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IR study on hydrogen bonding in epoxy resin–silica nanocomposites

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Abstract

The chemical and physical interactions between ingredients in composites play an important role in the improvement of service properties. The nucleophilic addition between polymer and isophoron diisocyanate molecules was monitored by FT-IR technique. The intensity loss of isocyanate absorption band in conjunction with the intensity growth of carboxyl absorption band indicates the progress of reaction. FT-IR spectroscopy was also adopted to examine the intermolecular hydrogen bonding of epoxy resin with silica as well as intramolecular one within polymer matrix. The vibration frequency of carboxyl group (—C=O) and hydroxyl group (—OH) shifts from 1736 to 1728 $\mathrm{cm}^{-1}$and 3420 to 3414 cm^{-1}, respectively, indicating the occurrence of hydrogen bonding between —C=O and —OH. The vibration frequency of Si—OH moves from 3435 to 3414 cm^{-1}, suggesting the involvement of silica. Whereas the vibration frequency of pending —OH in polymer chain moves from 3435 to 3420 cm^{-1} or 3414 cm^{-1}, proposing that this kind of interaction can also happen within polymer matrix.

Keywords: Hydrogen bonding; FT-IR; Epoxy resin; Silica

1. Introduction

Silica has been widely used to create high-performance or high-function materials over the last few decades. Silicon alkoxide and silica can be used in sol-gel processes to synthesize organic/inorganic composites [1,2]. Silica has also been successfully used to control the rheology of organic/inorganic hybrids, through research concerning storage modulus [3], shear thickening and thinning behaviour [4,5], thixotropy, and yield point [6]. Additionally, silica particles can be used for reinforcement of polymer matrices to lower shrinkage on curing, decreasing thermal expansion coefficients [7], and improving adhesion properties, mar (abrasion resistance) [8] and corrosion resistance [6]. Silica is valued in inkjet printing technology to speed up ink drying time and increase edge definition of printed materials [9–13]. Recently, silica has been involved in the generation of conductive polymer composites [14,15]. In our previous work we found that the incorporation of silica into the composites imposes a pronounced effect on the conductivity of composites [16]. On the other hand, in order to improve the service properties of such composites, it is critical to develop excellent chemical and physical interactions between host polymer matrix and solid fillers [17]. This work will provide an insight into the chemical reaction between polymer molecule and isophoron diisocyanate, and the hydrogen bonding between polymer matrix and silica as well.

2. Experimental

Silica (EH5) was kindly supplied by Cabot Corporation. Ethyleneglycol-*n*-butylether acetate, glycidyl end-capped poly (bisphenol A-co-epichlorohydrin), isophorone diiso-

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cyanate, and all general purpose chemicals were obtained from Sigma–Aldrich.

Of the 1.6378 g Phenolic resin was mixed with 0.9038 g silica in 40 ml 2-butoxyethyl acetate and 1.6 ml isophoron diisocyanate. The mixture was heated to reflux and then a trace amount was taken at 10, 30, 60, 90 min to conduct IR analysis on FT-IR Spectrum BX (Perkin Elmer, UK).

3. Results and discussion

3.1. Chemical reaction between polymer molecule and isophorone diisocyanate

Polymer molecules, glycidyl end-capped poly (bisphenol A-co-epichlorohydrin), have active lone pairs of electrons attached to the most electronegative element oxygen (—OH). And these molecules also have one hydrogen atom attached to the oxygen. When thermally activated, the nucleophile ($—O^{-}H$) will attack the partially positive carbon (—N=C=O) to make the intermediate with the full negatively charged nitrogen. The nitrogen then becomes protonated to yield the amide (see Fig. 1).

To obtain more information regarding the pathway of this nucleophilic addition, the reaction status was evaluated through the monitor of absorption bands by FT-IR technique. Since the variation of intensity of the absorption band is directly correlated with the variation of the amount of molecules involved. The first band monitored was used to evaluate the loss of reactant. This band occurs at 2259 cm^{-1} and results from the vibration of —N=C=O in isophoron diisocyanate. The second absorption band monitored was the absorption band at 1743 cm^{-1}, arising from the vibration of —O—C(O)-group. With reaction time going on, different samples were taken from the system and analyzed by FT-IR technique. The intensity of absorption peak at 2960 cm^{-1} arising from the vibration of methyl group ($—CH_3$) is chosen as the internal standard since the concentration change of methyl is negligible during the process. By calculating the peak height, relative intensity values of characteristic absorption bands are obtained and plotted in Fig. 2.

Fig. 2 clearly shows that the relative vibration intensity of isocyanate decreases as time passes by, indicating the loss of reactant. Also the vibration intensity of carboxyl group increases with reaction time, suggesting the generation of product. A combination of these two events partly confirms the nucleophilic addition mechanism. It can also be found that the intensity of absorption bands monitored changes remarkably during the first 30 min and then changes insignificantly from 60 to 90 min, which not only proposes that the reaction mainly progresses in the first 30 min and nearly reaches endpoint after 60 min, but also that the reaction is incomplete. The latter is as expected presumably due to the steric barrier of starting polymer and products generated.

3.2. Inter- and intramolecular hydrogen bonding

Under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them. This is called the hydrogen bond [18].

3.2.1. The occurrence of hydrogen bonding

It was observed that the infrared spectra of composites with and without silica showed somewhat differences for the characteristic absorption bands. The spectra are depicted in Fig. 3.

It can be seen that the absorption band of carboxyl group (—C=O) in epoxy resin/silica composites appears at relatively low frequency (1727 cm^{-1}), compared with the counterpart (1736 cm^{-1}) when no silica was employed, i.e. $\Delta\upsilon$ 9 cm^{-1}. This peak (1727 cm^{-1}) is also widened and the intensity is increased. In the meantime, the absorption band of hydroxyl group (—OH) moves from 3420 to 3414 cm^{-1}. All these are the basic characteristics of the occurrence of hydrogen bonding, and a combination of the above phenomena enables us to propose the happening of hydrogen bonding in the resin/silica composites.

3.2.2. Involvement of silica in the formation of hydrogen bonding

To understand the role of silica in this process, a comparison of spectra of silica and composite with silica was performed (see Fig. 3) and it was found that the absorption band of hydroxyl group (Si—OH) decreases from 3435 to 3414 cm^{-1}, $\Delta\upsilon$ 21 cm^{-1}, which suggests that silica gets involved in the formation of hydrogen bonding. Unfortunately, no significant frequency shift of absorption band of Si—O—Si can be observed, although a small shoulder peak appears at lower wavenumber (around 1050 cm^{-1}). This may be explained in terms of the strong and wide absorption peak of Si—O—Si (1103 cm^{-1}), which will blur or hide any weak and narrow peaks.

The aforementioned interaction between silica and polymer is expected. Since hydrogen (Si—OH) is attached to electrical negative oxygen atom and carboxyl oxygen (C=O) can serve as the electron donator, it is possible for the occurrence of hydrogen bonding (—Si—O…H…O=C—) between these species [19,20], as schematically depicted in Fig. 4. This kind of interaction between hydrogen atoms (Si—OH) and other functional groups has been observed elsewhere [2,21,22].

3.2.3. The formation of intramolecular hydrogen bonding

As stated previously, the low vibration frequency of C=O may be ascribed to the formation of intermolecular hydrogen bonds between silica and polymer matrix. Nevertheless, the intramolecular hydrogen bonding between active groups in polymer matrix may also contribute to the ‘red shift’ of carboxyl group (C=O). The intramolecular hydrogen bonds may exist in the following form (see Fig. 5).

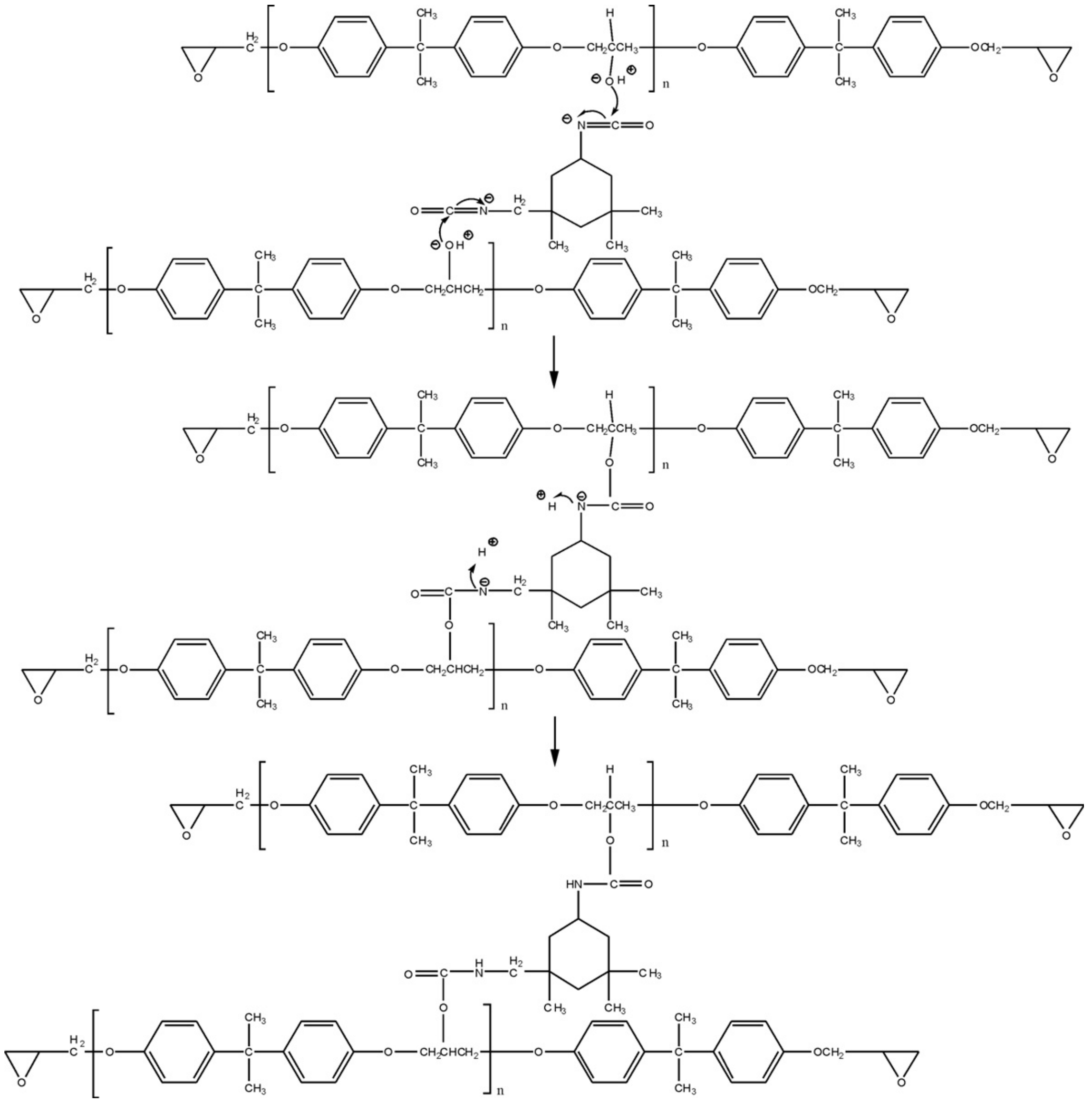

Fig. 1. Nucleophilic addition of hydroxyl group to imine.

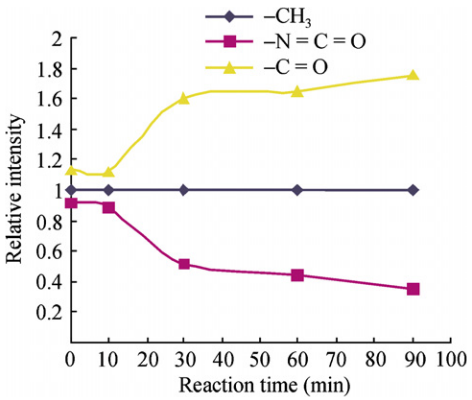

Fig. 2. Change of relative intensity of characteristic absorption bands with time.

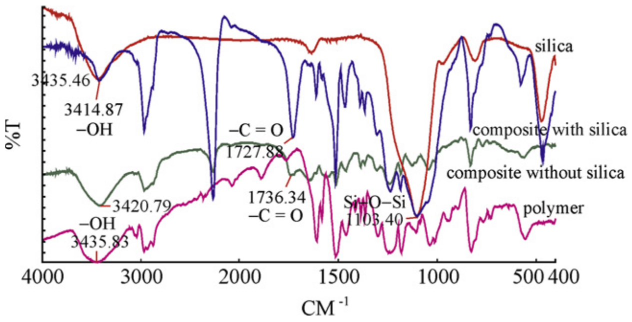

Fig. 3. Infrared spectra of composites, polymer and silica.

To further confirm this, FT-IR analysis of polymer was performed, which is diagrammatically shown in Fig. 1. It was found that the stretching frequency of hydroxyl group decreases from 3435 to 3414 cm^{-1}in composite with silica and 3420 cm^{-1} in composite without silica. This is one of the basic IR characteristics of

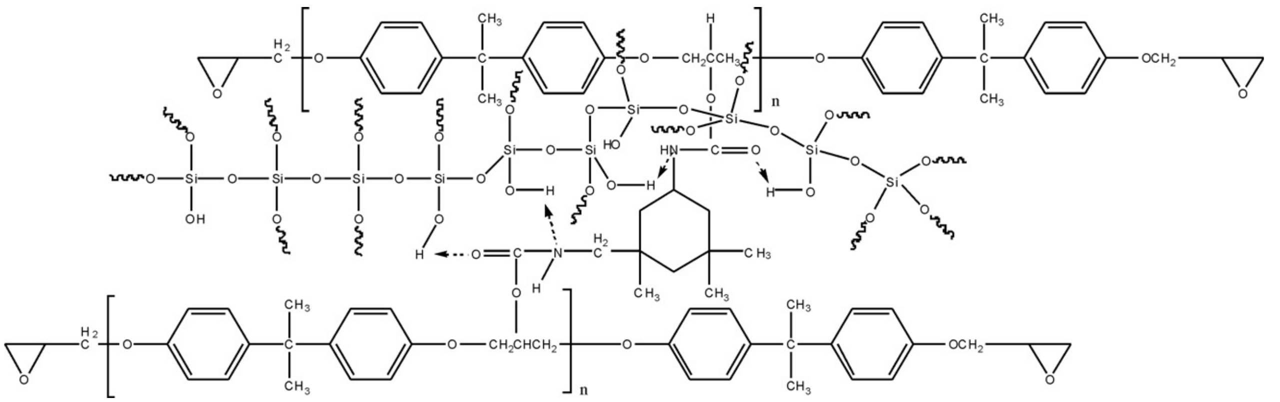

Fig. 4. Schematic representation of occurrence of intermolecular hydrogen bond between silica and polymer matrix.

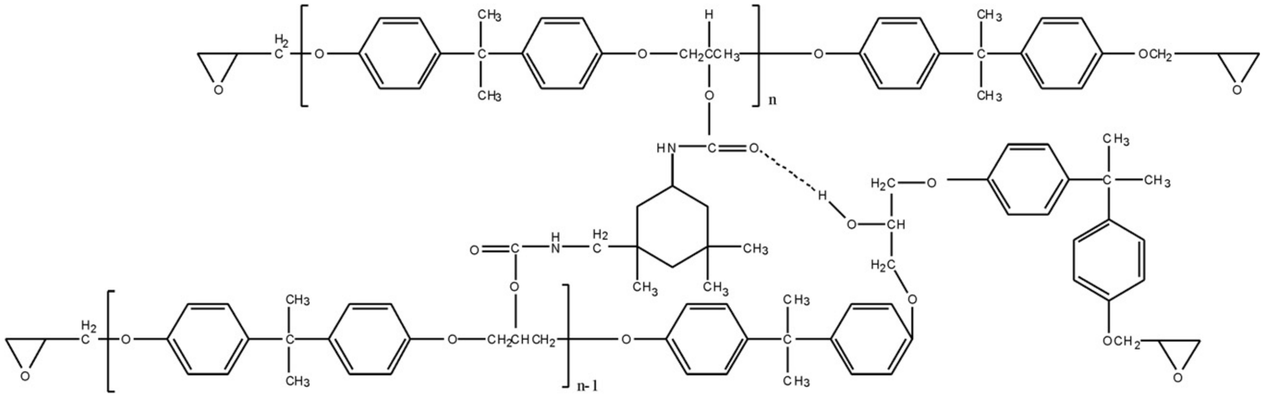

Fig. 5. Schematic representation of occurrence of intramolecular hydrogen bond in polymer matrix.

formation of hydrogen bonds, apart from the frequency shift of corresponding Lewis base. It seems that the pending hydroxyl group in polymer matrix gets involved in the formation of intramolecular hydrogen bonding.

In addition, the frequency shift of hydroxyl group (polymer-OH) in composite with silica ($\Delta \upsilon$ 21 cm^{-1}) is more obvious in contrast to the corresponding one in composites without silica ($\Delta \upsilon$ 15 cm^{-1}). This indicates that the hydrogen bonding may also form between silica and polymer matrix in the form of —Si—O…H—O— polymer, in which oxygen connected to silicon atom provides the shared lone pair electrons. As a consequence, the absorption band of hydroxyl group appears at lower frequency in composite with silica.

4. Conclusion

Nucleophilic addition of polymer hydroxyl group to isocyanate will occur when the composites are heated. The FT-IR analyses provide evidence for supporting this reaction pathway. The active hydrogen in hydrogen bonds has the ability to form hydrogen bond with other functionalities and may come from two resources in present systems, i.e. silica and polymer. This indicates that 'red shift' of carboxyl group from 1736 to 1727 cm^{-1} may result from both inter- and intramolecular hydrogen bonding. The formation of hydrogen bonding will strengthen the interaction between the ingredients in composites and reinforce the polymer matrix.

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