PATENT SPECIFICATION (11) 1 581 641

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(21) Application No. 38076/76 (22) Filed 14 Sep. 1976
(23) Complete Specification Filed 7 Sep. 1977
(44) Complete Specification Published 17 Dec. 1980
(51) INT. CL.^{3} C08J 7/02
(52) Index at Acceptance
B5B 351 352 353 360 363 368 369 902
FB
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(54) IMPROVEMENTS IN OR RELATING TO METHODS OF HEAT TREATMENT OF GRAFT POLYMER FILMS

(71) I, SECRETARY OF STATE FOR DEFENCE, London, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention is concerned with methods of heat treatment of graft copolymers.

Graft copolymers are well known and preparative methods are well documented, for example in "Graft Copolymers" by H.A. Battaerd and G.W. Tregear (Vol 16 of Polymer Reviews) published in 1967 by Interscience, "Radiation Chemistry of Polymeric Systems" edited by A Chapiro (Vol 15 of High Polymers) published in 1962 by Interscience, and "Modern Plastics", *35* (1957) page 171-176. They are conveniently prepared by polymerisation of a monomer in the presence of a polymeric substrate using initiation means, generally irradiation, which generates free radical sites on the backbone of the exisitng polymer which initiate copolymerisation of the monomer. A certain amount of cross-linking and homopolymerisation may also take place.

Amongst the most important of these graft copolymers are those in which a hydrophobic backbone, eg polyethylene, is grafted with a hydrophilic monomer, eg acrylic acid, resulting in materials having uses as semi-permeable membranes in dialysis separators, in water purification apparatus by the phenomena of ultrafiltration or reverse osmosis, and as anolyte-catholyte separators in electrochemical systems. The use of these materials in primary and secondary alkaline and acid batteries is to replace the long established and somewhat unsatisfactory cellulosic separator as indicated in "Zinc-Silver Oxide Batteries" edited by A Fleisher and J Lander and published by J Wiley & Sons in 1971. (see particularly page 271).

In accordance with the present invention a method of treating a graft copolymer film comprising a hydrophilic polymeric material grafted on a hydrophobic backbone material includes the step of immersing the graft copolymer film at an elevated temperature, in a liquid treatment medium as defined hereafter capable of swelling the hydrophilic polymeric material. The liquid treatment medium is preferably removed by quenching and washing in cold water or by quenching and washing in dilute alkaline solution. It has been discovered that the treated material may be quenched directly in either dilute alkali or in distilled water at about room temperature or it may be quenched to about room temperature in air, after which it is washed.

Preferably the treatment temperature is above the crystalline melting point of the hydrophilic polymeric material and the optimum temperature for a particular treatment will vary depending upon the identity of the hydrophilic polymeric material being treated and the properties desired in the final material. The temperature is likely to be above 80°C.

In a preferred embodiment of the invention the graft copolymer film consists of a hydrophilic polymeric material grafted on to any of the polyolefins or copolyolefins, for example polyethylene (low, medium or high density), polypropylene, poly 4-methylpentene-1 (and copolymers of these polyolefins), products of other vinyl polymerisations, for example polyvinylacetate as well as the halogen containing polymers or copolymers, for example polyvinylchloride, chlorinated rubbers, and polytetrafluorethylene, polychlorofluoroethylene, products of condensation polymerisations, for example polyamides or copolymides, ie the nylons, or the saturated and the un-saturated polyesters, or a mixture of any of these polymers. The hydrophilic comonomer may be any reactive polar vinyl monomer selected from acrylic acid, methacrylic acid, other ethylenic carboxylic acids, for example itaconic acid, ethylenic carboxylic acid amides, for example acrylamide and methacrylamide, and ethylenic carboxylic acid amines, for example butylamine acrylate, and organic bases capable of quaternisation for example vinylpyridine or vinylpyrrolidone. Of these acrylic acid and methacrylic acid are preferred and acrylic acid is the most commonly used.

These graft copolymers may be polymerised by any suitable method although the preferred technique is radiation initiated grafting with high energy radiation, for example gamma photons or accelerated electrons. The copolymers may include additives such as filler particles or other additives such as thermal or oxidation stabilisers, dyes, and pigments.

The hydrophilic polymeric material should be adequately cross-linked to ensure the integrity of the film during treatment. In certain instances, for example graft copolymers using acrylic acid as the comonomer, sufficient cross-linking is normally introduced during the grafting process. If sufficient cross-linking is not present in the polymer then it may be introduced, for example by irradiation, or possibly by chemical means using divinyl benzene, for example, as cross-linking agent. The presence of cross-linking may be checked by a conventional gel test in a solvent. In this way the mechanical integrity of the film of hydrophilic polymeric material may be ensured during the reaction.

The liquid treatment medium is a hydroxyl containing organic liquid. Suitable liquids include alkanols, for example octanol or decanol, polyhydric alcohols, for example glycerol, mono-, di-, and tri- ethylene glycol and polyethylene glycol and azeotropic mixtures of alkanols and polyhydric alcohols containing less than 20% by weight of water. Preferably the liquid treatment medium is normally substantially non-aqueous. The preferred liquid treatment medium is glycerol. The liquid treatment medium may include up to 5% molar of an alkali or alkaline earth metal hydroxide and potassium hydroxide is preferred.

The object of the process of the present invention is to improve certain properties of the graft copolymer so as to make it more useful as a battery separator material. The process produces film material which tends to have a decreased electrical resistance, increased hydroxyl ion permeability, increased rate of wetting out (as defined hereinafter) and an increased equilibrium water content (as defined hereinafter) when compared with the untreated film.

The optimum time of heat treatment varies with the values of the various parameters employed, eg temperature of treatment bath, identity of heat treatment medium and it is believed that in each instance there is a particular time after which no improvement takes place. The optimum time tends to be measured in minutes rather than hours in most instances.

It is believed that the present process achieves its beneficial effects by relieving stresses and strains in the molecular structure through increasing molecular movement and permitting reorientation and rearrangement of the molecular structure. X-ray crystallography shows that there is no marked reduction in total bulk crystalline content although there is a marked reduction in the degree of preferred molecular orientation originating in the base film from which the copolymer was made. The process is usually accompanied by changes in the dimensions of the material in length, breadth and thickness, further indication of a relaxation and reordering of structure.

It has been discovered that no chemical interaction occurs between the copolymer and the treatment medium in the process of the present invention as determined by spectrophotometric analysis before and after treatment; neither is there a weight loss of copolymer during processing indicating that the process is not leaching out treatment producing pores or voids in the material by removal of matter. The foregoing discussion of the postulated reaction mechanism is not to be construed as defining the extent or scope of the invention in any way.

The present invention will now be described by way of example only with reference to the following Examples.

The degree of grafting as used in the following is defined as

$$(W_F - W_I)/W_F \times 100\%$$

where W_F is the weight of the copolymer and W_I is the weight of the original polymer film and the equilibrium water content of the copolymer film is defined as

$$(W_W - W_D)/W_D \times 100\%$$

where W_W is the weight of the sample after having been equilibrated in distilled water for 20 hours and W_D is the weight of the same sample after drying in an oven in the presence of silica gel for 20 hours at 45°C.

The electrical resistivity of the material is determined by the method outlined on page 258 of "Alkaline Storage Batteries" by Falk & Salkind published by J Wiley & Sons in 1969 in conjunction with a Wayne-Kerr Autobalance bridge using 30% aqueous Potassium hydroxide solution at 25°C as electrolyte.

Wetting-out rate values refer to the time taken for the resistivity of the sample to fall from infinity at the moment of introduction of the electrolyte to a value 10% above the final equilibrium value. It is a measure of the rate of absorption of electrolyte by the separator and is related to porous structure and hydrophilic nature of the separator.

The hydroxyl ion permeability is measured at the rate at which hydroxyl ions migrate across the separator, at 25°C, from a cell compartment containing a 10 molar aqueous potassium hydroxide solution to a cell compartment containing initially only distilled water. The rate is measured titrimetrically using *N* hydrochloric acid with phenolphthalein as indicator.

EXAMPLE 1

A 12μ thick low density polyethylene film (supplied by British Visqueen Ltd) having a size of 5 feet by 1 foot was rolled up with a single ply Blue Tissue paper interleaving and placed in a glass tube 22 inches x 1.5 inches, which was then filled with 500 ml of a 25% by volume aqueous solution of acrylic acid and containing 4g/1 of Analar (Trade Mark) ferrous sulphate. The tube and contents were evacuated by water pump for 20 minutes at the end of which time it was back filled with nominally oxygen-free nitrogen and sealed. The tube was irradiated with gamma rays from a ^{60}Co source at 20°C to a total absorbed dose of 6×10^5 rad at a dose rate of 3.5×10^4 rad per hour. The graft copolymerised LDPE film was removed from the tube, washed three times with distilled water and air dried in a hot air oven. The weight of copolymerised acrylic acid was found to be 31.2% by weight, being an homogeneous graft.

The copolymer was subjected to heat treatment by immersion in a bath of Glycerol A.R. (ex BDH) at 122°C, for 5 minutes. Following immersion the film was quenched in 0.1N aqueous potassium hydroxide solution at 25°C for 10 minutes and then air dried at 45°C.

The properties defined above were measured and the results listed in Table 1 below.

TABLE 1

	Electrical resistivity (Ω cm^2)	Hydroxylion permeability (ml.M KOH cm^{-2} min^{-1})	Equilibrium water content %	Wetting-out rate (secs.)
Before heat treatment	0.08	0.39	72	72
After heat treatment	0.03	0.53	135	12

EXAMPLE 2

A 38μ thick low density polyethylene film (supplied by Metal Box Co Ltd) was graft polymerised to a level of 32.5% with acrylic acid in the manner of example 1.

The heat treatment was carried out by immersion in Glycerol A.R. at 120°C for 4 minutes followed by quenching and drying as in example 1. The properties were determined as above and are listed in Table 2 below.

TABLE 2

	Electrical resistivity (Ω cm^2)	Hydroxylion permeability (ml.M KOH cm^{-2} min^{-1})	Equilibrium water content %	Wetting-out rate (secs.)
Before heat treatment	0.18	0.12	70	440
After heat treatment	0.09	0.20	105	68

EXAMPLE 3

A 19μ high density polythene film (supplied by Dickinson Robinson Ltd) was copolymerised with acrylic acid to a level of 28.3% by the technique of example 1.

The copolymer was subsequently heat treated by immersion in Glycerol A.R. at 120°C for 5 minutes, quenched in dilute alkali and dried. The properties were determined as above and are listed in Table 4 below.

TABLE 3

	Electrical resistivity (Ω cm^2)	Hydroxyl ion permeability (ml.M KOH cm^{-2} min^{-1})	Equilibrium water content %	Wetting-out rate (secs.)
Before heat treatment	0.12	0.29	48	560
After heat treatment	0.12	0.27	62	100

EXAMPLE 4

A 25μ polytetrafluoroethylene film (supplied by Polypenco Ltd) was grafted, in a similar manner to example 1, with acrylic acid to a level of 12.4%.

The copolymer film was heat treated by immersion in Glycerol A.R. at 120°C for 4 minutes, followed by quenching in dilute alkali and air drying. The properties were determined as above and are listed in Table 4 below.

TABLE 4

	Electrical resistivity (Ω cm^2)	Hydroxyl ion permeability (ml.M KOH cm^{-2} min^{-1})	Equilibrium water content %	Wetting-out rate (secs.)
Before heat treatment	0.18	0.18	29	127
After heat treatment	0.18	0.20	31	90

EXAMPLE 5

A 40μ thick film of polyamide (GRILAMID L25 Nylon 12) film (supplied by Grilon Plastics Ltd) was graft copolymerised to a level of 41.5% with Acrylic Acid in the manner of example 1.

The heat treatment was carried out by immersion in Glycerol AR at 190°C for 5 minutes followed by quenching and drying as in Example 1 and the properties determined and listed in Table 5 below.

TABLE 5

	Electrical resistance (Ω. cm^2)	Hydroxyl ion permeability (ml.*N* KOH cm^{-2} min^{-1})	Equilibrium water content %	Wetting-out rate (secs.)
Before heat treatment	0.16	0.10	26	425
After heat treatment	0.04	0.60	915	15

EXAMPLE 6

A 32μ thick cast polypropylene film (supplied by Shorko Films Ltd) was graft copolymerised to a level of 33.5% with Acrylic acid in the manner of example 1.

The heat treatment was carried out by immersion in glycol AR at 190°C for 5 minutes followed by quenching and drying as in example 1 to give material having the properties listed in Table 6 below.

TABLE 6

	Electrical resistance ($\Omega . cm^2$)	Hydroxyl ion permeability (ml. N KOH $cm^{-2} min^{-1}$)	Equilibrium water content %	Wetting-out rate (secs.)
Before heat treatment	0.11	0.25	27	120
After heat treatment	0.08	0.37	142	45

EXAMPLE 7

A 19μ thick cast film of high density polyethylene (supplied by Dickinson Robinson Group Ltd, Packaging Division) was graft copolymerised to a level of 55.3% with Acrylic Acid.

The heat treatment was carried out by immersion in glycerol AR at 190°C for 5 minutes followed by quenching and drying as in example 1 to give material having the properties listed in Table 7 below.

TABLE 7

	Electrical resistance ($\Omega . cm^2$)	Hydroxyl ion permeability (ml. N KOH $cm^{-2} min^{-1}$)	Equilibrium water content %	Wetting-out rate (secs.)
Before heat treatment	0.04	0.46	43	20
After heat treatment	0.02	0.52	207	10

EXAMPLE 8

A 38μ thick cast low density polyethylene (supplied by Dixons Ltd) was graft copolymerised to a level of 43.8% with Methacrylic Acid in the manner described in Example 1.

The heat treatment, quenching and drying was carried out in the manner of example 1 to yield material having the properties set out in Table 8 below.

TABLE 8

	Electrical resistance ($\Omega . cm^2$)	Hydroxyl ion permeability (ml. N KOH $cm^{-2} min^{-1}$)	Equilibrium water content %	Wetting-out rate (secs.)
Before heat treatment	2.0	0.01	15	>1000
After heat treatment	0.8	0.07	81	>1000

EXAMPLE 9

This example illustrates three difference methods of quenching the material after the heat treatment of the present invention.

A 25μ thick film of low density polyethylene film (supplied by British Visqueen Ltd) was graft copolymerised to a level of 34.8% with acrylic acid as described in Example 1.

The heat treatment was carried out by immersion in glycerol AR at 120°C for 5 minutes followed by one of the following quenching treatments:-

(a) quenched in 0.1N aqeuous potassium hydroxide solution at 25°C for 10 minutes followed by drying in air at 45°C.

(b) quenched in distilled water at 20°C for 10 minutes followed by drying in air at 45°C.

(c) Air cooled in contact with glycerol AR from 120°C to 25°C followed by washing in 0.1N aqueous KOH solution at 25°C. Air dried at 45°C.

The properties of the products were determined and are listed in Table 9 below.

TABLE 9

Sample	Electrical resistance ($\Omega \cdot cm^2$)	Hydroxyl ion permeability (ml. N KOH $cm^{-2} min^{-1}$)	Equilibrium water content %	Wetting-out rate (secs.)
Before heat treatment	0.11	0.20	25	145
After quenching treatment (a)	0.06	0.37	88	44
After quenching treatment (b)	0.06	0.44	68	47
After quenching treatment (c)	0.05	0.40	94	41

As will be seen all three methods of quenching give similar results but generally method (a) is preferred.

EXAMPLE 10

This example illustrates the use of heat treatment media other than glycerol.

A 25μ thick low density polyethylene film (supplied by British Visqueen Ltd) was graft copolymerised to a level of 34.8% with Acrylic Acid in the manner of example 1 and samples were subjected to each of the following heat treatments:-

(a) Immersion in a bath of diethylene glycol (supplied by Koch Light Laboratories) at 120°C for 5 minutes

(b) Immersion in a bath of polyethylene glycol (Code No. 200 supplied by BDH Ltd) at 120°C for 5 minutes.

After the heat treatment the materials were then quenched and dried as described in Example 1 and the properties determined to give the results quoted in Table 10 below.

TABLE 10

Sample	Electrical resistance ($\Omega \cdot cm^2$)	Hydroxyl ion permeability (ml. N KOH $cm^{-2} min^{-1}$)	Equilibrium water content %	Wetting-out rate (secs.)
Before heat treatment	0.11	0.20	25	145
After heat treatment and quench (a)	0.05	0.50	113	18
After heat treatment and quench (b)	0.05	0.49	116	17

EXAMPLE 11

This example illustrates the addition of alkali metal hydroxide particularly potassium hydroxide to the heat treatment medium.

A 12μ thick low density polyethylene film (ex British Visqueeen Ltd) was graft copolymerised to a level of 31.2% with Acrylic Acid as in example 1.

The heat treatment was carried out by immersion in Glycerol AR in which had been dissolved 5% weight for volume of "Analar" Trade Mark (ex BDH Ltd) potassium hydroxide, for 5 minutes at 122°C, followed by quenching and drying as in example 1 and the properties of the material are given in Table 11 below.

TABLE 11

	Electrical resistance (Ω . cm^2)	Hydroxyl ion premeability (ml. *N* KOH cm^{-2} min^{-1})	Equilibrium water content %	Wetting-out rate (secs.)
After treatment in Glycerol only	0.03	0.53	135	12
After treatment in Glycerol & 5% w/v KOH	0.02	0.58	140	10

This illustrates a marginal improvement in the properties of the film with the addition of potassium hydroxide to the heat treatment medium.

EXAMPLE 12

This Example illustrates the effect of temperature upon the process of the present invention.

(a) A 19μ thick cast film of high density polyethylene (supplied by Dickinson Robinson Group Ltd, Packaging Division) was graft copolymerised to a level of 55.3% with Acrylic Acid similarly to Example 1.

Heat treatment was carried out in a bath of Glycerol AR at temperatures of 120°C and 190°C for 5 minutes. Quenching and drying were carried out in the manner of example 1 and the properties of the products are given in Table 12 below.

TABLE 12

	Electrical resistance (Ω . cm^2)	Hydroxyl ion permeability (ml. *N* KOH cm^{-2} min^{-1})	Equilibrium water content %	Wetting-out rate (secs.)
Before heat treatment	0.04	0.46	43	20
After heat treatment at 120°C	0.03	0.51	78	13
After heat treatment at 190°C	0.02	0.52	207	10

(b) A 32μ thick cast polypropylene film (supplied by Shorko Films Ltd) was graft copolymerised to a level of 33.5% with Acrylic Acid in the manner of example 1.

Heat treatment was carried out in a bath of Glycerol AR at temperatures of 120°C and 190°C for 5 minutes. Quenching and drying were carried out as in example 1 and the properties of the products are given in Table 13 below.

TABLE 13

	Electrical resistance ($\Omega . cm^2$)	Hydroxyl ion permeability (ml. N KOH $cm^{-2} min^{-1}$)	Equilibrium water content %	Wetting-out rate (secs.)
Before heat treatment	0.11	0.25	27	120
After heat treatment at 120°C	0.16	0.21	79	180
After heat treatment at 190°C	0.08	0.37	142	45

(c) A 40 μ thick polyamide (Grilamid L25 Nylon 12) supplied by Grilon Plastics Ltd was graft copolymerised to a level of 41.5% with Acrylic Acid in the manner of Example 1.

Heat treatment was carried out in a bath of Glycerol AR at temperatures of 120°C and 190°C for 5 minutes. Quenching and drying were carried out as in Example 1 and the properties of the products are given in Table 14 below.

TABLE 14

	Electrical resistance ($\Omega . cm^2$)	Hydroxyl ion permeability (ml. N KOH $cm^{-2} min^{-1}$)	Equilibrium water content %	Wetting-out rate (secs.)
Before heat treatment	0.16	0.10	26	425
After heat treatment at 120°C	0.20	0.20	64	580
After heat treatment at 190°C	0.04	0.60	915	15

The base polymers used in this example (a) cast high density polyethylene, (b) cast polypropylene, and (c) nylon 12 have crystalline melting points of 127°C, 159°C, and 175°C respectively. The crystalline melting points of the respective graft copolymers are 127°C, 157°C, and 174°C. The results quoted in Tables 12 to 14 indicate that the best improvement in properties is obtained when the heat treatment temperature is above the crystalline melting point of the copolymer. It has been found that below the crystalline melting point, the results are variable.

WHAT I CLAIM IS:

1. A method of treating a graft copolymer film comprising a hydrophilic polymeric material grafted on a hydrophobic backbone material which includes the step of immersing the graft copolymer film at an elevated temperature in a liquid treatment medium (as hereinbefore defined) capable of swelling the hydrophilic polymeric material.

2. A method as claimed in claim 1 and wherein the heat treatment is at a temperature in excess of 80°C.

3. A method as claimed in claim 1 or claim 2 and wherein the liquid treatment medium is removed by quenching and washing in cold distilled water.

4. A method as claimed in claim 1 or claim 2 and wherein the liquid treatment medium is removed by quenching and washing in dilute alkaline solution.

5. A method as claimed in claims 1 or 2 and wherein the treated graft copolymer film is quenched to about room temperature in air and washed in either dilute alkali or distilled water.

6. A method as claimed in claim 1 or claim 2 and wherein the heat treatment is at a temperature in excess of the crystalline melting point of the hydrophilic polymeric material.

7. A method as claimed in any one preceding claim and wherein the hydrophobic

backbone material is a polyolefin or copolyolefin or a condensation polymer or a mixture thereof.

8. A method as claimed in claim 7 and wherein the base polymer is low, medium, or high density polyethylene, polypropylene, poly-4-methylpentene-1, polyvinylacetate, polyvinylchloride, chlorinated rubber, polytetrafluoroethylene, polychlorofluoroethylene, polyamides, copolyamides, saturated and unsaturated polyesters, or mixtures or copolymers of the preceding materials.

9. A method as claimed in any one of the preceding claims and wherein the comonomer from which the hydrophilic polymeric material is derived is acrylic acid, methacrylic acid, itaconic acid, acrylamide, methacrylamide, butylamine, acrylate, vinyl pyridine, or vinyl pyrrolidone.

10. A method as claimed in any one preceding claim and wherein the liquid treatment medium is an alkanol, a polyhydric alcohol, an ethylene or a polyethylene glycol.

11. A method as claimed in any one of claims 1 to 9 and wherein the liquid treatment medium is octanol, decanol, glycerol, diethylene glycol, or polyethylene glycol.

12. A method as claimed in any one preceding claim and wherein the liquid treatment medium also contains up to 5% molar of an alkali metal or alkaline earth metal hydroxide.

13. A method as claimed in claim 12 and wherein the alkali metal hydroxide is potassium hydroxide.

14. A method substantially as hereinbefore described and with particular reference to the accompanying examples.

15. A graft copolymer film when produced by a method as claimed in any one preceding claim.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1980.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.