METHOD OF QUANTITATIVE ANALYSIS OF POLYOXADIAZOLE FIBRES IN A MATERIAL

FIELD

This invention relates to a method of quantitative analysis of polyoxadiazole fibres in a material.

BACKGROUND

Apparel worn by persons in low temperature environments to reduce heat loss from the person to the environment typically comprises three layers: an inner lining worn against the skin or another layer of clothing, an outer layer typically referred to as the shell, and a thermal insulation layer provided between the lining and the shell. The layer of thermal insulation serves to reduce heat loss from the person via irradiation, thermal conductivity and convection.

Polyoxadiazole has recently been introduced as one of the materials used in the thermal insulation layer of apparel worn in low temperature environments, mixed with other materials such as polyester to form a non-woven composite material comprising fibres of two or materials. For manufacturing control purposes and for research development, there is thus a need to have a method of quantitative analysis of polyoxadiazole fibres in a material, and particularly in fabric materials such as non-woven composite insulation materials as there is currently no available method for quantitative analysis of the amount of polyoxadiazole in such polymer-based fabrics.

SUMMARY

According to a first aspect, there is provided a method of quantitative analysis of polyoxadiazole fibres in a material, the method comprising the steps of:

(a) immersing a sample of the material in a solvent to obtain a mixture, the solvent being unable to dissolve polyoxadiazole fibres and selected to dissolve other materials in the sample;

(b) filtering the mixture to obtain a residue;

(c) washing the residue;

(d) drying the washed residue; and

(e) performing thermogravimetric analysis on the dried residue in air to determine

quantity by weight of any polyoxadiazole fibres present in the sample.

The solvent may comprise trifluoroacetic acid.

Step (e) may comprise heating the residue in air from room temperature to 700 °C at a heating rate of 10 °C/min.

Step (c) may comprise washing the residue twice with the solvent followed by washing the residue three times with water.

Step (d) may comprise heating the washed residue in an oven to dry the residue until the dried residue obtained is at a constant weight. The heating may be at 70 °C.

The quantity by weight in step (e) may be defined as weight loss from the residue in a temperature range from 450 °C to 650 °C during the thermogravimetric analysis.

BRIEF DESCRIPTION OF FIGURES

In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary embodiments of the present invention, the description being with reference to the accompanying illustrative drawings.

FIG. 1 is a flow chart of an exemplary method of quantitative analysis of polyoxadiazole fibres in a material.

FIG. 2 is a graph of TGA analysis of pure polyoxadiazole fibres in air.

FIG. 3 is a graph of TGA analysis of a non-woven material containing 90% polyester fibres and 10% polyoxadiazole fibres using the exemplary method of FIG. 1.

DETAILED DESCRIPTION

Exemplary embodiments of a method 100 of quantitative analysis of polyoxadiazole fibres in a material will be described below with reference to FIGS. 1 to 3.

The method 100 of quantitative analysis of polyoxadiazole fibres in a material comprises two broad steps 200, 300 as shown in FIG. 1. In the first step 200, a sample of the material

is prepared for the second step 300 by first immersing the sample in a solvent for polymers such as polyester 202 (for example trifluoroacetic acid (TFA), chlorobenzene, nitrobenzene, dimethylformamide, and so on) in order to dissolve polyester fibres and other additives that may be present, while retaining any polyoxadiazole fibres which are insoluble in the solvent, to obtain a mixture. The solvent should be one in which polyoxadiazole fibres cannot be dissolved, while being able to dissolve other polymers such as polyester that may be used together with polyoxadiazole to form the material. The material is typically a non-woven polyester-based composite fabric, although the method 100 is also applicable for materials such as fabrics that are woven, knitted, crocheted or formed by any other means.

The sample may comprise a representative amount of the material that is cut off from a roll of the material, preferably from the centre of the roll. An amount of the material to be used as the sample preferably contains at least 1% or more of polyoxadiazole fibres by weight. This 1% should be visible when performing the method 100 and also detectable by an analytical balance. In practice, it was found that for reliable data analysis, at least 10 mg of polyoxadiazole should be obtained when the method 100 is performed, regardless of the weight of the sample. Thus, if 10 mg of polyoxadiazole forms at least 1% by weight of the sample, a good minimum sample weight would be at least 1 g. If there is preliminary data that the amount of polyoxadiazole fibres in a particular sample is high, i.e., significantly greater than 1% by weight, then the amount of that particular sample taken for analysis can be reduced while still being able to obtain at least 10 mg of polyoxadiazole from that particular sample when the method 100 is performed. A sample of the material that is taken for analysis, which may in practice weigh from 500 mg to 1000 mg, should be dried (preferably in an oven at 105 °C) until a constant weight is achieved. Weighing of the sample is preferably performed using a digital microbalance with 5 digits accuracy.

After immersing the sample in the solvent 202 for a few minutes to dissolve polymers other than polyoxadiazole, the mixture is filtered 204 to collect any undissolved polyoxadiazole fibres as residue. The residue is then washed 206, for example twice with the solvent and three times with water. The washed residue is dried 208 (preferably in an oven at 70 °C) until the dried residue has a constant weight.

It is noted that during washing 206, there may be sedimentation of other material in the residue (for example undissolved polyester, and other materials such as polypropylene or polyaliphatic fibres that are insoluble in the solvent), so that any polyoxadiazole fibres present in the residue may be contaminated with other undissolved or solvent-insoluble materials in the material sample. Thus, it can be seen the first step 200 is insufficient to determine an exact amount of polyoxadiazole fibre in the sample. However, the first step 200 is still useful to verify whether the sample contains any polyoxadiazole fibres at all, as complete dissolution of the sample in the solvent leaving no residue after filtration will indicate absence of polyoxadiazole fibres in the sample.

In the second step 300, thermogravimetric analysis (TGA) is performed in air 300 on the dried residue obtained from the first step 200. TGA is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes, and is performed using a thermogravimetric analyser. Performing TGA in the second step 300 ensures that other materials that may be present in the dried residue other than polyoxadiazole are destroyed in order to obtain an accurate weight of the actual amount of polyoxadiazole that may be present in the sample. This is because polyoxadiazole is by comparison much more thermally stable than other natural or synthetic materials (such as wool, polyethylene and so on) as polyoxadiazole decays in air only at temperatures from 450 °C upwards whereas most other materials that may be present in the sample would have decayed by 400 °C.

As polyoxadiazole starts degrading during TGA in air only from 450 °C upwards (as shown in FIG. 2), this allows it to be separated from all other synthetic and natural fibres that may be present in the sample and which degrade completely at significantly lower temperatures (as shown in FIG. 3). Performing TGA in air may comprise heating the dried residue in air from room temperature to about 700 °C at a heating rate of 10 °C/min. The amount of polyoxadiazole fibres in the sample analysed by TGA is defined as the weight loss in the TGA temperature range from to 650 °C.

In the present method 100, it is not advisable to perform the TGA in a nitrogen atmosphere as this gives rise to formation of polyaromatic residue (about 10% by weight) which makes data interpretation difficult if not impossible. Performing TGA in air leads to complete

oxidation and destruction of all polymers without formation of residue.

Experimental Example

An experimental example of the method 100 was performed on six samples of non-woven composite materials containing different amounts of polyester fibres and polyoxadiazole fibres, all the fibres having a linear density of 1.5 denier. The six samples were prepared to contain percentage weight ratios of polyester to polyoxadiazole in the non-woven materials as shown in Table 1 below:

Sample	Polyester weight : polyoxadiazole weight (%)
1	100 : 0
2	97.5 : 2.5
3	95 : 5
4	92.5 : 7.5
5	90 : 10
6	80: 20

Table 1

The six samples were prepared by homogenously mixing appropriate amounts of polyester fibres and polyoxadiazole fibres (according to Table 1 above) using a carding machine, resulting in formation of samples of non-woven composite materials with a linear density of 100 g/m^2. The shape of the obtained samples was fixed by glue bonding using preferably about 10 wt% of glue. After glue bonding, the samples were dried in an oven at 120 °C for about 10 minutes.

From each sample, a small piece of about 700 mg to 800 mg was cut and immersed in 20 mL of TFA 202 to obtain the mixture. The mixture was stirred until all the polyester fibres were dissolved. The mixture was then filtered 204 and the residue washed 206 twice using TFA and three times with water. TFA is a preferred solvent as it is readily available and can dissolve polyester readily at room temperature. The washed residue was dried 208 in an oven at 70 °C overnight or at least until the dried residue had a constant weight.

TGA measurements were carried out 300 on the dried residue to quantitatively determine the amount of polyoxadiazole fibres in each sample. The samples were analysed under

TGA in air from room temperature to 700 °C at a heating rate of 10 °C/min. Results of the analysis are presented in Table 2 below:

Sample	Amount of polyoxadiazole fibres used in formation of sample (%wt)	Original total weight of sample (mg)	Real weight of polyoxadiazole fibres used in sample (mg)	Weight of dried residue after dissolution in TFA, filtering, washing and drying (mg)	Calculated amount of polyoxadiazole fibres from TGA (mg)
1	0	600	–	0	–
2	2.5	714	**16.7**	30.5	**18.00**
3	5	691	**32.0**	36.4	**30.76**
4	7.5	774	**54.1**	61.9	**53.23**
5	10	790	**73.0**	88.2	**70.38**
6	20	720	**131.4**	154.5	**132.56**

Table 2

TGA measurements were performed three times for each of the six samples and standard deviation of the results obtained, as shown in Table 3 below:

Sample	Amount of polyoxadiazole fibres used to form sample (%wt)	Calculated amount of polyoxadiazole fibres from TGA (% average from three measurements)	Standard deviation
1	0	0	-
2	2.50	2.69 (2.48; 2.79; 2.79)	0.179
3	5.00	4.81 (4.71; 4.78; 4.93)	0.112
4	7.50	7.38 (7.4; 7.29; 7.44)	0.078
5	10.00	9.64 (9.63; 9.69; 9.59)	0.050
6	20.00	20.18 (20.22; 20.13; 20.18)	0.045

Table 3

As can be seen in Table 3, accuracy of the TGA measurements increases with increasing amount of polyoxadiazole fibres in the material. The TGA measurements accord well with the actual amounts of polyoxadiazole fibres used to prepare the samples, thereby confirming the above described method 100 as a successful method of quantitative analysis of polyoxadiazole fibres in a material, regardless of the presence or absence of other fibres in the material.

Whilst there has been described in the foregoing description exemplary embodiments of the present invention, it will be understood by those skilled in the technology concerned that many variations and combination in details of design, construction and/or operation may be made without departing from the present invention.

CLAIMS

1. A method of quantitative analysis of polyoxadiazole fibres in a material, the method comprising the steps of:
   (a) immersing a sample of the material in a solvent to obtain a mixture, the solvent being unable to dissolve polyoxadiazole fibres and selected to dissolve other materials in the sample;
   (b) filtering the mixture to obtain a residue;
   (c) washing the residue;
   (d) drying the washed residue; and
   (e) performing thermogravimetric analysis in air on the dried residue to determine quantity by weight of any polyoxadiazole fibres present in the sample.

2. The method of claim 2, wherein other materials in the sample include at least polyester.

3. The method of claim 1, wherein the solvent comprises trifluoroacetic acid.

4. The method of any one of the preceding claims, wherein step (e) comprises heating the dried residue in air from room temperature to 700 °C at a heating rate of 10 °C/min.

5. The method of any one of the preceding claims, wherein step (c) comprises washing the residue twice with the solvent followed by washing the residue three times with water.

6. The method of any one of the preceding claims, wherein step (d) comprises heating the washed residue in an oven to dry the residue until the dried residue obtained is at a constant weight.

7. The method of claim 6, wherein the heating is at 70 °C.

8. The method of any one of the preceding claims, wherein the quantity by weight in step (e) is defined as weight loss from the residue in a temperature range from 450 °C to 650 °C during the thermogravimetric analysis.