3], it consists in changing the molecular structure of PVC by chemical methods such as copolymerization, macromolecular reaction and so on. Although the chemical modification methods of PVC toughening effect are ideal, however, the cost is high, and it is difficult to achieve toughening effect by complex chemical reaction, which is not the most economical choice.

### 2.2. Physical Modification

Physical modification is a physical method, which does not need to change the molecular structure of PVC, and can achieve the effect of toughening. Physical modification is usually divided into three types, filling, compounding and blending. One of the most widely used, the most economical is the blending modification. Blending modification can be divided into four kinds of solution blending, emulsion blending, melt blending, dry powder blending. In the blend system, PVC is the main body, which forms a continuous phase, which is called matrix, and the blend (other resin or inorganic) is the dispersed phase, and the interface between two phases is formed because of its self compatibility or compatibility. When the blend is subjected to external forces, two phases separated and absorbed energy, this is the basic mechanism of physical modification. In the blending process, there is not only the physical meaning of the dispersion and mixing of the components, but also the synergistic effect and the chemical reaction, which is the breakage and recombination of polymer chains.

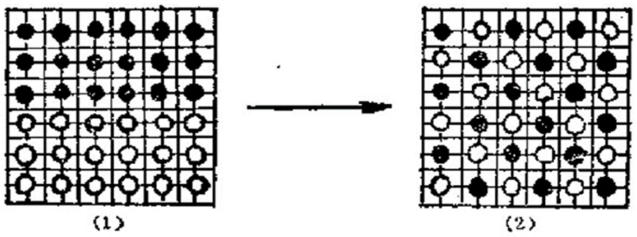


*Figure 2. Blending function.*

## 3. PVC blending Modification

PVC formula is as follows.

*Table 1. PVC basic formula.*

| formula | function | Examples |
|---|---|---|
| plasticizer | To reduce the softening temperature of polymer | epoxidized soybean oil DINCH |
| stabilizer | To Inhibit or neutralize HCl | Ca/Zn |
| antioxygen | To remove free radicals or prevent fracture of molecular chains | bisphenol A |
| lubricant | To reduce the friction between the molecules of PVC resin and the friction between the processing equipment | calcium stearate polyethylene wax |
| filler | To improve the processing performance of PVC | Nano-$CaCO_3$ nano-$BaSO_4$ |

The research progress of PVC blending modification was discussed from three aspects: the blend of the elastomer, the rigid particles and the blend of nano particles.

### 3.1. PVC/ Elastomer Blending System

PVC and elastomer blend modification is a mature and extensive research. Two kinds of toughening mechanisms were found. One is the network toughening mechanism, The elastic body forms a continuous network structure[4], which encapsulates the PVC matrix primary particle. When the blend is impacted by the energy, the elastic body network absorbs energy firstly, then the PVC matrix primary particles will be impacted by residual energy. The whole blend material is not easy to be destroyed by the external energy, and the toughness is enhanced. Its representative elastomer is CPE, NBR, etc.. The other is the crazing-shear yielding mechanism, Elastomer particles is dispersed uniformly in the PVC matrix, elastomer particles and PVC matrix form sea-island structure, The PVC matrix is the continuous phase of the sea, and the elastomer particles are the islands[5]. When subjected to external forces, the elastomer particles become stress concentration, PVC matrix produced a large amount of craze and shear belt to absorb energy, and the elastic body particles can prevent the development of the craze and shear belt, in addition, the shear belt will also prevent the development of the craze and small cracks, and the brittle-ductile transition will be appeared, then PVC matrix toughness is enhanced. Its representative elastomer is ABS, MBS, etc..

#### 3.1.1. PVC/Nitrile Rubber (NBR) Blending System

PVC has a certain polarity, and the compatibility of PVC and NBR with strong polarity is excellent, and its oil resistance, wear resistance and corrosion resistance are very good, so it developed early and used widely as a toughening agent. N.R.MANO et al[6] got the PVC/NBR blends by melt blending at 150℃，they found that, in a certain degree, the tensile strength of NBR was positively related to the tensile strength of the blends, and the tensile strength was negatively related to the tensile strength. When PVC and NBR were 75/25, the tensile strength of the blend reached 32MPa, the elongation at break reached 175%, and the toughness was good. Ali Shokri Ahmad et al[7] studied the NBR form (powder and bale) on the mechanical properties of NBR/ PVC system, they found that the effect of powder NBR on PVC was obviously better than that of bale NBR. This is due to the enhancement of the interfacial bond between the powder NBR and PVC. Schwarz H F et al[8] got the carboxylated nitrile rubber (XNBR)/PVC blends and compared the toughening effect of NBR and XNBR. They found that the toughening effect of XNBR is more obvious, the impact strength, tensile strength and modulus of the blends are higher, and the wear resistance is better.

### 3.1.2. PVC/CPE Blending System

CPE is a polymer material with excellent weather resistance, flame resistance, chemical resistance and ozone resistance , it is prepared by high density polyethylene (HDPE) through chlorination reaction. Its toughness is good, the structure of molecular chain is similar to PVC, it can be used as the toughening agent of PVC. The content and distribution of chlorine in CPE has great influence on its performance, In general, the content of chlorine in CPE is between 35%--40%. Zhou Li-ling et al[9] got the PVC and CPE blends by melt blending method. The morphology of the blends was studied by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). CPE molecular chain was found to form network structure in PVC matrix. Its compatibility with PVC was good. The shear yield and toughness of the PVC matrix were enhanced. The effect of CPE content on the rigid PVC/CPE system was studied by Chen Shaohui et al[10].They found that with the increase of the amount of CPE, the system has a brittle ductile transition, and the impact strength increases, when the amount of CPE reaches 16phr, the impact strength is 8 times that of the unmodified, and the toughness enhances.

### 3.1.3. PVC/ABS Blending System

ABS is a graft copolymer of acrylonitrile, butadiene and styrene, with three kinds of monomers, and has a core-shell structure. The polybutadiene is core, has the toughening effect, acrylonitrile styrene copolymer (SAN) is a shell that is grafted on the surface of PB, which has the function of increasing the compatibility of the blends, and can enhance the interfacial adhesion[11-12]. It has high strength, good toughness, easy processing and forming, it is a kind of very wide application of thermoplastic engineering plastics. Y J Shur et al[13]studied the PVC/ABS blends, they found that at room temperature and above, there is only one Tg. But Haaf[14] et al, in the study of SAN/PVC copolymer, they found that when the mass ratio of styrene and acrylonitrile is 75/25 in SAN, SAN and PVC matrix are uniformly distributed and have good compatibility. Qiao Weiwei et al[15]prepared PVC/ABS blends by means of melt blending method in the extrusion machine, and studied on its mechanical properties. they found that the mechanical properties of PVC/ABS system have been improved with the increase of ABS content, and when ABS content is between 20-60, the SAN of ABS forms the network structure with PVC, the impact strength and tensile properties of the system are improved. Zhou Li-ling et al[16] studied the impact fracture surface by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM), they found that PVC/ABS blend system is a kind of semi compatible system, which is formed by two phases. ABS is the stress concentration body, which lead to the silver pattern, which promotes the brittle ductile transition and toughness enhancement of the matrix.

### 3.1.4. PVC/MBS Blending System

MBS resin is a graft copolymer of methyl methacrylate, butadiene and styrene, it has a core-shell structure, in which PB is the core, PS and PMMA as the shell structure. It can be used as impact modifier for PVC[17]. The solubility parameter of MBS is similar to that of PVC, and the compatibility is good. The refractive index is also similar to that of PVC, and blending will not affect the transparency of PVC, and can be prepared transparent materials[18].

Effects of St and MMA content on the properties of PVC/MBS blends were studied by Zhu Ming-li et al[19]. They found that with the increase of the content of MMA, the compatibility of the system changes, the impact strength increases, the maximum reached 1117.74j/m. When the MBS was grafted with a small amount of St, the system had a ductile fracture, and the impact strength was 1039.33j/m. However, when MBS was grafted with a large number of St, the system had an inner containment and was not conducive to the improvement of toughness. He Jie et al[20] prepared PVC/MBS blends by melt blending process, and the effect of MBS content on the properties of the blends was studied. They found that with the increase of MBS content, the tensile strength and bending strength of the system decreased, but the impact strength increased sharply. When the dosage of MBS was 9 phr to 10 phr, the impact strength increased from 18kj/m$^2$ to 50 kj/m$^2$, which was obviously brittle ductile transition, and more than 10 phr, the system reached super toughness.

## 3.2. PVC/Rigid Particle Blending System

Rigid particle (RF) toughening was found and raised by Kurauchi and Ohta et al in 1984. When they studied PC/ABS and PC/AS blends, they found that the tensile strength, elongation at break and yield stress of the blends is obtained for a raise, so they put forward the brittle plastic particles and Matrix Toughness blend can greatly improve the material performance. After them, many scholars such as Inoue, Angola, K.Koo and so on did a further research on the basis of their research, until 1988, the rigid particle toughening polymer technology officially put forward[21-24].

The current RF mainly has two kinds of organic rigid particles (ROF) and inorganic rigid particles (RIF).

### 3.2.1. PVC/Inorganic Rigid Particles Blending System

RIF toughening mechanism: (1) when the blend is subjected to external forces, the RIF is a stress concentration, which causes the PVC matrix to produce a silver pattern, shear band, and cavitation, which absorbs energy and enhances toughness. (2) Then pinning - climbing or pinning - crack two triggered effect is occurred to consume energy and hinder crack growth[25].(3) At the interface, the cavitation is formed and the passivation crack is prevented from developing into a destructive crack[26].

RIF toughening modifier mainly has layered silicate, nano calcium carbonate, nano silica, etc..

The properties of the surface modified attapulgite (AT) and PVC blends were studied by Zhang Qi-wei et al [27]. They first used silane coupling agent and methyl methacrylate (MMA) on the surface of the attapulgite (AT) surface modification, then the modified AT and PVC were blended by melt blending and the mechanical and thermal properties of the test were tested. They found that in a certain range (at the mass fraction of less than 15%), with increase of AT content, the blends pulled strength, impact strength, bending strength and thermal stability increased. Over a certain range (AT's mass fraction is greater than 15%), the performance of the blends decreased. AT can improve the performance of PVC.

Nano particles have a great effect on the improvement of the properties of the polymer, but the key is how to make the nano particles disperse uniformly in the matrix and the interfacial bonding well. Nano calcium carbonate is a kind of commonly used PVC toughening agent, but in order to improve the dispersion and interfacial adhesion, it is necessary to surface modification[28-29].

The toughening modification of nano calcium carbonate to PVC was studied by Gao Guang-tao et al [30]. First, the surface modification of nano calcium carbonate was carried out, then the composite materials were prepared by blending with PVC and ACR and the structure and mechanical properties of the blends were studied. It was found that the modified nano calcium carbonate was dispersed well in the matrix, and the ductile fracture was found. Moreover, with the increase of the content of nano calcium carbonate, the breaking elongation and bending modulus of the system increased, the tensile strength decreased slightly. The impact strength increased first and then decreased, when the nano calcium carbonate was 15phr, the maximum reached 3 times of the matrix PVC (5.4 KJ/m$^2$).

The toughening modification of PVC by nano silica was studied by Tian Man-hong et al[31]. First, the surface modification of nano silica was carried out by ultrasonic and vibration grinding. After prepared nano-$SiO_2$/PVC composites by melt blending, the properties and the fracture surface is studied. It is found that the surface modification of nano-$SiO_2$ can solve the agglomeration phenomenon in PVC matrix, and improve the mechanical properties of the blends. Surface treatment time has a certain effect on the properties of the blends, and when the treatment time is 6h, the modified effect is the best.

### 3.2.2. PVC/Organic Rigid Particles Blending System

Organic rigid particles(ROF) toughening mechanism: There are two kinds of ROF toughening mechanism, one is drawn mechanism for better compatibility of the system, the other is a hole toughening mechanism applicable to poor compatibility system[32-35].

ROF toughening agent mainly includes PS, PMMA.

The effect of very fine polystyrene (UPS) particles on the properties of PVC/CPE blends was studied by Qiong Zhou[36] etc. Firstly, a series of UPS and PVC/CPE (100/10) blends were prepared by melt blending, and the mechanical properties and fracture surface structure of the blends were tested. They found that, with the increase of UPS content, the tensile strength of the blends decreased, but the impact strength has greatly improved, increased from 16 to 34KJ/m$^2$ (UPS 2.5phr), then decreased. In addition, electron microscope observation found that UPS can enhance the network structure between PVC and CPE. The effect of PMMA based core-shell structure organic rigid particles and common organic rigid particles on the properties of PVC/CPE (100/10) blends was studied by Wu Qiye[37] et al. The ordinary organic rigid particles of SAN and PMMA based core-shell structure organic rigid particles were blended with PVC/CPE blends respectively, after that they were tested for performance. They found that the PMMA based core-shell structure organic rigid particles (particle size 100nm) was found to have a more significant effect on the toughness of PVC/CPE blends than SAN, When the amount of the PMMA based core-shell structure organic rigid particles in the matrix is 1phr, the impact strength of the system is 41.6MPa, which is higher than that of 9.9MPa of the pure PVC/CPE.

## 4. Cold Resistance Modification of PVC by Blending Method

The impact strength of PVC is low, especially at low temperature, with the temperature decreasing PVC quickly becomes brittle and hard, then brittle fracture occurs. This will affect its application in many aspects, especially in medical apparatus and instruments. How to modify the performance of the PVC to enhance the cold resistance, while retaining its original transparency, is a subject of research in the direction of medical apparatus and instruments. Here is a brief introduction to the research on this aspect.

The method of improving the cold resistance of PVC is consistent with the toughening methods. On the basis of improving the cold resistance, ensure the transparency to meet the requirements, the requirements of process and formulation are higher.

Nowadays, the research on the cold resistance and the transparent modification of PVC is few, and the commonly used cold resistant and transparent modifiers are MBS, Elvaloy, etc.

### 4.1. PVC/MBS Cold Resistant and Transparent Blending System

MBS has been introduced in the paper, which is an important part of PVC toughening agent, and it is also a kind of cold resistant and transparent modifier. The plasticizing effect and refractive index of MBS is closely related to the methyl benzoic acid methyl ester, butadiene and styrene content in MBS. The effects of the number of parts of the three components in MBS on the properties of MBS/PVC blends were studied by D.Dompas[38] et al. It was found that when the ratio of methyl phenyl methyl ester, butadiene and styrene was 25:60:42, the blends showed good compatibility and transparency, and the mechanical properties were also very good.

There are three factors that affect the properties of MBS and PVC/MBS blends, the first one is the content of the three components in MBS, and the second is the process of preparing styrene butadiene latex, and the last one is the coagulation process of methyl methacrylate, butadiene and styrene. The effect of MBS polymerization on the properties of PVC/MBS blends was studied by L.Terlemezyan[39] et al. MBS was prepared by emulsion graft polymerization, and then the PVC/MBS blends were prepared by melt blending. It was found that the impact strength of the blend system can be reached by the MBS by two step emulsion graft polymerization, and the transparency of PVC can be kept.

### 4.2. PVC/Elvaloy Cold Resistant and Transparent Blending System

Elvaloy is a new type of PVC modifier, which is based on EVA. It is the three elements of ethylene, vinyl acetate and carbon monoxide. The glass transition temperature is low; the solubility parameter is about 9.2-9.3, it is similar to the PVC and because of the introduction of a ketone carbonyl, the compatibility with the PVC is very good[40].

The effect of Elvaloy on the performance of PVC was studied by Li Xiran[41] et al. They first used the melt blending method to blend the Elvaloy and PVC, and then carry on the performance test. It was found that the transmittance of the blend decreased with the increase of Elvaloy number, but it can be maintained at 76% or above, the brittle temperature decreases, when Elvaloy is 20phr, the brittle temperature decreases by 12.5℃, and the impact strength can be increased by more than 2 times.

### 4.3. PVC/Styrene Graft Copolymers Cold Resistant and Transparent Blending System

Styrene Graft Copolymers is a new type of PVC modified agent, which is prepared by ɑ-methyl methacrylate (ɑ-MS) and rubber by Graft Copolymerization. It is a colorless or light yellow viscous liquid, can be dispersed in PVC matrix. The effect of Styrene Graft Copolymers on the properties of PVC was studied by Li Xiran[42] et al. First, a series of PVC/ Styrene Graft Copolymers blends were prepared by double roller mill. After that, the optical performance, mechanical properties, low temperature performance and so on were tested. It was found that the transparency of the blend system was good and the impact strength of the blends increased with the increase of the amount of styrene. The impact strength decreased with the increase of the amount of styrene. When the Styrene Graft Copolymers was 8phr, the impact strength was 1.6 times higher than that of unmodified, and the brittle temperature decreased by 13 degrees Celsius.

## 5. Peroration

The toughening modification of PVC has received extensive attention from the last century, until now, the modification of PVC research has been prolonged. PVC's toughening modification method is also such, one after another, but the blending modification is still the most important and the most promising method to improve the PVC performance. With the continuous research of many scholars, PVC blend modification will be further developed, and the application of PVC will be more and more extensive.

## References

[1] Xiong C X, Wang T, Liu Q H,et al. Study on Preparation and Structure Characterization of Nano-crystalline poly(vinyl chloride)[J]. J Appl Polym Sci, 2004.19(1):563-569.

[2] Nakamura Y, KanbeM, TakekuniE, etal. Effects of Particle Size and Interfacial Slope Structure on the Mechanical and Faracture Properties of PVC filled with cross linked PMMA particles [J]. ComposInterf,2001,8:367-381.

[3] Herrero M, Tiemblo P, Reyes-Labarta J, et al. PVC modification with new functional groups. Influence of hydrogen bonds on reactivity, stiffness and specific volume [J]. Polymer, 2002, 43(9): 2631-2636.

[4] Liu Z H, Zhang X D, Zhu X G, et al. Effect of morphology on the brittle ductile transition of polymer blends: 3. The influence of rubber particle spatial distribution on the fracture behaviour of poly (vinyl chloride)/nitrile rubber blends [J]. Polymer, 1998, 39(21): 5027-5033.

[5] Zulfiqar S, Ahmad S. Thermal degradation of blends of PVC with polysiloxane—1[J]. Polymer degradation and stability, 1999, 65(2): 243-247.

[6] N R Mano, P P De， et al. Self-crosslinkable Plastic-Rub2ber Blend System Based on Poly (vinylchloride) and Acry-lonitril-$CO_2$-Butadiene Rubber [J]. J Polymer Science, 1993, (49): 132.

[7] Ahmad Ali Shokri, Gholamreza Bakhshandeh, Tahereh Darestani Farahani. An Investigation of Mechanical and Rheological Properties of NBR/PVC Blends: Influence of Anhydride Additives, Mixing Procedure and NBR Form[J]. Iranian Polymer Journal 15 (3), 2006, 227-237.

[8] Sellwarz H F, Indian Rubber Manufaet Urers.ResearchAssoe.,Thana,1983:45

[9] ZHOU Li-ling, WANG Xin, LIN Yu-sheng et al, Microstructures and Properties of PVC/ CPE and PVC/ ABS Blends [J]. Journal of Qiangdao University of Science and Technology, 2003, 24(1):48-52.

[10] CHEN Shao-hui , SONG Y- hui et al, Mechanical Properties of PVC/ CPE/ $CaCO_3$ Composites [J]. Journal of Materials Science & Engineering, 2011, 29(6):829-832.

[11] Kim H, Kerkkula H, Paul D R. Effect of acrylonitrile content on the toughness of ABS materials[J].Polymer,1991,32(8):1447-1455.

[12] Daniels E S,Dimonie V L, Vanderhoff J W. Preparation of ABS(acrylonitrile/butadiene/styrene) latexes using hydroperoxide redox initiators [J]. J Appl Polym Sci,1990,41(9):2463-2477.

[13] Shur Y J, Randy B. Gas permeation of polymer blends. IV. Poly (vinyl chloride) (PVC)/acrylonitnle-butadiene-styrene(ABS) terpolymer [J]. J Appl Sci,1976,20(11):3121-3128.

[14] Breuer H, Haaf F, Stabenow J. Stress whitening and yielding mechanism of rubber-modified PVC[J].J Macromol Sci Phys,1977,14(3):387-417.

[15] QIAO Wei-wei, WANG Guo-ying, HUANG Yan. Mechanical Properties of PVC/ABS Blending System [J]. Plastics, 2005, 33(6): 71-73.

[16] Zhou Liling, Lin YuSheng et al. Toughening effect of crazes in PVC/ABS blends [J]. Engineering Plastics Application, 2002, 8: 005.

[17] Zhou C, Chen M, Zhang H X. The influence of arrangement of St in MBS on the properties of PVC/MBS blends [J]. european Polymer Journal, 2006,42(8):138-139.

[18] Si Q B, Zhou C, Yang H D, et al. Toughening of Poly(vinyl chloride) by Core-shell Particles: Influence of the Iternal Structure of Core-shell Particles[J].European Polymer Journal,2007,43(7):3060-3067.

[19] CHU Mingli, LIU Zhe , LI Hongquan et al. Morphology and Mechanical Properties of PVC/MBS Blends [J]. CHINA PLASTICS, 2010，24(3):25-28.

[20] HE Jie, QIN Shuhao et al. Preparation and Performance of Super-Tough PVC/ MBS Alloy[J].Plastics, 2009，38(2): 5-6.

[21] Kurauchi T, Ohta T. Energy absorption in blends of polycarbonate with ABS and SAN [J]. Journal of materials science, 1984, 19(5): 1699-1709.

[22] Gawade A R, Lodha A V, Joshi P S. PVC/ABS Blends: Thermal and morphological studies [J]. Journal of Macromolecular Science, Part B, 2007, 47(1): 201-210.

[23] Quintens D, Groeninckx G, Guest M, et al. Mechanical behavior related to the phase morphology of PC/SAN polymer blends [J]. Polymer Engineering & Science, 1990, 30(22): 1474-1483.

[24] Angola J C, Fujita Y, Sakai T and Inoue T. J Polym Sci, Polym Phys, 1988, 26( 5) : 807.

[25] Li Fengling, Wang Jianmin et al. Developing situation of PVC toughened with rigid particles [J]. Modern Plastics Processing and Applications, 1999 ,11 (2) :47

[26] MENG Ji-ru, LIANG Guo-zheng, QIN Hua-yu, ZHAO Lei. Toughening and Reinforcing Effect of Rigid Fillers for Polymers [J]. Plastics, 2002, 31(2): 47-50.

[27] ZHANG Qi-wei, ZHANG Yong-hua et al. tudies on the Preparation and Properties of Rigid Poly (vinyl cholride) Filled by Surface Grafting Polymerized-Attapulgite [J]. CHINA PLASTICS, 2002,16 (9): 49-52.

[28] Gonzal EZ J, Albano C, Ichazo M, et al. Effects of coupoling agents on mechanical and morphological behavior of the PP/HDPE blend with different $CaCO_3$ [J]. Eur Polym J, 2002,38: 2465-2475.

[29] Wu Wei, Lu Shouci. Mechno-chemical surface modification of calcium carbonate particles by polymer grafting [J]. Powder Technol, 2003, 137:41.

[30] GAO Guangtao , ZHANG Yong. Study on Toughening of PVC by Modified Nano-$CaCO_3$ [J]. CHINA PLASTICS INDUSTRY, 2008, 36(1):49-52.

[31] TI AN Man - hong , GUO Shao- yun. Study on nano-$SiO_2$ reinforcing and toughening polyvinyl chloride composites [J]. Polyvinyl Chloride, 2003,1:26-32.

[32] Agari Y, Anan Y, Nomura R, et al. Estimation of the compositional gradient in a PVC/PMMA graded blend prepared by the dissolution–diffusion method [J]. Polymer, 2007, 48(4): 1139-1147.

[33] Dompas D, Groeninckx G, Isogawa M, et al. Miscibility behaviour of blends of poly (vinyl chloride) with poly (methyl methacrylate-co-styrene) copolymers[J]. Polymer, 1997, 38(2): 421-429.

[34] Rhoo H J, Kim H T, Park J K, et al. Ionic conduction in plasticized PVCPMMA blend polymer electrolytes [J]. Electrochimica acta, 1997, 42(10): 1571-1579.

[35] Li W, Yuan M, Yang M. Dual-phase polymer electrolyte with enhanced phase compatibility based on Poly (MMA-g-PVC)/PMMA[J]. European polymer journal, 2006, 42(6): 1396-1402.

[36] Qiong Zhou, etc. Modification of poly(vinyl chloride)/chlorinated polyethylene blends with ultrafine particles of polystyrene[J].European Polymer Journal,2000,36:1735-1740.

[37] WU Qi-ye, GAO Wei-ping, W ANG Qing-guo, QIAO Ling-ling, YU Qing-shan. Toughening of R-PVC /CPE blend by PMMA-basic core-shell rigid organic filler [J]. PO LYMER MAT ERIALS SCIEN CE AND EN GIN EERIN G, 2000,16 (6): 105-108.

[38] D. Dompas, G. Groeninckx, M. Isogawa, T. Hasegawa， M. Kadokura. Toughening behaviour of rubber-modified thermoplastic polymers involving very small rubber particles: 3. Impact mechanical behaviour of poly (rmvinyl chloride)/methyl methacrylate-butadiene-styrene graft copolymer blends[J]. Polymer, 1994, 35(22): 4760-476.

[39] L. Terlemezyan, M. Mihailov, L. Kamburova. Preparation an investigation of methacrylate — butadiene — styrene graft copolymers and their mixtures with poly (vinyl chloride) [J]. Acta Polymerica, 1989, 40: 279-281.

[40] An Q F, Qian J W, Sun H B, et al. Compatibility of PVC/EVA blends and the pervaporation of their blend membranes for benzene/cyclohexane mixtures[J]. Journal of membrane science, 2003, 222(1): 113-122.

[41] LI Xiran, DING Xuejia et al. Effect of Elvaloy on Properties of PVC [J]. CHINA PLASTICS, 2012, 26(12):25-28.

[42] LI Xiran, DING Xuejia et al. Influence of Styrene Graft Copolymers in Properties of PVC [J]. CHINA PLASTICS INDUSTRY, 2013,41(3):43-46.