



# Rigid cross-linked PVC foams with high shear properties: The relationship between mechanical properties and chemical structure of the matrix



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## ABSTRACT

Semi-IPN PVC foams with cross-linked polyurea network modified by epoxy resin (E51) were prepared in this work. Chemical structure and H-bonding of the foam matrix were characterized by FTIR. The effects of E51 content in the starting mixtures on tensile, compressive and shear properties of the resultant foams were studied. The changing trend of energy absorption capacities of the foams showed an inflection point at the content of 2 wt% E51. In this case, the foam with the density of 65 kg/m<sup>3</sup> presented a 35% shear failure strain with shear modulus of 25 MPa and shear strength of 1.05 MPa. Its energy absorption capacity was 1.8 times as that of the foam without E51. The relationship between mechanical properties and chemical structure of the matrix was discussed.

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## 1. Introduction

Although polyvinyl chloride (PVC) is a common resin, rigid cross-linked PVC (c-PVC) foams with an essentially closed cell structure show high performance, which is widely used as core materials in sandwich structures for the applications where damage tolerance and weight saving are required, for example, wind energy, transport, and industry applications [1,2]. A key factor for preparing high-performance c-PVC foams is the formation of cross-linked network within PVC matrix under the preconditions of good cellular structure. There are two kinds of method for preparing c-PVC foams: one of them is based on PVC grafting reaction of an unsaturated acidic anhydride (such as maleic anhydride) and a monomer (such as styrene) following the cross-linked reaction between acidic anhydride and isocyanate compounds [3]; the other is the formation of a semi-IPN (interpenetrating polymer network) 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) [4]. It can be seen that acidic anhydride is a necessary component in the two methods for the preparation of c-PVC foams.

In the foregoing part of this work [5], we found that the replacement of acidic anhydride by epoxy compounds is feasible to prepare c-PVC foams with high mechanical properties. Especially, the addition of epoxy compounds could obviously improve shear toughness of c-PVC foams without the sacrifice of strength and stiffness. By analyzing the chemical structure of cross-linked network in this modified c-PVC foam, it was found that the epoxy components were connected into polyurea cross-linked network by the formation of allophanate group, which changed the performance of cross-linked network. As a result, the mechanical properties of c-PVC foams were improved, especially shear properties. It was found that c-PVC foams with high shear strain and high shear modulus resulted from the formation of modified polyurea network by epoxy compounds in the semi-IPN PVC foams.

Considering that the amount of epoxy compounds in the starting mixture probably affected the formation of polyurea network, in this work, the influence of the content of epoxy compounds in the formulation of the starting mixtures on the mechanical properties of c-PVC foams was studied. However, as we know, the microstructure of foam (such as cell size and shape) has an important influence on mechanical properties [6–9], and the situation is similar in the case of PVC foams [9–11]. Thus we prepared a series of c-PVC foams with similar cell structure to study the effect of the chemical structure of the matrix on mechanical properties. A possible explanation about the changing trend of mechanical properties with the content of E51 was proposed.

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## 2. Materials and methods

### 2.1. Materials

Polyvinyl chloride (PVC) from Shenyang Chemical Company was used as matrix. Toluene-diisocyanate (TDI) 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 was purchased from Blue Star New Chemical Materials Company. Azodiisobutyronitrile (AIBN) from Tangshan Chenhong Industrial Company and azodicarbonamide (AC) from Hangzhou Haihong Fine Chemical Company) were used as blowing agents. Phthalic anhydride (PA) from Sinopharm Chemistry Regent Company was used to prepare comparison sample.

### 2.2. Preparation of rigid cross-linked PVC foams (c-PVC foams)

In the preparation of starting mixture, first 330 g TDI and a certain amount of E51 were preferably mixed under 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). The mold containing the starting mixture was heated to 175 °C and kept for 10 min under a pressure of 15 MPa. In the subsequent step, the plastic mass was cooled and solidified, and the pressure was gradually reduced until the atmospheric pressure was reached. 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 obtained foam samples were defined as xE, here x represents the loading of E51 in the starting mixtures. For example, 0E means that the loading of E51 was zero in the formulation of the obtained foam, and 30E means that the loading of E51 was 30 g in the formulations. The density of the resultant foams was about 65 kg/m<sup>3</sup>.

### 2.3. Characterizations

Tension, compression and shear tests were performed on foam samples using a screw-driven Instron 5869 test machine. The detail was shown in [supporting information](#). Scanning Electron Microscope (SEM, XL30 ESEM, PHILLIPS) was used to characterize the morphology of foam. Dynamic mechanical analysis was performed using ARES-G2 from TA instruments. Round samples (25 mm in diameter × 2 mm in thick) was held between two torsion clamps with a diameter of 25 mm. Tests were run from 30 to 150 °C with a temperature increases of 10 °C·min<sup>-1</sup> and a fixed oscillatory shear frequency of 1 rad·s<sup>-1</sup> under 1% strain amplitude. The loss factor tan δ (the ratio of the loss modulus to the storage modulus) were plotted as a function of temperature. The peak was defined as the glass transition temperature ( $T_g$ ) of foam. Chemical reactions during the preparation of c-PVC foams were investigated by Fourier transform infrared spectrometer (FTIR, VERTEX 70, Bruker).

## 3. Results and discussion

### 3.1. Cellular morphology of c-PVC foams

Generally, the mechanical properties of a foam depend on not only foam cellular structure but also chemical structure of polymer matrix [12]. The change in the composition of the starting mixtures will probably change the cross-linked network and foaming

behavior. To investigate the influence of polymer network on the mechanical properties, here we prepared a series of c-PVC foams with the density of 65 kg/m<sup>3</sup>. Fig. 1 shows SEM micrographs of c-PVC foams. All the foams presented the morphologies of polyhedron cells. The average diameter of cell was about 600 μm in spite of the uneven distributions in some samples. The change of cell sizes with the loading of E51 was not obvious. This showed that the addition of E51 component in the starting mixtures did not change the foaming behavior under the controlled foaming conditions. Therefore, we can study the relationship between mechanical properties of the foams and cross-linked network of the foams, in which all the foams have the same density and the same (or very close) cell structure.

### 3.2. Chemical structure analysis

The resultant foams were extracted by alcohol and acetone, respectively. Nothing could be extracted by alcohol from all the foams, indicating that all the E51 molecules took part in the cross-linking reaction completely. Only a trace of PVC was extracted by acetone from 0E, 10E and 20E. The amount of soluble fractions in acetone from 50E is less than 1 wt%. Fig. S1 (in the [supporting information](#)) shows FTIR spectra of the soluble fractions and the residue. The absorption peak at 915 cm<sup>-1</sup> (50E-L curve in Fig. S1) implied the presence of epoxy group in soluble fractions. These epoxy groups probably result from the incomplete reaction products of E51. The absorption peak at 830 cm<sup>-1</sup> (50E-G curve in Fig. S1) was ascribed to the p-substituted benzene ring structure from E51. Although the characteristic absorption peak at 915 cm<sup>-1</sup> could not be distinguished from the peak at about 910 cm<sup>-1</sup>, it is reasonable that some of epoxy groups existed in the cross-linked fractions of 50E. The presence of a large amount of E51 can block the decomposition of PVC (reaction (1) in [Scheme S1 of the supporting information](#)), which leads to the decrease of the amount of HCl originated from the decomposition of PVC. As a result, the amount of the product b (reaction (2) in [Scheme S1](#)) will increase. However, the product b cannot contribute to the cross-linking bridge (reaction (4) in [Scheme S1](#)). So the excessive E51 acts as “termination agent” to reduce cross-linked bridges.

Fig. 2a shows FTIR spectra of 0E, 20E and 20E-p foams. The 20E-p is the prefoam of 20E. There was an absorption peak at 1728 cm<sup>-1</sup> in the 20E-p (Fig. 2b), which was ascribed to the carbonyl group of allophanate [5]. Compared to 20E-p, the 0E and 20E showed a stronger absorption in the N-H stretching region from 3200 to 3500 cm<sup>-1</sup>. Furthermore, the absorption peak shapes of C=O from 1620 to 1800 cm<sup>-1</sup>, resulting from the reaction between isocyanate and water, were obviously different in the three samples (Fig. 2b). The fitting curves of C=O absorption band for the samples 0E, 10E, 20E and 50E through second-derivative spectroscopy method were used to analyze the change of C=O absorption peak [13–16]. The results are shown in Fig. S2 in the [supporting information](#). According to the assignment made by Priester et al. [17,18], free urea appeared at ~1715 cm<sup>-1</sup> and loosely H-bonded urea appeared at 1700–1650 cm<sup>-1</sup>, while H-bonded urea appeared at ~1640 cm<sup>-1</sup>. The assignments of absorption bands of the carbonyl in the FTIR spectra were listed in [Table S1 in the supporting information](#). The region from 1620 to 1700 cm<sup>-1</sup> was due to ordered and disordered H-bonded urea carbonyl [19]. Particularly, the peak at 1643 cm<sup>-1</sup> resulted from urea carbonyl forming ordered H-bonding [19], and other three peaks (1652, 1667, and 1685–1700 cm<sup>-1</sup>) were ascribed to urea carbonyl forming disordered H-bonding [14,20]. The peak at 1713 cm<sup>-1</sup> of 0E was ascribed to free urea carbonyl [21,22]. The peaks at about 1725 cm<sup>-1</sup> and 1746 cm<sup>-1</sup> were ascribed to the free allophanate carbonyl [5,23], and the one at ~1776 cm<sup>-1</sup> was ascribed to the carbonyl of TDI dimer [24]. The amount of free carbonyl in the

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