Preparation and Chemical Reactions of Rigid Cross-Linked Poly(vinyl chloride) Foams Modified by Epoxy Compounds

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ABSTRACT: A novel method to prepare semi-interpenetrating polymer network rigid cross-linked poly(vinyl chloride) (c-PVC) foams with improved shear toughness in the absence of anhydride components is reported. The cross-linked network structure in the c-PVC foams was composed of polyurea network modified by epoxy structure. The cellular morphology was characterized by scanning electron microscopy. Tensile, compressive, and shear properties of the foams were studied. The obtained c-PVC foams showed high shear properties compared with the comparative samples with the same density and cellular morphology. Possible reactions during the preparation of c-PVC foams were studied by means of Fourier transform infrared spectrometry and nuclear magnetic resonance measurements through the model experiments. The results showed that allophanate structure resulting from the reaction between isocyanate compounds and epoxy compounds formed in the molding step, which was included into the final cross-linked network in the cross-linking step. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40567.

INTRODUCTION

Rigid polymer foams are often used as a core in the sandwich structure of composites.[1] Besides reducing the weight of structure, the main functions of core are to separate and support face sheets, and transfer shear force between the face sheets when the sandwich structure is subjected to bending loads.[2] Thus, core materials should have enough strength and toughness to satisfy practical requirements. Although many foams (such as linear poly(vinyl chloride) [PVC] foam,[3] styrene acrylonitrile foam,[4] and polyethylene terephthalate foam[5]) have a higher shear strain, their shear strength is low. Rigid cross-linked PVC (c-PVC) foam is widely used as core material in sandwich structures for the applications where damage tolerance and weight saving are required; e.g., wind energy, aerospace, transport, etc.

So far there are two kinds of known methods for preparing c-PVC foams with an essentially closed cell structure.[6–11] A common method used in the industry for a long time was reported by the French company "Kleber Colombes."[12] To prepare high-performance c-PVC, a cross-linked structure linked to PVC matrix was formed by grafting reaction of an unsaturated acidic anhydride (such as maleic anhydride) and a monomer (such as styrene) after the cross-linking reaction between acidic anhydride and isocyanate compounds.[6] Another method for preparing c-PVC foams is the formation of a semi-interpenetrating polymer network (IPN) structure in the final c-PVC foams, in which a cross-linked network interpenetrating with PVC matrix results from the reaction between isocyanate (or/and polyisocyanate) and water or both water and acidic anhydride (such as phthalic anhydride [PA]).[13] In the above two methods, some chemical propellants were also added to control foam cellular structure via releasing gases (acting as foaming agents) at a certain temperature, such as azobutyronitrile, isobutyronitrile, or azodicarbonamide (AC).

The current commercially available c-PVC foams are produced using the second method based on the cross-linking system of PA and isocyanate.[13] Scheme 1 shows the main reactions in the preparation of c-PVC. When isocyanate reacts with water, diamines and carbon dioxide are initially formed (Reaction 1). Then these diamines can further react with excess isocyanate to yield a linear or branched polyurea (Reaction 2).[7] Another reaction between isocyanate and phthalic acid (from the hydrolysis of PA) results in the formation of amide bond (Reaction 3).[13]
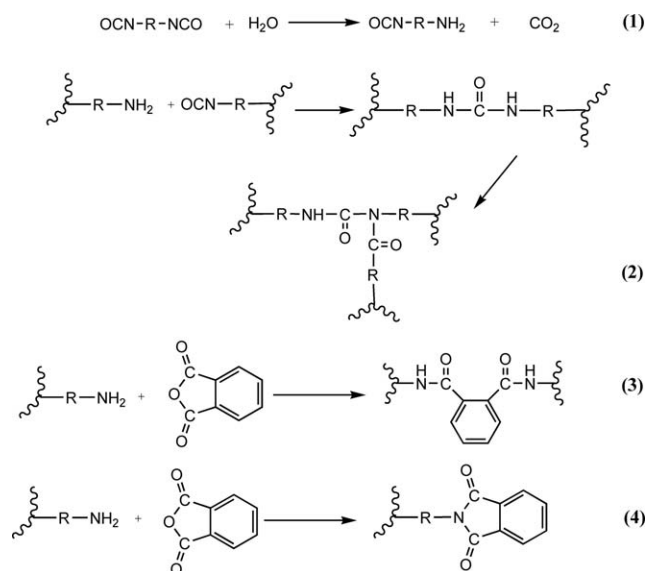
Scheme 1. Main reactions in the preparation of cross-linked poly(vinyl chloride) foam.

Moreover, the amide units become imide units via further cyclization and release of water (Reaction 4). Thus, in this case, the cross-linked network consists of the units of urea, amide, and imide.[14]

Compared with linear PVC foam, the presence of cross-linked network structures markedly strengthen and stiffen the frame structure of PVC foam. However, the foam prepared by the reported method is brittle, and impact strength or resistance to the rupture of foam core is not satisfactory for some applications involving dynamic loading,[10] probably resulting from too high rigidity of cross-linked networks within the frame structure (lack of flexibility). As a result, it fails in a resolved tension mode in a direction close to that of the major principal stress when subjected to shear loading or a combined stress.[15] Thus, how to modify the cross-linked network within c-PVC foams is a key factor to prepare a product with high strength and high toughness.

Some reports have shown that other kinds of foams, such as the shape memory polymer based self-healing syntactic foam[16–18] and functionally graded syntactic foam,[19,20] could be improved by designation of structure or material selection. However, for c-PVC foam, the cross-linking network is mainly concerned because the incorporation of isocyanate components and anhydride components with different chemical structures can effectively affect the mechanical properties of c-PVC foams. For example, the addition of tetrahydrophthalic anhydride and methyltetrahydrophthalic anhydride could improve the shear strain at failure.[8] Recently, the reactions involved in methyltetrahydrophthalic anhydride addition were reported,[9] and the epoxy compounds[10] or melamine[11] was used to modify PVC foam cross-linked by isocyanate–anhydride system. Although a higher shear failure strain was obtained, the strength and stiffness of the foams (such as compressive strength and shear modulus) were reduced greatly.[10] The epoxy compounds could react not only with amines from the hydrolysis of isocyanate, but also with organic anhydrides.

In this study, we explored a novel method to prepare c-PVC foams with improved impact strength in the absence of anhydride components, compared with c-PVC foams based on the isocyanate–anhydride system. The resultant c-PVC was a semi-IPN structure, in which the cross-linked network structure interpenetrating with PVC matrix was formed from the reaction between epoxy compounds and isocyanate compounds. In this case, the cross-linked network structure was polyurea modified by the addition of epoxy compounds. Thus, the flexibility of the cross-linked structure could be improved. Chemical structure of the isocyanate–epoxy c-PVC foams and possible chemical reactions involved in the preparation process were investigated in detail.

EXPERIMENTAL

Materials
Poly(vinyl chloride) (PSH-30, degree of polymerization 1630–1830) from Shenyang Chemical Company was used as the matrix. Toluene-diisocyanate (TDI), which consisted of 80 wt % of toluene-2,4-diisocyanate and 20 wt % of toluene-2,6-diisocyanate, was obtained from Mitsui Takeda Chemicals Inc. Epoxy resin (E51) with epoxy value of 0.52 mmol/100 g and hydroxyl value of 0.04 mmol/100 g was purchased from Blue Star New Chemical Materials Company. Azodiisobutyronitrile (AIBN) from Tangshan Chenhong Industrial Company and AC from Hangzhou Haihong Fine Chemical Company were used as blowing agents. PA from Sinopharm Chemistry Regent Company was used to prepare comparison sample.

Preparation of PVC Foams
In the preparation of starting mixture, 330 g TDI and a certain amount of E51 were first mixed with stirring; then, 610 g PVC, 50 g AIBN, and 10 g AC were added and mixed again. The obtained liquid starting mixture was put into a compression mold with a sealed cavity (220 mm × 220 mm × 25 mm). This mold was heated to 175°C and kept for 10 min under a pressure of 15 MPa. In the next step, the plastic mass was cooled and solidified, and the pressure was gradually reduced to the atmospheric pressure. Then the molded sample was removed from the mold and immersed into a water bath of 95°C. After expanding to a required size, the sample was removed into the surroundings with water vapor at 65°C and was kept for 10 days.

The amount of added E51 was changed in the following order: 10, 20, 50, and 100 g, and the corresponding final foams were named 10E, 20E, 50E, and 100E, respectively. The density of all the foams was about 65 kg/m^3 except for 100E (60 kg/m^3). The comparative foams 0E-65 and 20PA-65 were designed without E51 and with 20 g PA instead of E51, respectively. The density of the two foams was 65 kg/m^3.

Extraction of the Resultant Foams
The foam 100E was wrapped with a 120 mesh stainless steel screen cloth and was extracted with tetrahydrofuran (THF) to give the solid (F-G); then, the extracted solution was precipitated in diethyl ether to get the solid material (F-S), and the filtrate was evaporated to get the liquid material (F-L). The above separated substances were dried *in vacuo*.

Table I. Properties of Cross-Linked Poly(vinyl chloride) Foams

Foam	0E-65	20PA-65	20E-65	HP60[a]
E51 (%)	0	0	2	–
PA (%)	0	2	0	–
Density (kg/m^3)	64.0 ± 1.0	65.0 ± 0.5	65.5 ± 0.5	65
Compressive strength (MPa)	0.90 ± 0.02	0.95 ± 0.02	0.95 ± 0.02	0.95
Compressive modulus (MPa)	42 ± 3	40 ± 3	41 ± 3	–
Tensile strength (MPa)	1.87 ± 0.01	1.90 ± 0.01	1.96 ± 0.02	1.8
Tensile modulus (MPa)	81 ± 4	78 ± 4	84 ± 3	75
Yield shear strength (MPa)	0.75 ± 0.02	0.93 ± 0.02	0.90 ± 0.03	0.85
Ultimate shear strength (MPa)	0.78 ± 0.03	0.99 ± 0.03	1.05 ± 0.03	–
Shear modulus (MPa)	19 ± 1	20 ± 1	25 ± 1	20
Failure strain (%)	23 ± 2	22 ± 2	35 ± 2	23

[a] Divinycell HP60 from DIAB technical data.

Reaction between PVC and E51

PVC (61 g) and E51 (10 g) were mixed in blender at 175°C for 10 min, and the mixture was dissolved in THF and precipitated in ethanol for three times. The solid fraction (PVC/E-S) was filtrated, and the solvent was removed from the filtrate by rotary evaporator to give a viscous liquid fraction (PVC/E-L). The above separated substances were dried *in vacuo*.

Reaction between Hydrochloric Acid and E51

About 42.5 ml of 36% hydrochloric acid was added drop wise into the solution of 100 g E51 in 250 mL chloroform with stirring in an ice bath. Then the mixture was stirred at room temperature for 30 min. The chloroform phase was washed successively with water, aqueous sodium bicarbonate, and water, then dried with anhydrous sodium sulfate, and chloroform was evaporated to obtain an adduct (EOH) of hydrogen chloride (HCl) and E51.

Reactions of E51, EOH, and TDI

Three comparative experiments were conducted. The first was the system of TDI and E51 (T/E). The second was the system of TDI and EOH (T/EOH). The last was the system of only TDI. At first, the mixture of TDI and E51 or EOH in a weight ratio of 5 : 1 (T/E-a for the system containing E51 and T/EOH-a for the system containing EOH) was placed in a sealed mold. Then, the mold was heated to 175°C at 10 MPa pressure and kept for 10 min before being cooled to room temperature. The reaction mixture (T/E-b for the system containing E51 and T/EOH-b for the system containing EOH) was removed from the mold into a polypropylene container, and treated at 95°C vapor for 12 h to get a solid (T/E-c for the system containing E51 and T/EOH-c for the system containing EOH). After the third system (only TDI, without E51 and EOH) was subjected to the above process, a solid product (P-TDI) was obtained, which was used as the control.

Characterization

Chemical structure of c-PVC foam samples was investigated by Fourier transform infrared spectrometer (FTIR; VERTEX 70, Bruker). E51 and embryo were dissolved in THF, and two to three drops of the solution was deposited on a KBr plate to form a liquid film. After the solvent was evaporated, a thin film of sample was left. The cross-linked foam sample swelled in THF was ground with KBr. Then, the solvent was evaporated, and a KBr disk was obtained by pressing the mixture powder in a pellet die.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV 400, operating at 200 MHz for ^{1}H-NMR and ^{13}C-NMR. The analysis was carried out in CDCl$_3$, with tetramethylsilane as the internal standard. The ^{13}C cross polarization magic-angle spinning spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4-mm standard bore CPMAS probehead whose X channel was tuned to 100.62 MHz for ^{13}C and the other channel was tuned to 400.18 MHz for broad band ^{1}H decoupling, using a magnetic field of 9.39 T at 297 K. The dried and finely powdered samples were packed in the ZrO$_2$ rotor closed with Kel-F cap and were spun at 5 kHz rate. The experiments were conducted at a contact time of 2 msec. A total of 1500 scans were recorded, with 3 sec recycle delay for each sample. All ^{13}C cross polarization magic-angle spinning chemical shifts were referenced with the resonances of adamantane (C$_{10}$H$_{16}$) standard (δ(CH$_2$) = 38.5).

Mechanical property tests (tension, compression, and shear) were performed on foam samples using a screw-driven Instron 5869 test machine. The specimens were cut by a diamond tool. Tension tests were conducted according to ASTM C297, using cuboid specimens of gauge length 30 mm and cross-section of 50 mm × 50 mm for each foam sample. The specimens were adhered to the loading blocks using a two-part epoxy glue cured at room temperature. Loading was parallel to the rise direction of the foam at a displacement rate of 0.50 mm/min. Compression tests were conducted on cuboid specimens of gauge length 30 mm and cross-section 45 mm × 45 mm at a rate of crosshead displacement of 3 mm/min, with the loading direction parallel to the rise direction, according to ASTM D1621-04a. The displacement measurement was made using the test machine crosshead drive system. The tensile shear tests were performed on specimens 12 mm thick, 150 mm long, and 50 mm wide in accordance with ASTM 273. In specimen manufacturing, the
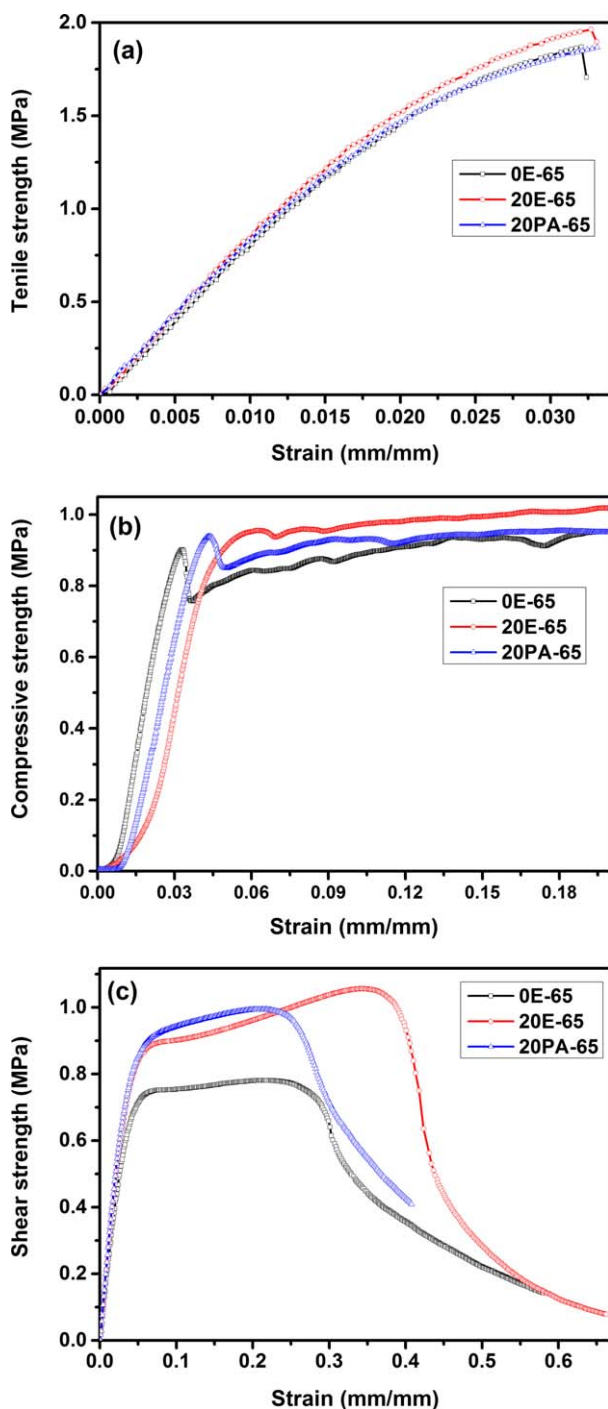
Figure 1. Stress–strain curves of the foams for (a) tensile, (b) compressive, and (c) shear strengths [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

steel surfaces of shear test rig were degreased and abraded, and the foam specimens were adhered to the grips using a two-part epoxy adhesive, with room temperature cure. The average value of the two extensometers fixed on both sides of grips was defined as the value of strain. The six specimens were tested for each samples of foam and each loading configuration, and the typical measured responses at room temperature were obtained. The scatter was found to be negligible: the peak strength in

tension, compression, and shear varied by only a few percentage for the identical specimens from the same sample.

RESULTS AND DISCUSSION

Mechanical Properties and Cellular Morphologies of c-PVC Foams

Table I shows the mechanical properties of c-PVC foams with different compositions. The stress–strain curves are shown in Figure 1. Here, the densities of all c-PVC foam samples were about 65 kg/m^3. With the addition of 2 wt % PA or E51 in the starting materials for the preparation of c-PVC foams, the mechanical properties increased to different degrees. For example, compared with 0E-65 sample, the compressive strength of 20E-65 (adding 2 wt % E51) increased from 0.90 to 0.95 MPa, and the tensile strength also increased. The foam 20E-65 presented about 35% failure strain, 1.5 times higher than that of the control samples (0E-65 and commercial product HP60). At the same time, this foam showed higher yield shear strength than that of the commercial product.

It is an interesting issue why the mechanical properties (especially shear properties) of 20E-65 are higher than those of 0E-65, although they show the same density. As we know, the mechanical properties of a foam depend on not only foam cellular structure but also chemical structure of the polymer matrix. Figure 2 shows the scanning electron micrographs of c-PVC foams. All the foams presented similar morphologies of irregular polyhedron cells. The average diameter of the cell was about 600 μm in spite of the uneven distributions in some samples. Thus, the difference in the mechanical properties of the foams cannot be ascribed to the foam cellular structure, which should be related to the chemical structure of the matrix in the c-PVC foams. Several chemical reactions are possible during the preparation process of c-PVC foams. The addition of epoxy components probably causes some change in the final matrix of c-PVC foams. Thus, possible chemical reactions and chemical compositions in the resultant c-PVC foams were studied in the following sections.

FTIR Characterization of c-PVC Foams

To analyze the chemical reactions occurring during the preparation of c-PVC foams, the foam sample (100E) was extracted using THF as the solvent. Three fractions were obtained after extraction: the fraction insoluble in THF (F-G, cross-linked network), the fraction insoluble in ether but soluble in THF (F-S), and the fraction soluble in both ether and THF (F-L), and their contents were 47, 44, and 9 wt %, respectively. The FTIR spectra for these fractions are shown in Figure 3. The FTIR spectrum of the F-G fraction was similar to that of P-TDI (a product from the reaction between isocyanate and water). This showed that the insoluble fraction in the c-PVC foam was mainly a reaction product of TDI with water. When compared with FTIR spectrum of P-TDI, there was an absorption peak at 1063 cm^{-1} in the F-G fraction. This vibration peak was assigned for aryl ether bonding,[21] indicating that there was a certain amount of epoxy structure in the cross-linked network of c-PVC foams. On comparing FTIR spectra of F-L fraction with those of E51, it was found that the epoxy absorption at 919 cm^{-1} still remained in the FTIR spectrum of F-L fraction, meaning that the main component of F-L was epoxy resin. However, the peak at 1725 cm^{-1} in the F-L fraction was
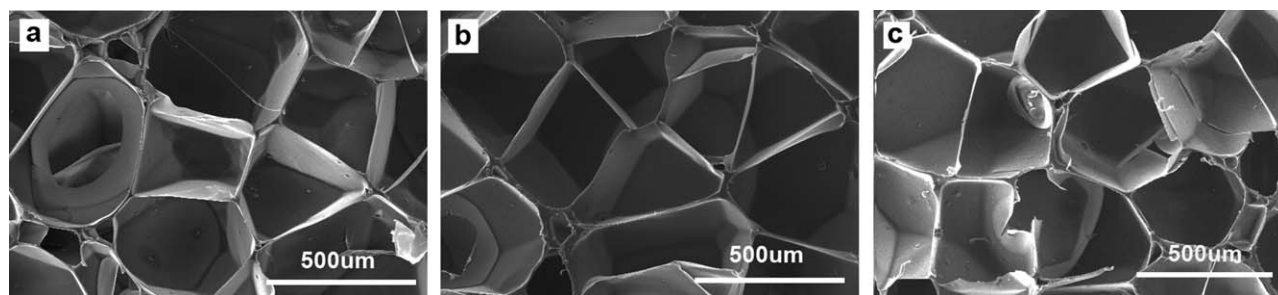
Figure 2. Scanning electron micrographs of cross-linked poly(vinyl chloride) foams: (a) 0E-65; (b) 20E-65; and (c) 20PA-65.

attributed to carbonyl group,[22] which resulted from urethane formed in the reaction between hydroxyl compound and isocyanate in the mixtures. The source of hydroxyl compound needs further investigation. From the FTIR spectra analysis, it was also inferred that F-S was mainly a PVC resin with some of the reaction product of TDI with water.

The Reaction Products between PVC and E51
As already known, PVC will degrade to release some amount of HCl at high temperature.[23] The released HCl probably reacts with the epoxy group of E51 during preparation of c-PVC foams. To obtain the reaction information between PVC and E51, FTIR and NMR were used to characterize possible reaction products. The ^{1}H-NMR spectra of the samples are shown in Figures 4 and 5. The chemical structures of E51 and EOH (E51 addition product with HCl) are presented in Figure 5. The formation of reddish brown reaction mixture between PVC and E51 implied a serious dehydrochlorination of PVC. The hydrogen signal from the benzene ring was not found in ^{1}H-NMR spectrum of PVC/E-S (Figure 4), implying that PVC/E-S was mainly composed of PVC. This confirmed that the grafting

reaction of epoxy component onto PVC, as described in the literature,[24,25] did not occur. However, the reaction between E51 and HCl from PVC to form EOH took place, because about 10 mol % EOH was found in the liquid fraction (PVC/E-L) according to its ^{1}H-NMR spectrum (Figure 5).

TDI Reactions with E51 and EOH
For more information about the reactions in the c-PVC foams, two model reactions were designed. The mixture of 50 g TDI and 10 g E51 (or EOH) was subjected to the same process as the preparation of c-PVC foams. The raw materials and the samples from different treatments were characterized by FTIR [Figure 6(a)]. Compared with that of E51, the absorption peak at 3510 cm^{-1} in the FTIR spectra of T/E-a (because of the presence of very small amount of OH in the E51) disappeared; meanwhile, a weak absorption band appeared at 1735 cm^{-1}. It was ascribed to free C=O from the reaction between the isocyanate and the hydroxyl of epoxy resin,[26] as there was no other reaction when the E51 was mixed with TDI in the first step if the water was completely removed. In contrast, there was an obvious absorption at 1735 cm^{-1} in T/EOH-a. Considering the presence of hydroxyl group in the EOH resulting from the reaction between E51 and PVC, it was reasonable that the
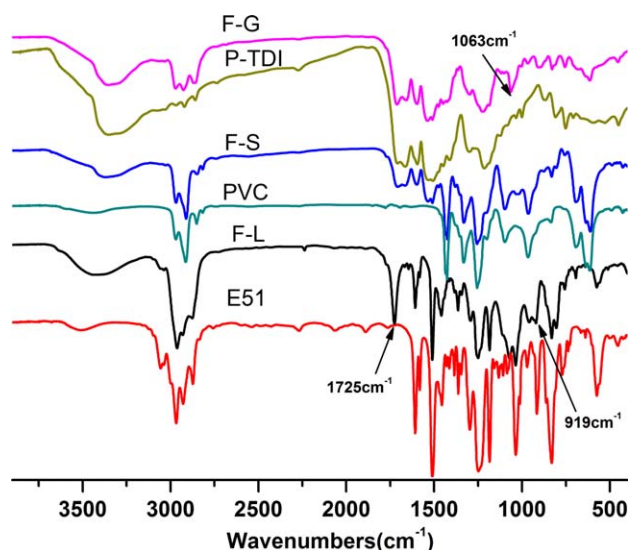

Figure 3. Fourier transform infrared spectra for E51, poly(vinyl chloride), P-TDI, and the components of foam 100E (F-G: fraction insoluble in tetrahydrofuran (THF); F-S: fraction insoluble in ether but soluble in THF; F-L: fraction soluble in ether) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
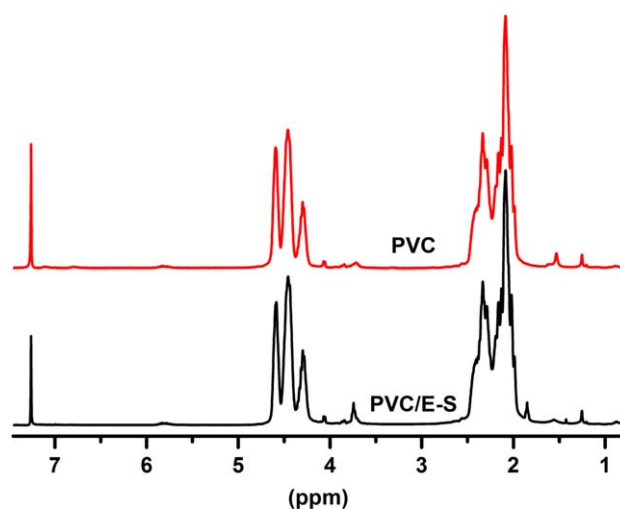

Figure 4. ^{1}H-NMR spectra of poly(vinyl chloride) (PVC) and the solid fraction from the reaction mixture of PVC with E51 after dissolution–precipitation purification (PVC/E-S) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
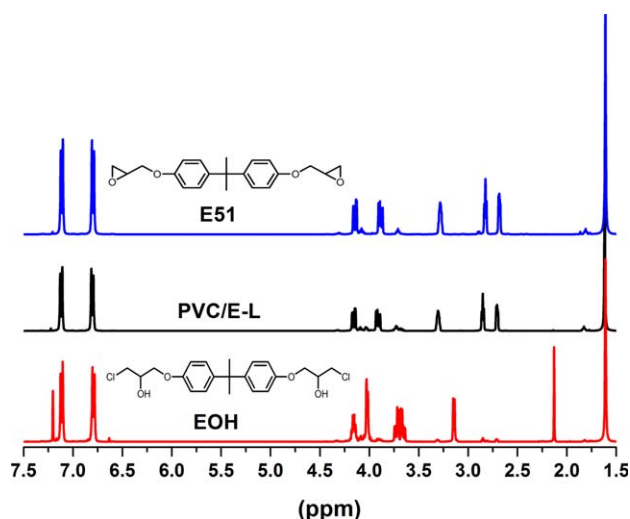
Figure 5. ^{1}H-NMR spectra of E51, EOH (the reaction product between E51 and hydrogen chloride), and the liquid fraction from the reaction mixture of poly(vinyl chloride) with E51 after dissolution–precipitation (PVC/E-L) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

absorption at 1735 cm^{-1} was from the reaction between isocyanate and EOH. In addition, there was a marked absorption at nearly 2271 cm^{-1} in the T/E-a and T/EOH-a because of the presence of the NCO group.

After heat treatment at 175°C, the absorption almost unchanged in the mixture of TDI and E51 (T/E-b in Figure 6), but the stronger absorption at 1728 cm^{-1} appeared in the prefoam of 20E (20E-p) when the absorption peak of benzene ring in E51 at 1618 cm^{-1} served as the reference. The ratio of TDI/E51 in the 20E and T/E-b was 165/10 and 50/10, respectively. Thus, the stronger free C=O absorption at 1728 cm^{-1} in the prefoam of 20E (20E-p) should result from the reaction between isocyanate and EOH formed *in situ* in the system.[27] Although there were the above chemical reactions in the T/E-a, T/E-b, and 20E-p, the absorption peak at 919 cm^{-1} (epoxy group) could also be observed in these samples [Figure 6(b)], meaning that some amount of epoxy structure still existed.[21]

Because E51 and EOH may react with TDI in the preparation process of c-PVC foams, to determine the chemical structure of the reaction products, EOH and E51 were mixed with TDI, respectively, and treated in accordance with the process of preparing the prefoam. ^{13}C-NMR and ^{1}H-NMR spectra were used to investigate the formation of urea, urethane, allophanate, and biuret linkages from the reaction between isocyanate and active hydrogen compounds.[28–32] Figure 7(a) shows the ^{13}C-NMR spectra of T/E-b and T/EOH-b. A very evident carbon signal of methylene attached to epoxy ring at 68.80 ppm (Scheme 2a) in the spectrum of the mixture of TDI and E51 (T/E-b) indicated that there was almost no reaction between TDI and E51. However, the signals of 154.91 and 151.06 ppm appeared clearly in the spectrum of the mixture of TDI and EOH (T/EOH-b), which corresponded to the two C=O carbons from allophanate (Scheme 2b), according to the literature.[33–35] The peak at 72.11 ppm was attributed to the tertiary carbon connected with oxygen

in allophanate. Enlargement of the N—H regions in the ^{1}H-NMR spectra for T/EOH-b is shown in Figure 7(a). The allophanate N—H proton resonances were found at 10.67 ppm (Scheme 2b).[35] The peak at 152.67 ppm was ascribed to the C=O carbon of urea from the reaction between isocyanate and the moisture during the preparation and the treatment.[27] The characteristic peaks (at 153.67 and 9.50 ppm) of the C=O carbon and N—H proton of urethane[35] were not found in the NMR spectra of T/EOH-b. Thus, the reaction products of TDI and EOH in the above process should be allophanate rather than urethane. Compared with the solid ^{13}C-NMR spectra of P-TDI, the spectra of 100E showed weak carbon signal peaks at 153 ppm (*) and 75 ppm (#) [Figure 7(b)], confirming the presence of allophanate cross-linked structure in the c-PVC foam.
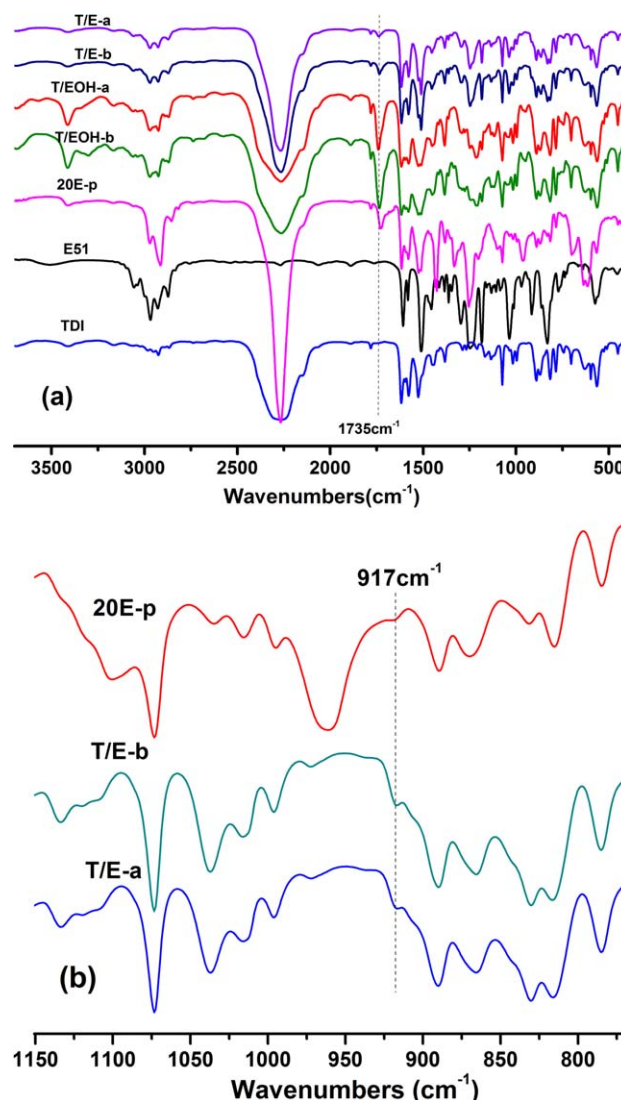
Figure 6. (a) Fourier transform infrared (FTIR) spectra of TDI, E51, 20E-p (20E prefoam), and the mixtures (TDI : E51 (or EOH) = 50 : 10 g) in the different steps: mixing at room temperature(T/E-a and T/EOH-a) and after treatment at 175°C for 10 min (T/E-b and T/EOH-b). (b) Zoom-in FTIR spectra of 20E-p, T/E-a, and T/E-b from 770–1150 cm^{-1} [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. (a) ^{13}C-NMR spectra of T/E-b and T/EOH-b and ^{1}H-NMR spectra of T/EOH-b. (b) Solid ^{13}C-NMR spectra of cured samples (T/E-c, T/EOH-c, P-TDI, and 100E) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scheme 2. Structures of (a) E51 and (b) allophanate.

Possible Reactions in the Preparation of PVC Foams

According to the above results, possible reactions during the preparation c-PVC foams are shown in Scheme 3. In the first step, water is completely removed, and there are no other reactions except that between the isocyanate and a small amount of hydroxyl of epoxy resin. If not, some polyurea is probably formed, and good foam cannot be obtained because of the lower elasticity of embryo. In the next step, the starting mixture is heated to a fixed temperature under a certain pressure. During this stage, AIBN decomposition occurs at first (Reaction 1). As the temperature increases continually, AC also begins to decompose (Reaction 2). PVC in the mixture will release HCl at high temperature (Reaction 3), and HCl can react with epoxy groups in the epoxy compounds to give hydroxyl compounds (Reaction 4). Because there is a large number of isocyanate group in the mixture, the hydroxyl formed *in situ* will react with isocyanate to give allophanate at high temperature (Reaction 5). As a result, one epoxy group is transformed into a structural unit with two isocyanate functional groups. In the next cross-linking treatment,

Scheme 3. Main reactions involved in poly(vinyl chloride) foaming process.

the isocyanate group including that from Reaction 5 will react with water to give amine and CO_2 (Reaction 6). The CO_2 can inflate the cell in the prefoam. In addition, the amine can react with isocyanate to form polyurea (Reaction 7). The biuret will be formed during further reaction between the isocyanate and urea (Reaction 8). The biuret linkage served as a cross-linked point in the network. The allophanate compounds with multi-isocyanate groups from Reaction 5 also contribute one or two cross-linked points. Thus, the epoxy compounds are introduced into the cross-linked network in the final c-PVC foams through the above reactions. The allophanate structure was included into the polyurea network, which will affect the mechanical properties of the final foam. A further investigation is going on in our laboratory.

CONCLUSIONS

A novel method to prepare semi-IPN c-PVC foams with improved shear toughness in the absence of anhydride components was successfully established. The cross-linked network in the resultant c-PVC consisted of polyurea cross-linked network modified by epoxy components. Possible reactions during the preparation of c-PVC foams were analyzed. Main reactions occurred during the heating molding step and the final cross-linking step. Allophanate structure was formed in the molding step, in which the reaction between isocyanate and the addition product of E51 and HCl (from the dehydrochlorination of PVC) resulted in the formation of allophanate. As a result, epoxy structure was connected into polyurea cross-linked network in the final c-PVC foams. Now we are studying the effects of E51 loading (epoxy compound) on mechanical properties and thermal properties of c-PVC foam. These results will be reported in the next article.

ACKNOWLEDGMENTS

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