Effect of Poly(epichlorohydrin) on the Thermal and Mechanical Properties of Poly(vinyl chloride)

Yiming Ren,[1] Guangfeng Wu,[2] Xiaoxing Zhao,[2] Xiaoli Liu,[1] Fengqi Liu[1]

[1]College of Chemistry, Jilin University, Changchun 130012, China
[2]Engineering Research Center of Synthetic Resin and Special Fiber, Ministry of Education, Changchun University of Technology, China

ABSTRACT: Five kinds of polyepichlorohydrin (PECH) of different molecular weights were synthesized and characterized by gel permeation chromatography (GPC). Mechanical blending was used to mix PECH and poly(vinyl chloride) (PVC) together. The blends of different PVC/PECH ratios were characterized by thermogravimetric analysis (TGA), tensile tests, differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). TGA results show the thermal stability of PVC/PECH blends is desirable. Tensile tests indicate elongation at break is raised by increasing both the amount and the molecular weight of PECH. DSC is used to determine the glass transition temperature of PECH, and a quite low T_g is obtained. DMA results indicate that PECH has a perfect compatibility with PVC, when PECH concentration is below 20 wt %. There is only one peak in each tan δ curve, and the corresponding T_g decreases as PECH amount increases. However, above 20 wt %, phase separation takes place. The molecular weight of PECH also has a great influence on the glass transition temperature of the blends. This study shows that PECH is an excellent plasticizer for PVC, and one can tailor the glass transition temperature and tensile properties by changing the amount and the molecular weight of PECH. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3416–3424, 2010

Key words: poly(vinyl chloride) (PVC); polyethers; polymer blends; cationic polymerization; plastics

INTRODUCTION

PVC is one of the most important plastics worldwide, which has a large number of output and consumption annually. It is used in many fields, such as automobiles, construction, cable, packaging, etc. The properties of PVC materials vary markedly as additives change, from soft to rigid, transparent to opaque, which endows PVC with a broad range of applications.

Plasticizer is mixed into some plastics to achieve good processability by lowering the melting and softening points and viscosity of the melts. The incorporation of a plasticizer into the plastic material matrix markedly decreases the second order transition temperature of PVC.[1] In general, plasticizers are solid with relatively low melting point or liquid with relatively high boiling point. They are well dispersed among plastic polymer molecules, and the polar groups of the plasticizer interact with the counterparts of the polymer molecules by supramolecular force, which is commonly considered as dipole–dipole interactions. The nonpolar sections of the plasticizer segregate polymer molecules and reduce the interactions between them. As a result, the mobility of polymer molecules are increased, which is especially helpful to processing.[2–4]

The most widely used PVC plasticizer is phthalates [e.g., di-(2-ethylhexyl) phthalate (DEHP), didecyl phthalate (DIDP), dibutyl phthalate (DBP), etc.], which have over 30 different kinds, and account for 92% of the world plasticizer market. DEHP alone, accounts for 51% of the total phthalates.[5] Phthalates have some desirable properties of a plasticizer such as satisfactory insulation for cables, good fusion properties, minimal interaction with resins at room temperature and low cost, etc.[6] The processability of PVC is also much improved.

The incorporation of plasticizers has brought about some problems, though the advantages above are obvious. As most of plasticizers are low molecular weight compounds, volatility and migration are matters of concern. This kind of plasticizer molecules can move freely in the PVC matrix. As time goes by, the plasticizer molecules diffuse from inside out to the surface of PVC. After that they volatilize into the air or may be rubbed away by human's touch. This leads to the brittleness of PVC, which largely reduces its lifetime. In addition, because some PVC products may be occasionally exposed to some nonaqueous solvents, extraction also becomes a factor that reduces the lifetime of the

Correspondence to: F. Liu (liufengqi@jlu.edu.cn).

materials. Because of these problems, phthalate plasticizers have been found in most environments, such as foods and animals.[7] When used in applications such as medical devices and children products, these problems become especially serious, which may cause the transfer of plasticizers into human bodies. Some western countries have already promulgated bans on the use of some certain phthalate plasticizers in toys and childcare articles.

To solve the problems above, scientists have tried many ways, such as surface crosslinking,[8] modification of surface hydrophilicity/lipophilicity,[9–13] surface coating,[14,15] and surface extraction.[16–18] Besides, polymeric plasticizers have also been of wide concern and study, because of their great advantages in low volatility and low migration rate. Polymeric plasticizer molecules have a much stronger dipole–dipole interaction with PVC molecules, accompanied by entanglement effect, which largely restricts the mobility of these molecules. Hence, the migration rate is reduced. Many literatures have reported the studies on the blending properties of PVC and its polymeric plasticizers, which include poly(butylene adipate) (PBA),[19,20] poly(propylene imine) dendrimers,[21] PMMA,[22] poly(butyl acrylate) (PBA),[23] acrylonitrile butadiene rubber (NBR), ethylene vinyl acetate (EVA),[24] aliphatic-aromatic copolyester (AAC),[25] polyesteramides,[26] epoxidized liquid natural rubber (ELNR),[27] to cite just a few. Blend of PVC and each plasticizer has its unique properties, on the basis of which different plasticizers can be used for different purposes.

In this work, we have developed a new PVC plasticizer, PECH, and studied the properties of its PVC blends. In general, polymeric plasticizers for PVC are mostly polyesters, while this new plasticizer is a type of polyether, which is quite different from traditional polyester. Polyesters have perfect compatibility with PVC through the dipole–dipole interaction of ester carbonyl group and C—Cl bond. However, there is no carbonyl group but a C—Cl bond in each unit of PECH chains, which is quite similar with that of PVC molecules. This similarity makes PECH and PVC have a perfect compatibility. C—Cl bonds on both PECH and PVC chains have strong interactions through dipole–dipole force and hydrogen bonding. The incorporation of PECH into PVC matrix lowers the glass transition temperature markedly, which favors the processability of PVC. The blends of them turn to have good tensile properties, which indicate its prospects of industrialization.

EXPERIMENTAL

Materials

PVC (SG5) was used in this study, a commercial product of Jilin Petrochemical Company. Epichloro-hydrin (ECH) was provided by Tianjin Fuchen Chemical Reagent Factory. Boron trifluoride ether solution used as the polymerization catalyst was supplied by Sinopharm Chemical Reagent (Shanghai). Ethylene glycol (EG) and methylenechloride were both purchased from Beijing Chemical Works, China. Dibutyltindilaurate used as a thermal stabilizer was provided by Ninghe Chemical (Shanghai).

Synthesis of PECH and preparation of testing sheets

Five PECHs with different molecular weights were synthesized, which are listed in Table I, whereas only the synthesis of PECH1 is described here because others were synthesized in similar ways. Fifty milliliter dry EG, 9.6 mL boron trifluoride ether solution and 100 mL dry methylene chloride were added into a 2000 mL three-necked flask. The mixture was stirred violently and kept under N_2 atmosphere for 20 min to get rid of water vapor. ECH (842 mL) and methylene chloride (850 mL) were mixed in a 2000 mL beaker and stirred well then poured into a 500 mL dropping funnel for several times. This solution was added drop by drop into the three-necked flask and the dropping rate was kept at one drop per second. The reaction was kept for 12 h at room temperature. All the reactants were dried before use. Fifty milliliter of ammonia was added into the flask with stirring after 12 hours' reaction. The resulting solution was washed with distilled water for three times to get rid of water-soluble impurities. Then it was filtrated, rotary evaporated and kept in the vacuum drying oven for 24 h. A buff and viscous fluid was obtained. As molecular weights increased, the viscosity increased and the color darkened.

A two-roll mill was used to make the PVC/PECH blends. The temperature was set at 175°C in the blending process. PVC and PECH were weighted 100 g totally with different ratios, and added into the mixture followed by vigorously stirring. To prevent possible degradation, 2 mL dibutyltin dilaurate was added to the blends. After blending, a hot-press molding machine was used to make plastic slabs at 185°C. In this article, PECHn-A/B is used to represent the blending samples, in which n is the number of PECH of different molecular weights, and A/B is the mass ratio of PVC/PECH.

Characterization of PECH and PVC/PECH blends

Gel permeation chromatography (GPC)

Average molecular weights of PECH samples were estimated by gel permeation chromatography (GPC) on Shimadzu LC-20A (Japan). The columns used were GPC-805 columns, which were packed with

PECH	M^a	M_n (g/mol)[b]	M_w (g/mol)[b]	PDI[b]	EG: ECH (mol : mol)[a]
PECH1	1170	2281	2409	1.06	1 : 12
PECH2	1910	2331	2461	1.06	1 : 20
PECH3	2840	2697	2933	1.09	1 : 30
PECH4	3760	2930	3775	1.29	1 : 40
PECH5	4690	3215	4406	1.37	1 : 50

[a] Average from synthesis batches.
[b] As calculated from GPC.

spherical porous gel made of a styrene-divinyben-zene copolymer. A small quantity of PECH was dissolved in tetrahydrofuran, which acted as a mobile phase, and injected into the instrument. The flow rate was set at 1 mL/min and the temperature was controlled at 40°C.

Thermogravimetric analysis (TGA)

Thermal stability was determined by using a Perkin–Elmer Pyris 1 thermogravimetric analyzer. The experiment was performed under N_2 atmosphere over the temperature range of 30–650°C at 10°C/min.

Tensile tests

The tensile properties of the plasticized samples were determined by using a universal tester (AG-I, 1KN, Shimadzu, Japan) at a cross-head speed of 10 mm/min. Measurements for all the samples were taken at 25°C. The PVC/PECH slabs were cut into dumbbell-shaped tensile samples, which were 30 mm long and 4 mm wide.

Differential scanning calorimetry (DSC)

Differential scanning calorimeter (DSC) was conducted with Mettler Toledo 821[e] and N_2 was used as the purge gas. The heating scans were performed at 10°C per minute over the range of −70 to 30°C for PECH.

Dynamic mechanical analysis (DMA)

The dynamic properties of the PVC blends were taken on the Perkin–Elmer diamond dynamic mechanical analyzer. The samples were heated from −60 to 110°C at the heating rate of 3°C/min with a fixed frequency of 1 Hz. The samples were 25 mm long, 4.0 mm wide and 1.0–1.5 mm thick.

RESULTS AND DISCUSSION

Studies of thermogravimetric properties

Thermogravimetric curves of PECH1, PECH2, PECH5, and pure PVC are shown in Figure 1. From the curves, we can clearly observe that there are two apparent steps of PVC degradation. During the first step, elimination of HCl at 238°C results in the formation of polyene sequences which then decompose to aromatic and aliphatic hydrocarbons at 425°C.[28] The three PECHs all start to lose weight below 100°C, which is possibly because of the evaporation of the residual solvent and monomer molecules, and the decomposition of oligomer resultants in the synthesizing process. As temperature increases, PECH1 firstly starts to lose weight at a faster rate at 189°C, while the other two plasticizers remain quite stable. This is because the molecular weight of PECH1 is quite low and relatively sensitive to temperature. When the temperature rises to 320°C round, all the PECHs begin to lose weight at a very fast rate, and the greatest mass loss is observed. This may be attributed to the dehydrochlorination of the plasticizer molecules, just similar with the mechanism of that of PVC. This onset temperature is 40 degrees
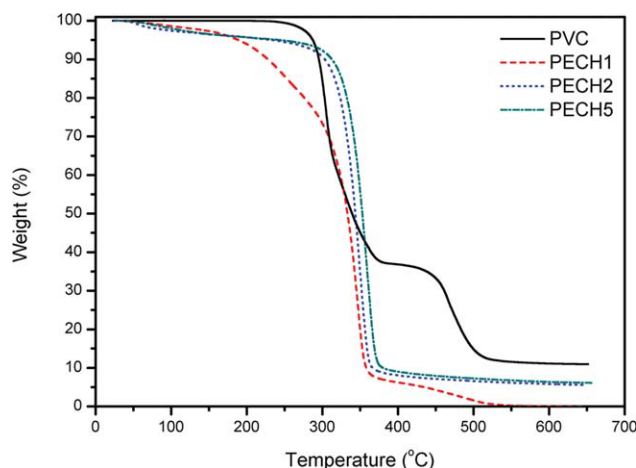

Figure 1 Thermogravimetric curves of pure PVC and three PECHs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
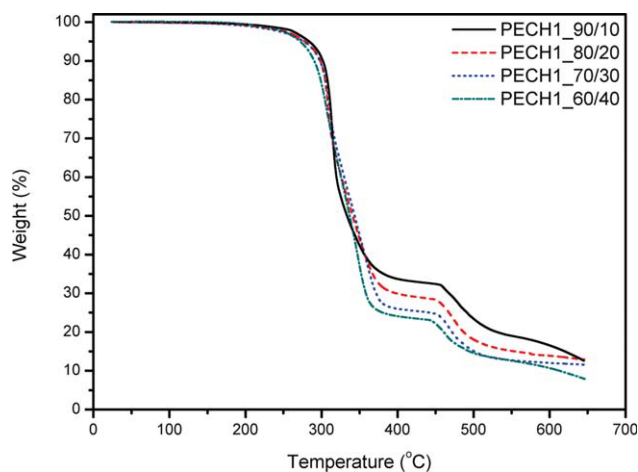
Figure 2 Thermogravimetric curves of blends of various mass ratios of PVC/PECH1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

higher than that of pure PVC, which may be because the polyene formation of PVC favors the degradation and makes it easier to decompose, but PECH can not form the polyene. PECH1 loses all its weight at 540°C and the other two PECHs change very little after 380°C. The plasticizers have only one step of degradation, which indicates that dehydrochlorination is the only way of weight loss for PECH and no polyene forms. The curves of PECH2, PECH3, PECH4, and PECH5 are quite alike. To make the curves more clear, only PECH2 and PECH5 were selected.

Thermogravimetric analysis curves of blends of various ratios of PVC/PECH1 are shown in Figure 2. From the curves, it is clearly observed that the onset temperatures of degradation ascend to 260°C. This temperature is much higher than that of pure PECH1 and only a little lower than that of PVC, which indicates that the thermal stability of PVC/PECH blends is much better than that of pure PECH. This may be attributed to the addition of dibutyltin dilaurate, which restrains the rupture of C—Cl bond and makes PVC difficult to degrade. Because of the similarity of PECH and PVC, this stabilizer is also effective to PECH and favors its thermal stability. Therefore, it does not need to add other stabilizers into the blend system when used. For the samples of four PVC/PECH1 ratios, the onset temperatures of degradation get a little lower as the plasticizer amount increases, but all of them are quite near. The curves have two steps, due to the addition of PVC. The onset temperatures of the second step are between 445 and 460°C, a little higher than that of pure PVC. This may be attributed to the reduction of the content of PVC compared to pure PVC in the blends. The residual weight percent after the first step of degradation

drops markedly as the plasticizer content increases, because PECH loses most of its weight in this step while PVC does not. The less the PVC mass content, the fewer residues left. After the second degradation step, samples of each ratio come to a minimum weight, about 11% of the initial one.

Studies of tensile properties

PECHs of different molecular weights were characterized by tensile tests. Only mass ratio of PVC/PECH-90/10 was selected, with the curves shown in Figure 3 and date shown in Table II. The relationships between yield stress, break stress, elongation at break and the corresponding M_n values are shown in Figure 4. It is found that the molecular weight of the plasticizer has a considerable influence on the tensile properties. With the increase of the molecular weights of PECHs, the stress tends to rise and becomes stable at about 35 MPa between the yield point and the break point. Strength is an important factor when evaluating plastics, which reflects the interaction between PVC and PECH. PECH has a long, soft chain which could entangle with other molecules, especially macromolecules, like PVC. Therefore, when increasing the molecular weight of PECH, the entanglements of the polymeric chains turn to be more significant, which leads to the increase of the strength. As a result, the strength of the blends rises with the molecular weight of PECH. However, the yield and the break strength both experience an extreme value over this molecular weight range. To interpret this phenomenon, compatibility is involved here. Small plasticizer molecules could easily penetrate into the polymer matrix, but large ones do not. They tend to agglomerate and
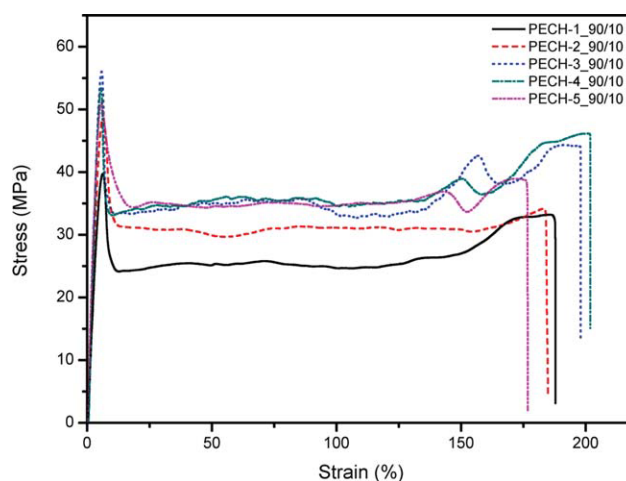

Figure 3 Stress–strain curves of PVC/PECH blends with various PECH molecular weights. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Tensile Data of PVC/PECH Blends

Samples	PVC/PECH (g/g)	Young's modulus (MPa)	Stress at yield (MPa)	Stress at break (MPa)	Elongation at break (%)
PVC	100/0	1064	53.4	49.4	70.4
PECH1	90/10	735	39.7	33.2	87.7
	80/20	369	19.3	24.6	166.0
	70/30	357	18.0	20.7	171.8
	60/40	333	16.8	17.3	161.5
PECH2	90/10	895	48.5	34.2	84.0
PECH3	90/10	1065	56.0	44.3	97.9
PECH4	90/10	1039	53.4	46.1	101.8
PECH5	90/10	993	51.0	38.9	76.6

are difficult to mix well with other polymer molecules. Thus, the compatibility becomes weak. For PVC/PECH system, the increase of the molecular weight of the plasticizer is also negative to the compatibility with PVC. The enhancement of strength with increasing the molecular weight and the resulting bad compatibility counteract with each other. As the two factors compete, the yield strength comes to the maximum at PECH3 and the break strength at PECH4. The elongation at break also experiences a maximum value at PECH4. The elongation at break of PECH5 is the lowest, which could be possibly interpreted by the same mechanism. The molecular weight of PECH5 is much higher than others, so interacts worst with PVC molecules. Therefore, it has the lowest elongation rate.

PVC/PECH1 blends of different ratios and pure PVC were also characterized by tensile tests, with the curves shown in Figure 5 and data shown in Table II. From the graph, it is obviously observed that the stress changes a lot when varying the PVC/PECH1 ratio. PVC is a kind of hard and brittle material, which has the highest tensile stress, but the lowest elongation at break in the graph. As the content

of PECH1 rises to 10 wt %, the stress decreases markedly, including stress at both yield and break. The elongation at break increases at the same time. As the plasticizer content continues to increase, the same trend is observed. The phenomenon is attributed to the plasticization of PECH to PVC. When mixing soft molecules into PVC matrix, like PECH, the original strong dipole–dipole interaction between PVC molecules is partially destroyed, and PVC-PECH interaction forms. PECH has an ether group in every unit, which could rotate freely and show soft properties. Therefore, PVC is provided with more free volume and mobility, and the material becomes soft and prone to deformation. The elongation at break also increases with the of PECH content. The sample of PVC/PECH1-70/30 has the highest elongation rate, 172% approximately. When increasing PECH amount to PVC/PECH1-60/40, the stress goes on decreasing, but elongation at break falls to 161%. This may be caused by phase separation. There is a concentration range for both polymers when mixing them together. If either
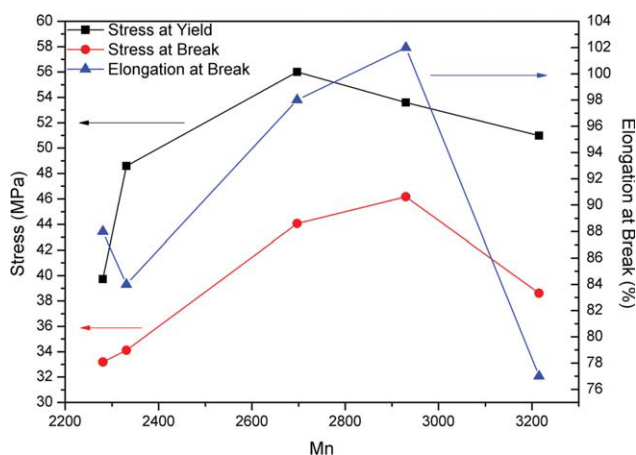

Figure 4 The yield stress, break stress and elongation at break as functions of M_n of PECHs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
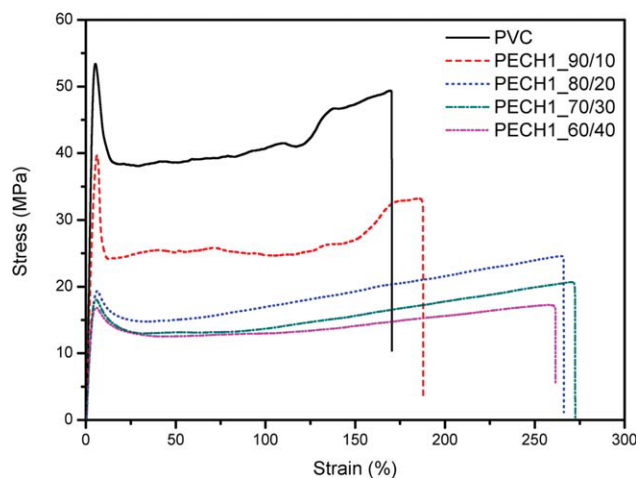

Figure 5 Stress–strain curves for samples of different PVC/PECH1 ratios: 90/10, 80/20, 70/30, and 60/40. Pure PVC here is taken as compare. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
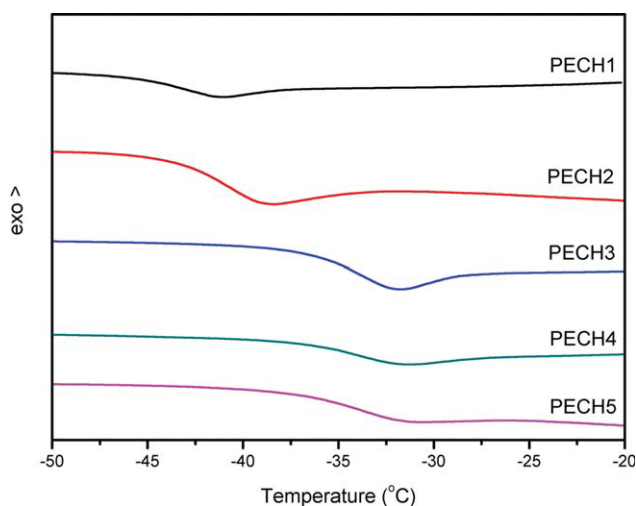
Figure 6 The differential scanning analysis curves of five PECHs of different molecular weights. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

component is over this range, they become incompatible and phase separation takes place. In the PVC/PECH system, the mass ratio of PVC/PECH1-60/40 may be out of the compatible range. Therefore, there is additional PECH in the matrix, which brings down the molecular interactions and impairs the tensile properties.

Phthalates, as traditional plasticizers for PVC, have been studied over decades of years. Crespo et al.[29] studied the tensile properties of PVC/DEHP blends. As the content of DEHP was varied from 30 to 100 p.h.r., the tensile strength of the blends dropped from 17.2 to 6.6 MPa, while the elongation at break increased dramatically from 185 to 500%. Pena et al.[24] investigated the effect of dioctyl phthalate (DOP) on the tensile properties of PVC. It was found that the tensile strength of the PVC/DOP blends dropped from 22.5 to 5 MPa as the content of DOP was varied from 20 to 50 wt %. The curve of elongation at break versus DOP contents quite resembles that of PVC/DEHP blends. For PVC/PECH system, the tensile strength is similar to those of PVC/DOP and PVC/DEHP systems; however, the elongation at break is far less than that of the latter ones. Thus it can be concluded that PVC/PECH blends can be applied as a kind of plastic which bears more stress but causes little strain.

Studies of the glass transition temperature of PECH

Figure 6 shows the differential scanning analysis curves of five PECHs of different molecular weights. The temperature range was set from -70 to $30°C$, but the glass transition temperatures (T_g) were all between -50 and $-20°C$. Therefore, only this narrow

temperature range was selected here. For each curve, there is a slope, and the midpoint of it corresponds to T_g, which is listed in Table III. The temperature range of the slope is $5°C$ round, a little big, because of the polydispersity index, especially PECH5 with the largest PDI. It is also observed that the molecular weight has a great influence on the glass transition temperature. At a relatively low M_n, the glass transition temperature is also very low, even up to $-44°C$. This quite low glass transition temperature endows the material with an inherent plasticizer potentiality. With M_n increasing, the glass transition temperature rises rapidly up to $-34°C$, and becomes stable. The chain-ends effect is involved here to explain the influence of the molecular weight of PECH on its glass transition temperature. Every chain end induces some free volume to the molecules. Low molecular weight plasticizer molecules can move more freely for it has more chain-ends, which brings about a drop of glass transition temperature. However, higher molecular weight of the plasticizer allows more entanglements and provides fewer chain-ends per mass plasticizer. Therefore, a rise of glass transition temperature takes place.

Studies of DMA properties

The storage modulus, loss modulus and tan δ values of various PVC/PECH1 ratios are shown in Figure 7(a–c), respectively. The T_g values obtained from both E'' and tan δ curves are shown in Table IV. It can be observed from Figure 7(a) that the storage modulus decreases with increasing the amount of PECH plasticizer, despite it is not obvious when PECH is below 10 wt %. This phenomenon corresponds to the softening effect of the plasticizer to PVC. The improvement of the mobility of PVC molecules brings the storage modulus down. However, the loss modulus plateau values experience a maximum at PVC/PECH1-80/20 in Figure 7(b). This may be interpreted that the friction resistance of polymer molecules increases firstly and then drops. The better PVC and PECH mix together, the more the friction resistance is. When PECH1 is over 20 wt %, the compatibility may fall. There is a peak in each loss modulus curve, and it comes to a lower temperature when the plasticizer amount increases. In the PECH1 concentration range from 0 to 10 wt %, this phenomenon is especially obvious. This is because

TABLE III
Glass Transition Temperature Values of Five PECHs of Different Molecular Weights Characterized by DSC

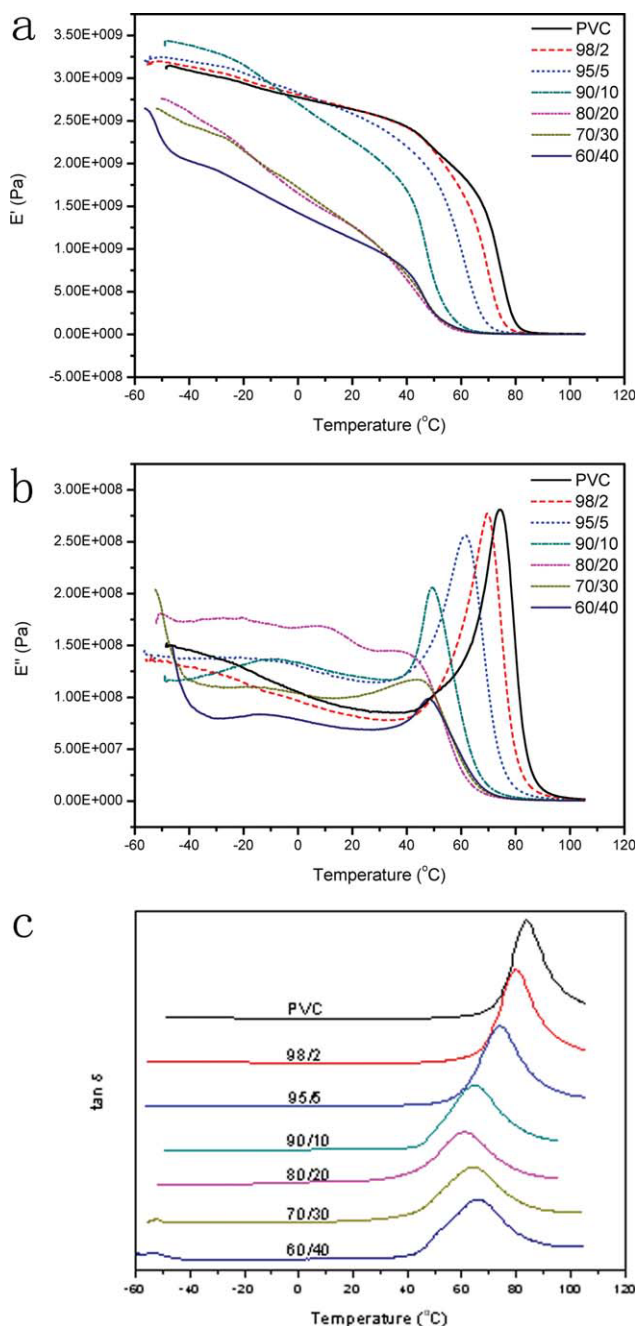| Plasticizer	PECH1	PECH2	PECH3	PECH4	PECH5
T_g (°C)	−42.9	−40.8	−33.9	−33.8	−33.8

a

b

c

Figure 7 The storage modulus E' (a), loss modulus E'' (b), and tan δ values (c) of samples of various PVC/PECH1 ratios, respectively, characterized by dynamic mechanical analysis. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

PVC is more sensitive to the addition of PECH1 in this range. When above 20 wt %, the peaks become small and the corresponding temperature increases with increasing the amount of PECH1. This seems a little abnormal for common plasticizers, and indicates that the compatibility becomes rather bad when the amount of PECH1 is above 20 wt %.

TABLE IV
Glass Transition Temperatures of PVC/PECH Samples Characterized by DMA

Samples	PVC/PECH (g/g)	T_g (°C)[a]	T_g (°C)[b] Phase 1	Phase 2
PECH1	98/2	69.7	79.7	–
	95/5	61.5	73.9	–
	90/10	49.5	64.7	–
	80/20	35.7	60.7	–
	70/30	43.9	63.9	−52.5
	60/40	47.9	66.0	−53.4
PECH2	90/10	50.8	68.2	–
PECH3	90/10	58.7	74.8	–
PECH4	90/10	59.9	75.3	–
PECH5	90/10	60.4	75.0	–
PVC	100/0	74.3	83.8	–

[a] Obtained from the peaks of E'' curves.
[b] Obtained from the peaks of tan δ curves.

It has been reported that both E'' (loss modulus) curves[30,31] and tan δcurves[32,33] can indicate the glass transition temperature. In our study, both E'' and tan δhave the same trend of T_g, however, tan δ curves are more distinct and easier to getan accurate T_g, especially T_g of PECH-rich phase. Figure 7(c) shows the relationship between tan δ values and the amount of PECH1 in the blends, and the curve of T_g versus PECH1 concentration is displayed in Figure 8. It is easily seen that the glass transition temperature decreases almost linearly before the concentration of 10 wt %. This drop continues till 20 wt %, and then $T_g$rises up with PECH1 amount increasing. However, for two samples of PVC/PECH1 (70/30) and (60/40), there is a little peak at −52°C round each, while there is no such a peak for other samples. Referring to the DSC curves of PECH, this peak refers to the glass transition temperature of PECH1. Therefore, it is distinctly concluded that when the
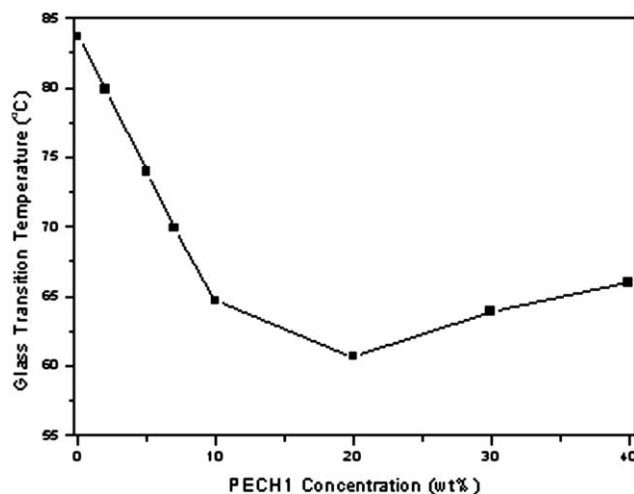

Figure 8 The relationship between PECH1 concentration and the glass transition temperature.
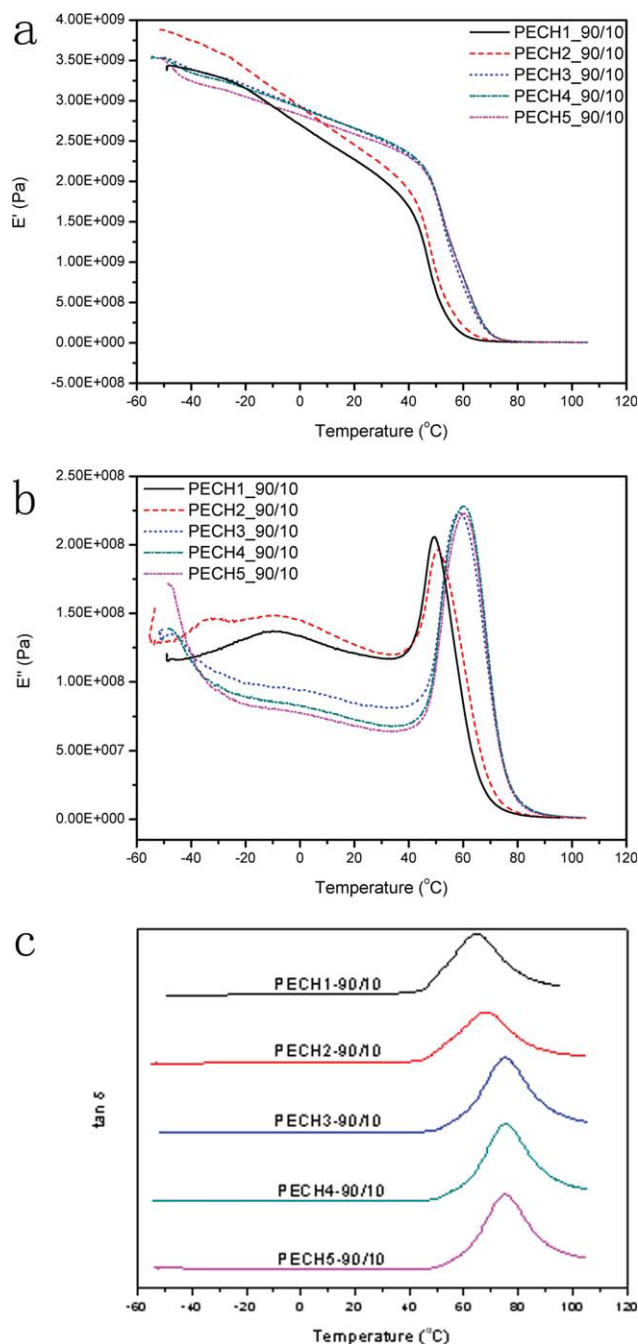
Figure 9 The storage modulus E' (a), loss modulus E'' (b), and tan δ values (c) of samples of various molecular weight PECHs and the same PVC/PECH ratio (90/10), respectively, characterized by dynamic mechanical analysis. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

concentration of PECH1 arrives at 30 wt %, the compatibility of two polymers can no more hold them together, and phase separation takes place, resulting in a PVC-rich-phase and a PECH1-rich-phase. Each phase is a mixture which includes both components. The blend of PVC/PECH1-80/20 is in a supersaturated state, and a little more addition of PECH1 results in the phase separation, and the concentra-

tion of PECH1 in PVC matrix decreases. The more amount of PECH1 added, the less amount of it left in PVC matrix. Therefore, when reaching 30 wt %, PECH1 phase occurs and takes some amount of PECH1 away from PVC matrix, and this reduces the plasticization efficiency. This conclusion well explains why T_g and the peak temperature of loss modulus curves get higher above PECH1 concentration of 20 wt %.

Figure 9 shows the variation of storage modulus, loss modulus and tan δ values with temperature for samples of PVC/PECH1, PVC/PECH2, PVC/PECH3, PVC/PECH4, and PVC/PECH5 of the same mass ratio 90/10. In Figure 9(a), it is observed that the molecular weight of PECH has a great influence on the storage modulus of the blends, which gets higher with the molecular weight. Figure 9(b) shows that the loss modulus values get lower with increasing the molecular weight of PECH, and the peak of the curve occurs at a higher temperature. The curves of PVC/PECH3, PVC/PECH4 and PVC/PECH5 in both Figure 9(a,b) are quite alike and nearly lap over each other.

The loss factor tan δ versus temperature for these samples is shown in Figure 9(c), with the data shown in Table IV. The glass transition temperatures of the blends get higher with increasing the molecular weight of PECH plasticizers. This may be because that the glass transition temperature of pure PECH also increases with the increasing of its molecular weight, according to the DSC results. When the molecular weight is great enough, the glass transition temperature becomes quite stable for both pure PECH and the blends.

From the DMA curves above, it could be seen that the compatibility between PVC and PECH is quite good. However, small molecule plasticizers, such as phthalates, have a better compatibility with PVC. Phthalates could be mixed up to 50 wt % of the blend, and a quite low T_g was obtained.[24,29] The reason for the difference lies in the large difference between their molecular sizes. Macromolecules, such as PECH, are rather difficult to penetrate into other polymer matrix, but small molecules are quite easy to disperse in it. Therefore, phthalate plasticizers could help PVC to reach a strikingly low T_g while PECH could not.

CONCLUSIONS

Different with traditional polyester PVC plasticizers, polyepichlorohydrin (PECH) was studied as a type of polyether plasticizer in this work. Due to its structural similarity with PVC molecules, there is very good compatibility between the two polymers. TGA was used to determine the thermal stability of pure PECH and its blends with PVC. The results show

that the thermal stability of pure PECH is undesirable, while PVC/PECH blends are rather stable to heat in the presence of organotin. Tensile tests indicate that PECH markedly plasticizes PVC and the elongation at break is improved, accompanied by the drop of tensile strength. DSC results indicate PECH has a relatively low glass transition temperature as a plasticizer. DMA characterization shows that when the concentration of PECH is below 20 wt %, it is well compatible with PVC and efficiently lowers the glass transition temperature of the blend. However, above 20 wt %, phase separation takes place, which worsens the mechanical properties of the material.

In addition, the impact of the molecular weight of PECH on the plasticization was investigated. Increase of the molecular weight of PECH makes more PVC molecules bind together onto PECH chains, which results in the rise of modulus, glass transition temperature, tensile strength as well as elongation at break. However, increase of molecular weight is rather adverse to the compatibility of both polymers. These properties are the consequence of the competition of the two factors earlier.

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