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Degradation of filled epoxy resin surfaces

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Abstract

Many components manufactured from polymeric materials have fillers incorporated into them, to improve the control of the manufacturing process and to assist with mechanical and electrical properties. Although the mechanical and electrical aspects of the inclusion of the filler material is given great consideration, little thought is given to the possible effects of the filler on the degradation processes. This work investigates the effect of three common fillers and identifies changes in the reaction of an epoxy resin to a range of possible environmental stresses. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polymers, such as epoxy resin, form a major part of many items used in industry and in the domestic market. The degradation of the polymer component reduces the appearance of the goods and can also cause a reduction in operating efficiency and, in extreme cases, failure.

To reduce the component costs, and to change the physical characteristics and appearance of the polymer, inorganic fillers are often added. The addition of fillers to polymerics, such as epoxy resins, also eases a number of difficulties in the production of moulded components. Parts manufactured with an inorganic filler have a lower volume of polymer which, in turn, lowers the volume of reactive material, reduces the degree of shrinkage and the heat build-up during epoxy cross-linking. As the thermal conductivity of filled materials is greater than that of pure resin, components can be designed and generated more simply, with a lower risk of deformation and a greater control over the chemical cross-linking reaction of the epoxy resin.

Although the production processes benefit from the inclusion of the filler materials, the fillers may have an adverse effect on the chemical reactions taking place under environmental stresses. To investigate the effect of filler materials, a bisphenol-A epoxy resin which has had one of three fillers added has been subjected to a range of chemical and radiative stresses. The fillers were selected to cover the range of shape of particle and acidity of filler material commonly in use in industry today. The three filler materials selected were alumina (Al_2O_3), silica (SiO_2) and wollastonite ($CaSiO_3$).

2. Background

In previous work by the authors [1–3], investigations have been carried out into the effect of electrical, chemical and radiation stressing on the surface chemistry of unfilled samples of this bisphenol-A epoxy and phthalic anhydride hardener combination. Linear anhydrides, acids and amines were identified on the surface of stressed resin samples. Chemical reactions were hypothesised which would account for the changes found at the surface of the stressed resin samples.

Observations by research teams involved in studies of polymeric materials suggest that filler materials will affect the physicochemical reactions occurring due to the range of stresses caused by electrical discharges. Under discharge stressing the surface of materials are exposed to electron, ion and excited molecular species impact, as well as to ultraviolet (UV) radiation. The interaction of the polymeric material and these reactive elements may be affected by the presence of inorganic fillers, e.g. fillers acting as catalysts or buffers. Possible examples of this can be seen in the following three exemplars.

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Firstly, a reversible swelling of epoxy resin is caused by moisture absorption [4–6], however, UV radiation causes water to dissociate to highly reactive radical species which can cause polymer degradation. Metal oxides, which are used as fillers in some applications of plastics, are known to catalyse the dissociation of water [7,8]. It is, therefore, considered likely that metal oxide filler materials will sensitise a filled resin to degradation.

Secondly, it is reported, in studies of the degradation of poly(ethylene terephthalate) in soil, that polymer breakdown is enhanced by the presence of metal ions [9]. The coordination of copper with ester and carbonyl functional groups is reported as significant in this respect. (It should be noted that copper electrodes are used in the experiments in this work and that both functional groups are present in the epoxy resin used.)

Thirdly, a particular type of fault, known as a water tree, has been studied in ethylene-propylene rubber (EPR) high power cables. It has been found that a large number of these faults initiated at sites containing transition metal particles (iron and vanadium) [10]. The discovery of organic and inorganic ionic species in the fault regions is taken as confirmation of electrochemical reactions occurring.

From the three cases given above, it can be seen that inorganic filler materials may have a deleterious effect on the reaction to applied stress in filled polymeric systems. Identification of differences in degradation between the various filled epoxy resins might indicate applications, or environmental situations, which would not be advisable for a particular filler/resin combination, given the stress conditions expected to be prevalent.

3. Experimental

The samples of filled resin were manufactured using a bisphenol-A epoxy and a phthalic anhydride hardener. The resin was combined with one of three common filler materials: silica, alumina and wollastonite. 1mm thick slices were cut from 25mm diameter tubes of filled resin to generate the standard sample form. The sample surfaces were examined by Attenuated Total Reflectance-Fourier Transform InfraRed (ATR-FTIR) microspectroscopic analysis both before and after the application of the three stress conditions to determine the changes in surface chemistry. A zinc selenide crystal, attached to a NicPlan infrared microscope on a 5DXC Nicolet bench, was used to collect the spectral data.

The following stress conditions were investigated.

3.1. Electrical discharge stressing

The wall of the test cell is a 100 mm long section of cylindrical pyrex glass, thickness 5 mm, it is enclosed top and bottom by 10 mm thick Perspex sheets. The filled resin samples were placed on the stainless steel plane electrode connected to ground, zero volts. The discharges were generated by applying 10kV ac to a conical copper electrode, the tip being 2 mm above the resin surface. The atmosphere used was room air at normal pressure and temperature. The samples were exposed for various times, the results shown are from samples exposed for 50 h.

3.2. Samples were exposed to nitric acid fumes

The samples of filled resin were suspended in a sealed, 1 l, clear glass container. The nitric acid fumes were produced by enclosing an open glass phial containing 50 ml of conc. nitric acid in the container. To allow the fumes to evolve from the acid and affect the resin samples, the samples were left in the container for 50 h.

3.3. Samples were exposed to UV radiation

The stress was applied by exposing samples to an ultraviolet lamp for 50 h. The samples were held 5 cm from the surface of the lamp. A 6 W Philips TUV lamp was used.

The nitric fumes and UV radiation were selected as representative of possible species generated by discharges in air.

In addition, a number of samples were stored in dry air to provide a background measure of the state of filled resin materials.

It was also decided that, in addition to the three stress conditions outlined above, a further investigation would be carried out. Samples of the three filled resins were subjected to thermogravimetric analysis (TGA), to determine whether there would also be a variation in the materials reaction to thermal stress.

4. Results

Attenuated total reflectance–fourier transform infrared (ATR–FTIR) microspectroscopic analysis of the electrical, chemical and radiative stressed samples was carried out.

The results are presented for samples stored in dry air and for those stressed under the conditions given above, i.e. nitric acid fumes, UV radiation and electrical discharge in air.

The samples in dry air show the ‘unstressed’ infrared data. Spectral information from pure resin samples is provided to indicate the changes to the epoxy resin spectrum caused by each filler material. Fig. 1 shows the spectra from samples stored in dry air. Fig. 2 shows the spectra from samples exposed to nitric acid fumes. Fig. 3 shows the spectra from samples exposed to UV radiation.

Fig. 4 shows the spectra from samples exposed to electrical discharges in air.

In each figure the upper spectrum (a) is unfilled resin, the second (b) is alumina filled resin, the third (c) is silica filled resin and the lower (d) is wollastonite filled resin.

Fig. 1 presents a spectrum from an unstressed sample of each type.

In Fig. 1(a), a spectrum of unstressed unfilled epoxy resin, the major infrared absorbance bands are: between 3000 and 2800 cm^{-1}, the absorbance bands due to methyl and methylene groups, at 1710 and 1260 cm^{-1} are those due to carbonyl groups, at 1630, 1610 and 1510 cm^{-1} are aromatic bands and at 1250, 1230, 1100 and 1035 cm^{-1} are the ether bands.

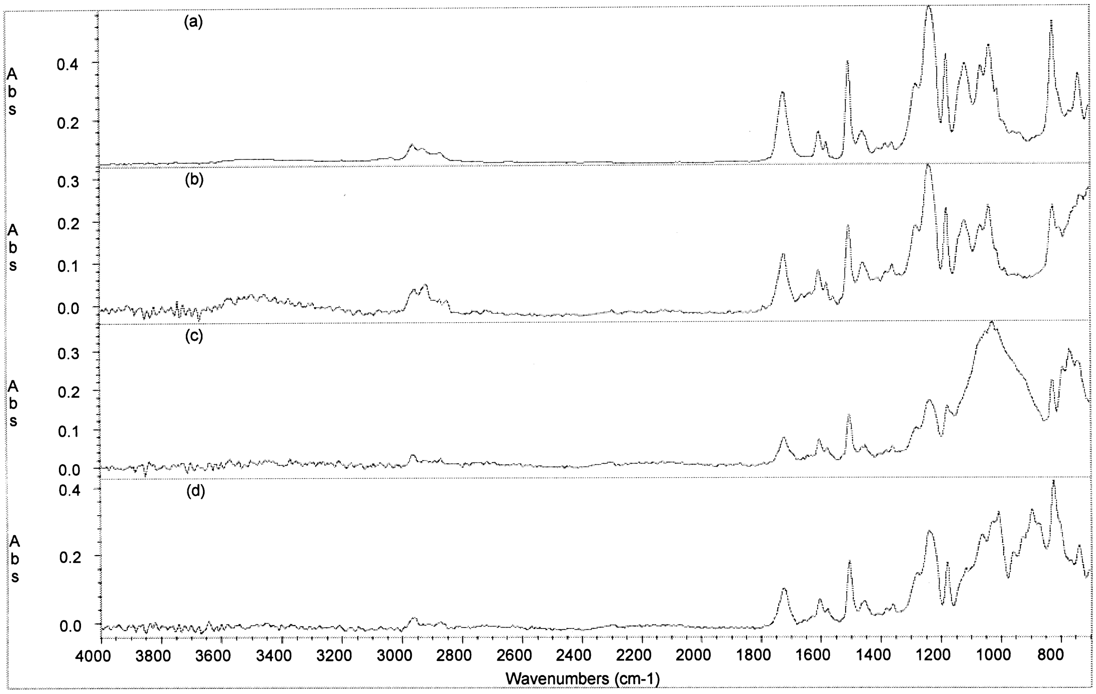

Fig. 1. Samples stored in dry air. (a) Unfilled resin, (b) alumina filled resin, (c) silica filled resin, (d) wollastonite filled resin.

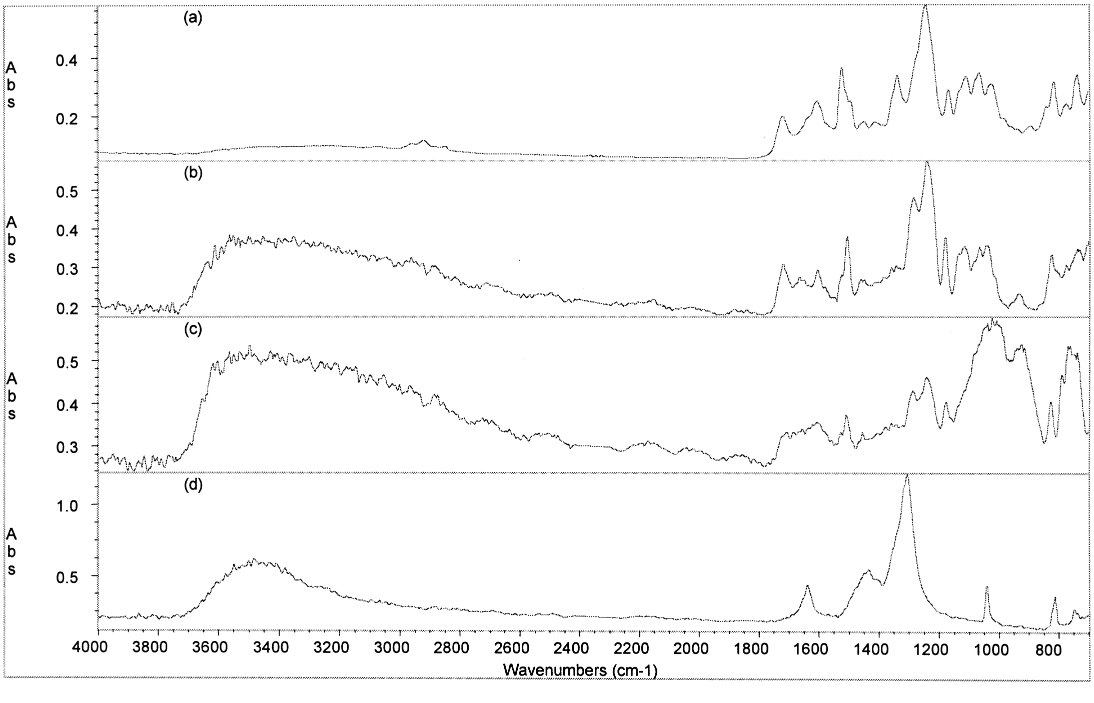

Fig. 2. Samples in nitric acid fumes. (a) Unfilled resin, (b) alumina filled resin, (c) silica filled resin, (d) wollastonite filled resin.

In Fig. 1(b) the alumina filler produces a broad absorbance band below 900 cm^{-1}.

In Fig. 1(c) the silica filler produces broad absorbance bands at 1050 and at 750 cm^{-1}. In Fig. 1(d) the wollastonite produces a number of absorbance bands between 1020 and 850 cm^{-1}.

Fig. 2 presents a typical spectrum from each set of samples after they have been exposed to nitric acid fumes for 50 h. From Fig. 1(a) to Fig. 2(a) the intensity of the methyl/methylene bands have decreased, that of the ether bands have decreased and there are additional absorbance bands around 1630, 1500 and

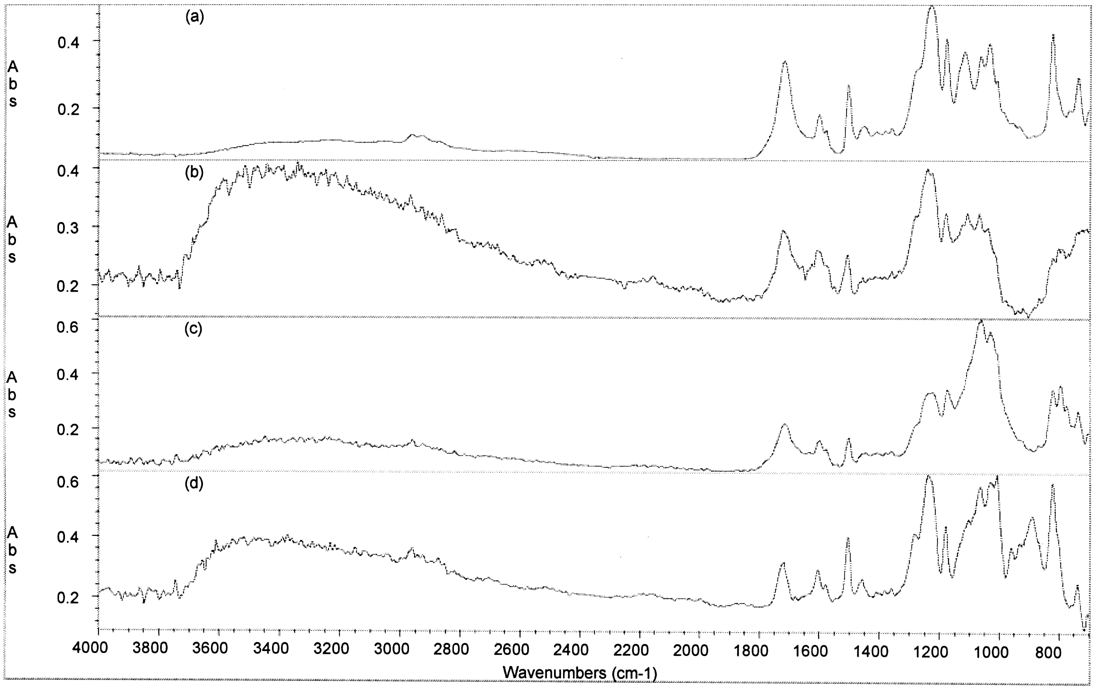

Fig. 3. Samples exposed to ultraviolet radiation. (a) Unfilled resin, (b) alumina filled resin, (c) silica filled resin, (d) wollastonite filled resin.

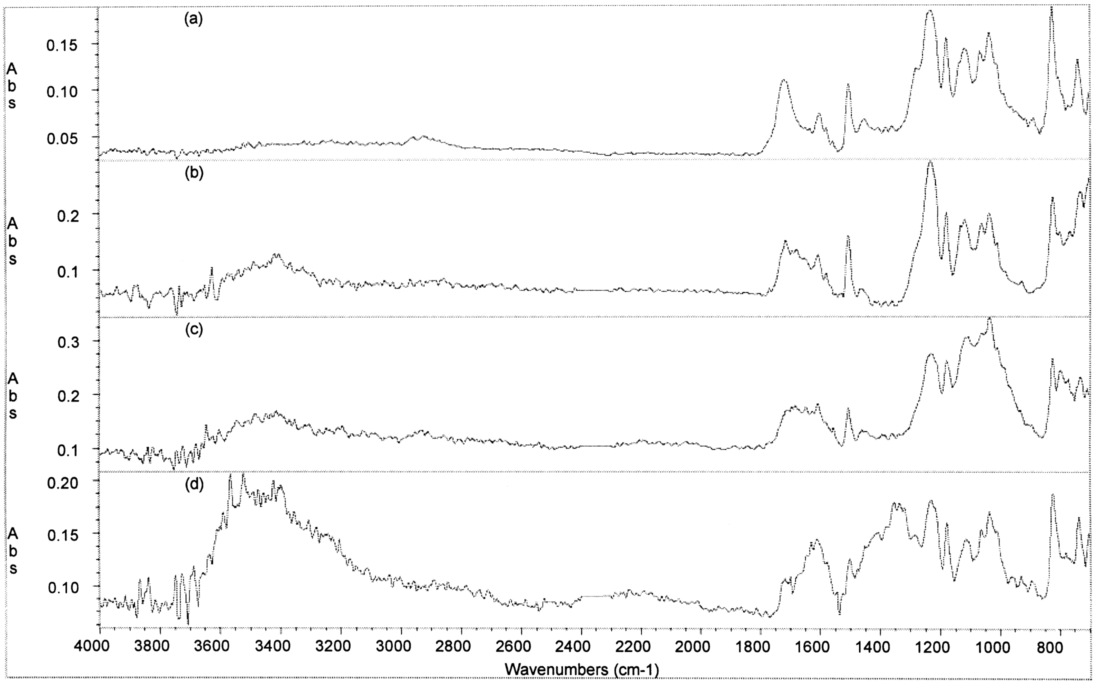

Fig. 4. Samples subjected to electrical discharge in air. (a) Unfilled resin, (b) alumina filled resin, (c) silica filled resin, (d) wollastonite filled resin.

1400 cm^{-1} indicating the presence of nitro and nitroso compounds. From Figs. 1(b) and 2(b) there is less evidence of nitrogen species and the broad bands from 3600 to 2800 cm^{-1} and around 1640 cm^{-1} indicate the presence of water, alcohol and acid, suggesting hydrolysis taking place. The reactions taking place at the surface of the filled resin are, therefore, different to those on unfilled resin. From Figs. 1(c) and 2(c), similar reactions to those in silica filled resin, though possibly stronger, are indicated by the spectral changes. The greatest spectral differences are between Figs 1(d) and 2(d). The spectrum in Fig. 2(d) indicates that the wollastonite has been degraded and a hydrated calcium-silica-nitrate has formed.

Fig. 3 presents a typical spectrum from samples irradiated with UV for 50 h. The differences between the unstressed, unfilled resin in Fig. 1(a) and the stressed resin in Fig. 3(a) show changes to the carbonyl band at 1710 cm^{-1} and to the ether bands around 1250 cm^{-1}. The changes indicate oxygen absorbance and suggest an increase in the resin crosslink density. The differences between unstressed and stressed alumina filled resin, Figs. 1(b) and 3(b), show the presence of hydroxy groups and indicate changes to the carbonyl and ether attachments. These changes indicate reaction with atmospheric moisture, the formation of alcohol and acid species and additional oxygen crosslinks. The silica filled resin spectra, Figs. 1(c) and 3(c), also show reactions with atmospheric moisture similar to those in the alumina case, though the hydroxyl groups are less intense. Although the wollastonite spectra, Figs. 1(d) and 3(d), show similar changes to those in the alumina and silica filled samples, the crosslink reaction appears suppressed.

Spectral data from samples subjected to electrical discharges in air are presented in Fig. 4. The spectra displayed were collected at a distance of 5 mm from the discharge axis. The reactions occurring at the surface of samples subjected to electrical stress changes with increasing distance from the electrode axis, i.e. annular degradation regions surround the discharge axis. Infrared spectra could not be gathered at the centre of degradation of the filled resin samples. Investigation of stressed filled samples by scanning electron microscopy showed that filler particles sit on the resin surface, indicating severe resin erosion in this region. This confirmed an earlier investigation of unfilled resin [1], where atomic force microscopy of the centre of the degradation indicated it to be lower than the surrounding resin. The erosion of the polymer stops the ATR crystal from making contact with resin in stressed filled resin samples. At 5 mm from the degradation axis, the erosion has reduced and resin spectra can be gained. To allow a direct comparison of the stressing effects on filled and unfilled resins, the spectra shown in Fig. 4 are all from this off-axis region.

In the unfilled resin samples the changes between Figs. 1(a) and 4(a) are very similar to those between Figs. 1(a) and 3(a). The ether band at 1300 cm^{-1} is affected to the same extent in both cases. The intensity of the carbonyl peak (1710 cm^{-1}) in the discharge stressed sample is, however, lower than that in the UV radiation stressed sample, though it has broadened to a greater extent. These differences suggest variations in oxygen absorbance.

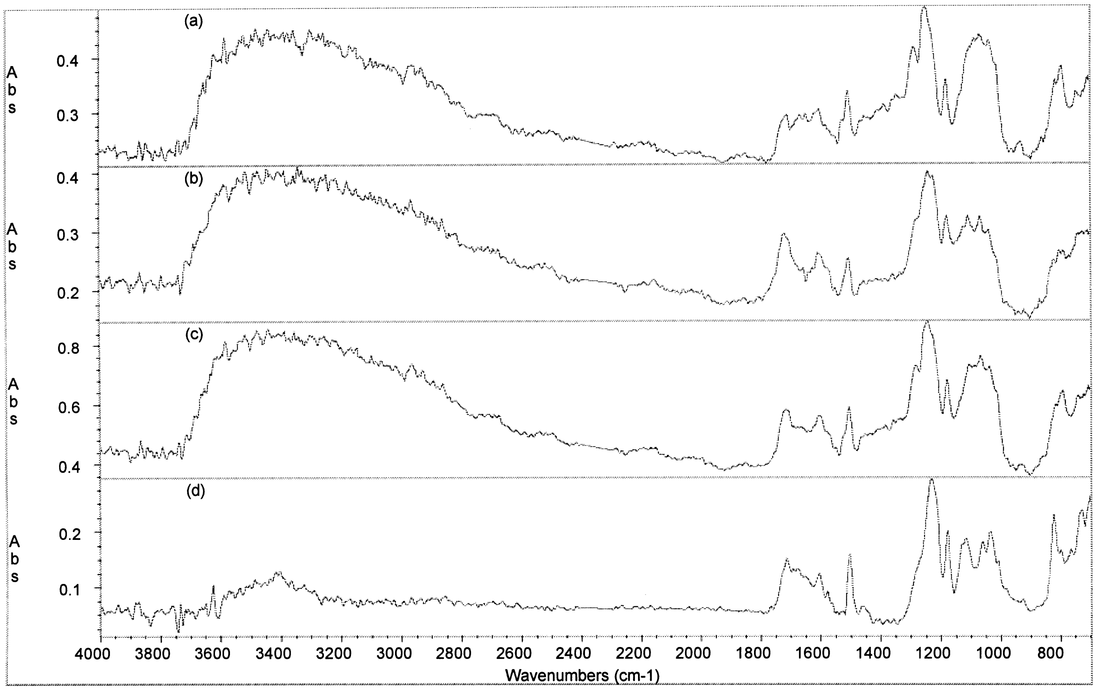

Fig. 5. Comparison of alumina filled resin samples. (a) Nitric fumes, (b) ultraviolet radiation, (c) addition of (a) and (b), (d) electrical discharge stressing.

The changes to the spectra in Figs. 4(b), (c) and (d) share, to a degree, aspects of the changes in Figs. 2(b) and 3(b), 2(c) and 3(c) and 2(d) and 3(d) respectively.

To determine whether there were any common features between the electrical discharge stressing and the nitric fumes and UV stressing, a comparison of the spectra was made. The degree of change between the original sample spectra and the spectra from the stressed samples was, however, too great to allow subtraction to be used to determine commonality of change, e.g. lack of common

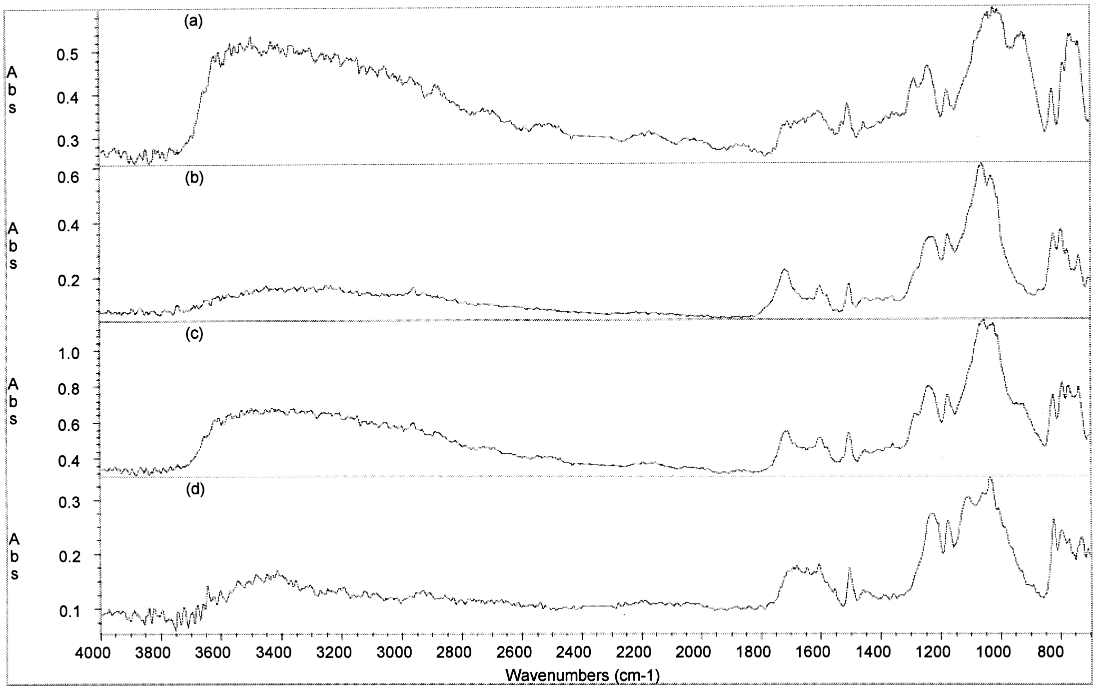

Fig. 6. Comparison of silica filled resin samples. (a) Nitric fumes, (b) ultraviolet radiation, (c) addition of (a) and (b), (d) electrical discharge stressing.

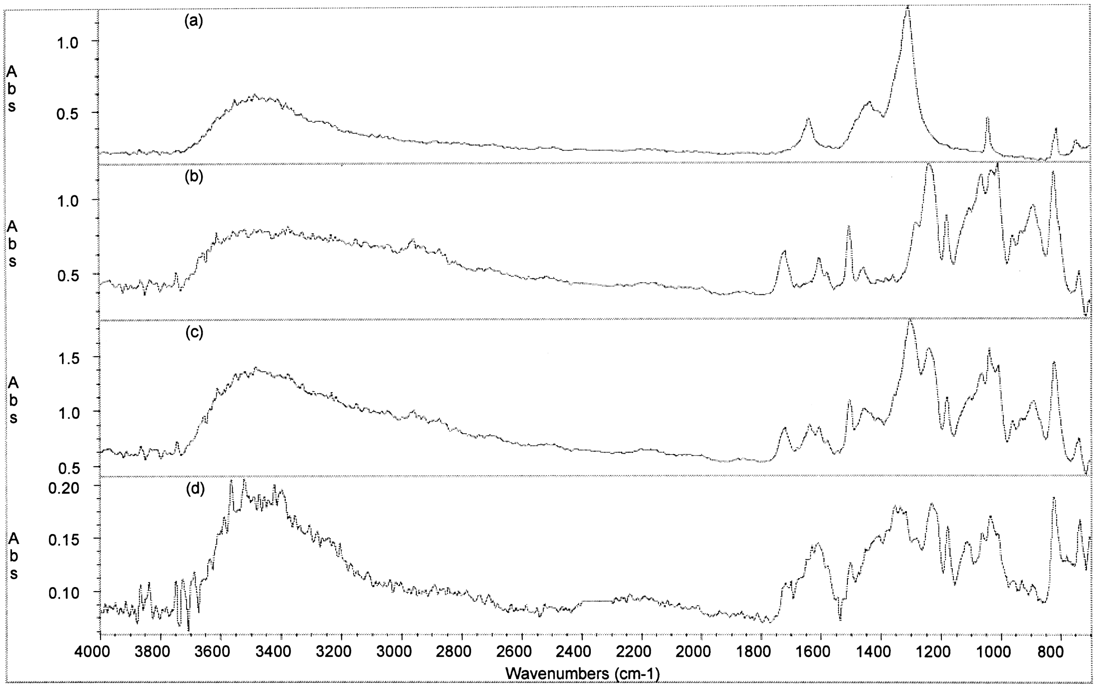

Fig. 7. Comparison of wollastonite filled resin samples. (a) Nitric fumes, (b) ultraviolet radiation, (c) addition of (a) and (b), (d) electrical discharge stressing.

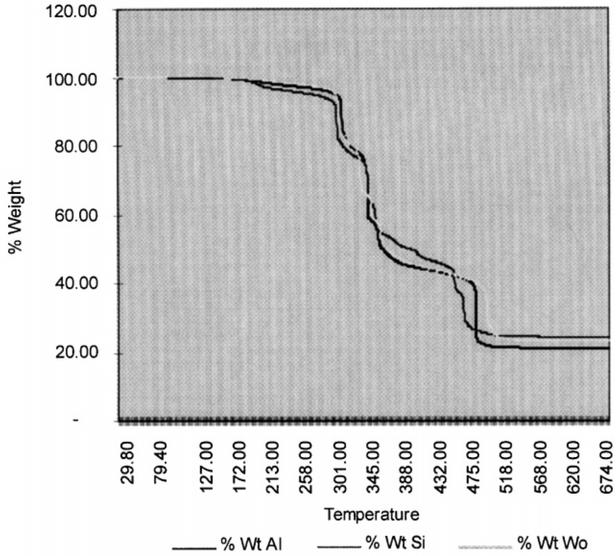

Fig. 8. TGA of three filled resin samples.

absorbance peaks between Figs. 1(d) and 2(d). An alternative approach at determining the similarity of effect of the stresses was taken, namely the spectra from the nitrogen stressed samples and UV radiation stressed samples were added and compared with the electrically stressed sample spectra. The data presented in Figs 5–7 show the two spectra to be combined, the resultant and the discharge stressed spectrum.

Figs. 5(c) and (d), the alumina samples, show that, although there are differences in the shape and intensity of the hydroxy absorption and in the intensity of ether and nitrogen absorption bands, all are present.

Figs. 6(c) and (d), the silica spectra, show that the absorption intensity due to the silica is reduced in the pd stressed sample. In common with the alumina samples, the width and intensity of the hydroxy, ether and nitrogen bands varies between the resultant spectra.

Figs. 7(c) and (d), the wollastonite spectra, in common with the other fillers, the band intensities are altered but still exist.

Fig. 8 demonstrates that there is indeed a variation in reaction to thermal stress among the three filled resin samples. The degradation steps, indicated by the loss in mass at given temperatures, can be seen to change with the filler material.

5. Conclusions

The use of filler materials to affect the mechanical and electrical properties of polymeric materials is common in industry. The effect of the filler material upon the reaction of the polymer to environmental stresses needs also to be addressed.

Alumina, silica and wollastonite have been shown to cause a variation to the reaction of an epoxy resin when chemical, radiative, electrical and thermal stresses are applied. It has also been shown that, under certain conditions, the reactions to individual stresses can be combined to mimic changes in situations where synergetic reactions may be occurring, e.g. the spectra from nitric fume and UV radiation stressed resin combined show similarities to that from electrical discharge stressing in air.

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