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The use of Raman spectroscopy to study the reaction between an amine-terminated thermoplastic and epoxy resins

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Abstract

Reactive thermoplastics are increasingly used as toughening modifiers for epoxy resins. A way to understand the influence of the reactive end-groups on the toughening and curing mechanisms is to observe in situ the reaction between the thermoplastic and the growing epoxy network. For this purpose, Raman spectroscopy has been used to follow the reaction of aromatic amines with epoxide monomers through the evolution of an amine-substituted aromatic vibration. A double shift of this peak was correlated with the formation of secondary and tertiary amines. Band assignment was confirmed by the study of model compounds. Through this method, qualitative observation of the reaction between an amine-ended copolyethersulphone thermoplastic and epoxide was performed. Unfortunately, in the studied blend containing the curing agent, a band appearing upon curing overlapped with the band characterising the end-group reaction. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive thermoplastic; Aromatic amine; Raman spectroscopy

1. Introduction

Thermoplastic modifiers, such as polyethersulphone (PES) and polyetherimide (PEI), are frequently incorporated into high performance epoxy resins in order to improve the thermoset toughness. The introduction of such a modifier can lead to different morphologies upon cure [1–4]. The observed toughening effect is related not only to the types and sizes of the microstructures, but is also enhanced by having good adhesion between the phases [5,6]. It has been shown that thermoplastic chain-ends reactive towards the epoxide greatly influence these properties [1,2,5–7]. Reactions of the thermoplastic with the growing epoxy network are assumed as well as the subsequent formation of copolymers [2,5,6,8]. There is thus an interest in following the occurrence of such reaction and in determining the conditions allowing it to take place.

In the absence of the curing agent, the possibility of a reaction between reactive thermoplastics and epoxide monomers has been investigated by Fourier-transform infrared spectroscopy (FTIR) [2,9–11] and high performance liquid chromatography [8]. For systems containing the curing agent, different strategies have been adopted to study the equivalent reaction. Kim et al. [2] end-capped the thermoplastic by pre-reaction of reactive chain-ends with epoxide monomers. The blending of this modified thermoplastic led to similar morphological results as the introduction of the unmodified reactive polymer. These observations suggested that reaction with epoxide groups took place in situ during curing. The presence of non-grafted thermoplastic was also assessed by solvent extraction performed on pulverised samples [11–13].

There is, however, still a need for direct evidence of the reaction between reactive thermoplastic and epoxy resins. For this purpose, Raman spectroscopy has been used in this work. This choice has been guided by the prospect of local characterisation of heterogeneous blends provided by Raman microscopy with a spatial resolution down to the micron-scale [14,15], however it has eventually not been exploited in this way here.

This paper presents a way of following, by Raman spectroscopy, the reaction between aromatic amines and epoxide groups. The method is based on a spectral band that is characteristic of the amine and sensitive to its reaction. It is supported by the study of model aromatic amine compounds. Characterisations of the reactions of aniline, amine-ended copolyethersulphone and its model compound are successively presented. A more complex system involving the curing agent has also been studied.

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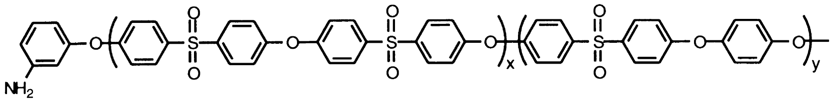
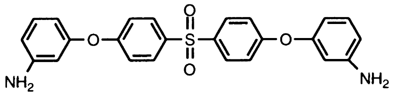
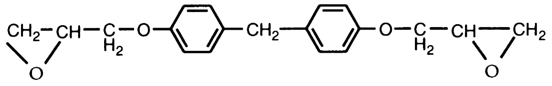


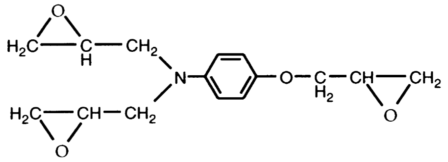
a) Amine-ended copolyethersulphone (PES-PEES-NH$_2$)



b) PES-PEES-NH$_2$ model compound



c)Diglycidylether of bisphenol F (DGEBF)



d) Triglycidylaminophenol (TGAP)

Fig. 1. Molecular structures.

2. Experimental

2.1. Materials

Aniline 99.8%, *N*-ethylaniline 98% and *N,N′*-diethylaniline 99%, were purchased from, respectively, Janssen Chemica, Acros and Aldrich.

Two types of thermoplastic copolyethersulphone were supplied by Cytecfiberite. The PES–PEES–NH$_2$, shown in Fig. 1a, is terminated with *m*-amine. As determined by nuclear magnetic resonance spectroscopy, 83% of the end-groups are amine whilst the remainder are *p*-hydroxyls. The PES–PEES–Cl material is 100% terminated with *p*-chlorine. Amine chain-ends are expected to react with epoxide groups whilst chlorine chain-ends are expected to be non-reactive towards epoxides. A model compound of the reactive thermoplastic with *m*-amine end-groups was supplied by Cytecfiberite. Its structure is shown in Fig. 1b.

The epoxide monomers used were a diepoxide, diglycidylether of bisphenol F (DGEBF, PY306 from Ciba-Geigy, Fig. 1c) and a triepoxide, triglycidyl *p*-aminophenol (TGAP, EPON 1076 from Shell, Fig. 1d). The aromatic diamine curing agent was 4,4′-diaminodiphenylsulphone (DDS, HT976 from Ciba-Geigy).

2.2. Sample preparation

Dichloromethane was used to ensure uniform mixing of the blend components. It was then evaporated overnight under vacuum at room temperature. Though dichloromethane is not a solvent for DDS, this curing agent dissolved in the presence of epoxide monomers.

For the samples described hereafter, several reaction times were investigated at a temperature of 180°C. This is the reference cure temperature for the studied epoxy resin–thermoplastic blends.

Reaction of the aniline: the diepoxide and the aniline were mixed at stoichiometry. Reactions were performed in stainless steel DSC pans in an oven. Products were transferred onto glass slides for analysis.

Reaction of the PES–PEES–NH$_2$ model compound: the model compound was mixed with the diepoxide monomer in a slight molar excess of epoxide groups in relation to amino hydrogens (1.15:1). Reactions were carried out between glass slides in a hot stage (Mettler FP 82 HT).

Reaction of the PES–PEES–NH$_2$ thermoplastic: a molar ratio epoxide/amino hydrogen of around 10:1 has been used for the reaction between PES–PEES–NH$_2$ and the diepoxide monomer. Reaction took place in sealed stainless steel DSC pans in an oven. Since these samples remained mainly soluble after reaction, they were dissolved in dichloromethane and cast as a film on an aluminium sheet. This procedure allowed for a reduction of the sample fluorescence affecting the Raman analysis.

Reaction in the blend containing the DDS curing agent: proportions were those used for the morphological study conducted in the framework of this project. The two epoxide monomers were used in a weight ratio close to 1:1. The excess of epoxide groups in relation to the amino hydrogens of the DDS corresponded to a ratio close to 1.4:1. The thermoplastic accounted for 20% of the total weight of the

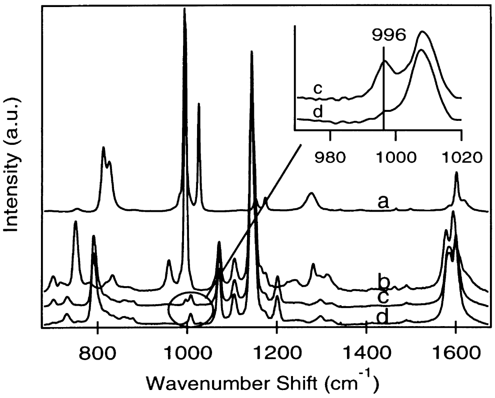


Fig. 2. Raman spectra of: (a) aniline; (b) model compound of the PES–PEES–NH_2; (c) PES–PEES–NH_2; and (d) PES–PEES–Cl.

blends. Reactions were performed in the hot stage between an aluminium sheet and a glass slide.

2.3. Testing technique

Samples were analysed by Raman spectroscopy using a Dilor Labram dispersive Raman spectrometer. The incident laser excitation wavelength was 632.8 nm from a He–Ne laser source. Instrumental parameters were fixed as follows. The 100 × magnification objective was combined with a pinhole diameter of 1000 μm. This corresponded to the analysis of a sample area close to 10 μm in diameter within a depth of around 15 μm. The slit entrance of the detector was set to 1000 or 200 cm^{-1} which gave rise to a spectral resolution of about 3 cm^{-1} in both cases. Centred on 1200 cm^{-1}, spectra were the average of 10 accumulations of 20–120 s.

It has been observed that the time of exposure to the laser before acquisition had to be controlled at least for the samples based on the PES–PEES with and without the DDS. Indeed, long times under the beam gave rise to increases in the intensity around 998 cm^{-1}. After periods during which the laser was switched off, the intensity around 998 cm^{-1} decreased but more slowly than the previous increase. This observation cannot be explained yet.

A polynomial baseline of the fifth order was subtracted from the spectra using the Dilor Labspec software. Normalisation was achieved through the height or the area of the sulphone peak located at around 1145 cm^{-1} (area from 1125 to 1160 cm^{-1}).

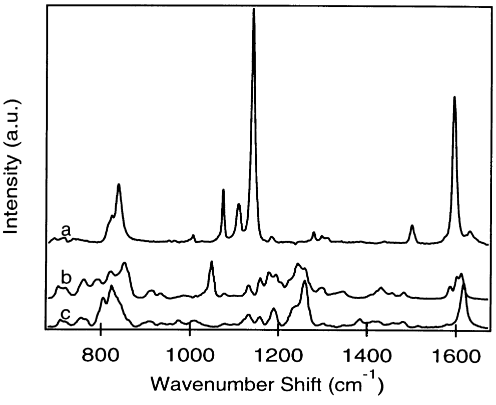


Fig. 3. Raman spectra of: (a) DDS; (b) diepoxide monomer (DGEBF); and (c) triepoxide monomer (TGAP).

3. Results and discussion

3.1. Characteristic peak of the aromatics carrying the amine end-groups

According to Varsanyi [16], mono-substituted, *m*-di-substituted or 1,3,5-tri-substituted benzene derivatives show a peak near 1000 cm^{-1} in Raman and infrared spectra. This peak is assigned to a skeletal vibration of the aromatic ring. For aniline, a mono-substituted aromatic compound, Varsanyi reports the peak at 996 cm^{-1}. For a *m*-di-substituted compound such as *m*-aminophenol, Varsanyi mentions the equivalent vibration at 1001 cm^{-1}.

We observed this aniline characteristic vibration at a wavenumber shift of 995 cm^{-1} (Fig. 2). This was very close to the Varsanyi's value.

The spectrum of the amine-terminated PES–PEES showed a small peak at 996 cm^{-1} (Fig. 2). It was assigned to the same vibration of the aromatic ring carrying the amine group in the *m*-position. The corresponding vibration was found at 995 cm^{-1} for the model compound of PES–PEES–NH_2 (Fig. 2). This peak was, of course, much more intense than for PES–PEES–NH_2 because of the higher proportion in *m*-amine substituted aromatic rings. No significant peak was observed at this location for the chlorine-ended PES–PEES, with the chlorine in the *p*-position (Fig. 2).

Spectra of the DDS curing agent and of both epoxide monomers are given in Fig. 3. It should be noted that the spectrum of the DDS curing agent did not show any peak near 1000 cm^{-1}. Indeed, the aromatic ring carrying the amine is *p*-substituted. The peaks of both epoxide monomers in the area around 1000 cm^{-1} were not supposed to interfere in this region because of their low intensities (Fig. 3).

3.2. Evolution of the aromatic amine peak with the amine reaction

3.2.1. Reaction of the aniline

Reaction between aniline and diepoxide caused the evolution of the Raman aniline peak located initially at 996 cm^{-1} and assigned, as above, to a vibration of the mono-substituted aromatic ring (Fig. 4). This peak vanished with the reaction while two peaks appeared progressively at lower wavenumber shifts, 991 and then 982 cm^{-1}. It is proposed here to relate these displacements of the aniline

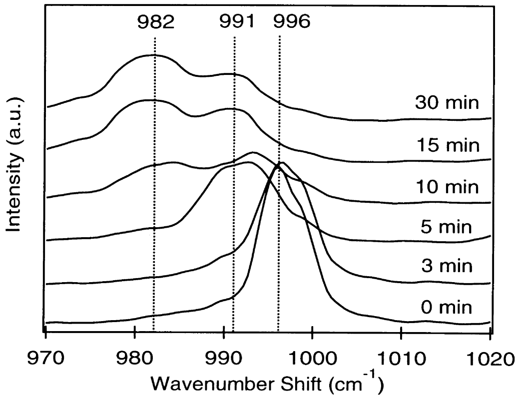


Fig. 4. Reaction between aniline and the diepoxide monomer: area of interest of the Raman spectra taken after several times of reaction at 180°C.

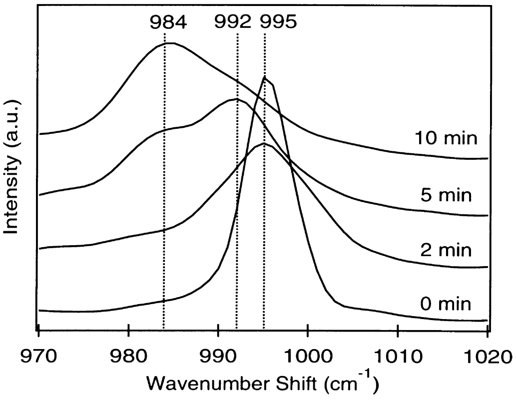


Fig. 6. Reaction between the model compound of the PES–PEES–NH_2 and the diepoxide monomer: area of interest of the Raman spectra taken after several times of reaction at 180°C.

peak to the following two transformations of the amine:

primary amine → secondary amine → tertiary amine

This assumption was supported by the Raman analysis of commercial model compounds. Two aniline derivatives were used: *N*-ethylaniline and *N*,*N*′-diethylaniline, respectively, as models for the secondary and tertiary amines. Raman spectra around 1000 cm^{-1} are given in Fig. 5. For each compound, one peak was observed in this region and assigned to the mono-substituted aromatic vibration. However, the different amine substitution states appeared to influence the peak position. Peaks were located at a lower wavenumber shift for a higher degree of amine substitution. These observations supported the assignment of the peak shifts of reacting aniline to the appearance of secondary and tertiary amines.

The possible determination of the amine substitution state can be useful in the study of epoxy–aniline systems used to model epoxide–amine reaction mechanisms [17].

3.2.2. Reaction of the PES–PEES–NH_2 model compound

The PES–PEES–NH_2 model compound has been reacted with an excess of diepoxide monomer. Raman spectra were taken after different times of reaction at 180°C (Fig. 6). The characteristic Raman peak was located at 995 cm^{-1} before reaction. With increasing times of reaction, a clear double shift of the peak was observed towards 992 and then to 984 cm^{-1}, assigned to the appearance of secondary and tertiary amines.

3.2.3. Reaction of the PES–PEES–NH_2 thermoplastic

The Raman spectra obtained for the mixture of PES–PEES–NH_2 and diepoxide monomer after different reaction times are presented in Fig. 7. Exposure time to the laser before acquisition of these spectra was set to 10 min. Despite the low intensity of the characteristic peak, a double shift of this peak can be detected, from 995 to 990 and 984 cm^{-1}. Related to the formation of secondary and tertiary aromatic amines, this shift has evidenced the reactions of the PES–PEES amine end-groups with epoxide rings.

Because of the small signal to noise ratio, quantitative

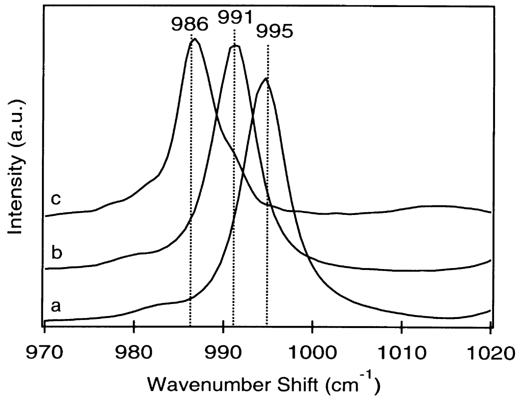


Fig. 5. Raman spectra of: (a) aniline; (b) *N*-ethylaniline; and (c) *N*,*N*′-diethylaniline in the vibration region characteristic of the mono-substituted aromatic ring.

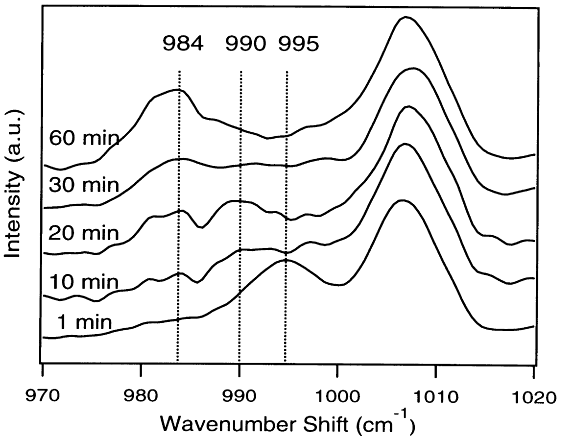


Fig. 7. Reaction between PES–PEES–NH_2 and the diepoxide monomer: area of interest of the Raman spectra taken after several times of reaction at 180°C.

determination of the extent of reaction cannot be obtained. However, Raman spectroscopy allows us to determine whether the reaction between PES–PEES amine end-groups and epoxide rings has taken place under the studied conditions.

3.2.4. Reaction in the blend containing the curing agent

A blend of PES–PEES–NH_2 with the two epoxide monomers and DDS was prepared since this aromatic amine hardener showed no peak in the area of interest. Curing of this system led to a homogeneous-looking network.

Raman spectra were acquired after the same exposure time to the laser but for different blend curing times. A peak around 996 cm^{-1} was observed and appeared more intense and broader with longer curing times. This vibration band could not be assigned. Spectra taken after varying exposure time to the laser revealed that more the sample was cured, more rapid was the peak increase along with the time under the laser. For the longest cured samples, it was not possible to take a spectrum showing a low intensity around 996 cm^{-1}, even after short exposure to the laser.

This broad peak around 996 cm^{-1} masked the shifts related to the reaction of the PES–PEES amine-ends. In the particular case of this blend, in situ characterisation of the thermoplastic reactivity could thus not be achieved, even qualitatively, with Raman spectroscopy.

4. Conclusions

A peak located near 996 cm^{-1} was observed by Raman spectroscopy for aniline and for the amine-ended copolyethersulphone (PES–PEES–NH_2) and its model compound. This vibration is assigned to an amine-substituted aromatic ring. Upon reaction of these amine compounds with epoxide groups, two vibrations at lower wavenumber shifts appeared. This paper shows that these shifts can be assigned to the formation of secondary and tertiary amines.

For the amine-ended PES–PEES, only qualitative analysis is possible because of the small signal to noise ratio in the interesting area of the spectra. Its reaction with epoxide monomers is, however, evidenced through the shift of the peak initially located near 996 cm^{-1}. The occurrence of this reaction at other time and temperature conditions can be investigated by this method. In the presence of the DDS curing agent, the reaction of the chain-ends cannot be followed anymore because of an overlapping broad peak increasing with curing.

Nevertheless for these systems, Raman spectroscopy allowed successful quantification of the epoxide conversion, as will be presented in future papers.

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