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RADIATION PROCESS OF PREPARING GRAFTED ELASTOMERIC FIBERS WHEREIN POST-DECRYSTALLIZATION IS EMPLOYED

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ABSTRACT OF THE DISCLOSURE

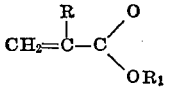
Cellulose-containing fibrous materials such as rayon yarn are converted into elastic materials by a process in which the fibrous materials are irradiated, an acrylate monomer is graft copolymerized onto the irradiated material and the product of the grafting process is treated with a decrystallizing agent. The elastic product obtained possesses good extensibility and elastic recovery and can be used in place of fibrous rubber in the preparation of elastic products.

The present invention relates to a method of imparting elastic properties to fibrous cellulose-containing materials by grafting acrylate compounds thereon.

Heretofore, acrylate monomers such as ethyl acrylate have been co-polymerized onto rayon for the purpose of producing elastic fibers, However, such efforts have either been unsuccessful or have achieved elasticity only after very large amounts of ethyl acrylate have been grafted onto the rayon.

An article by Nakamura et al. entitled, "Elastomers Based on Cellulose Fibers," Journal of Polymer Science, Part C, Number 23, pp. 629–645, 1968, discloses grafting ethyl acrylate onto rayon fibers using ceric ion initiation and indicates that high graft levels are required to obtain elasticity. The use of a pretreatment with a zinc chloride decrystallizing agent increases the elasticity at a given graft level to some degree, but still an extent of grafting of over 1000 percent was required to obtain rubber-like behaviour. In a subsequent article by Nakamura et al., entitled "Rheological Properties of Elastomers Based on Cellulose Fibers," Polymer Preprints, Vol. 11, Number 1, February 1970, Division of Polymer Chemistry, A.C.S., work is described wherein rayon yarn is irradiated prior to grafting ethyl acrylate thereon. This process increases the elasticity of the grafted product but still, even at high irradiation dosages, a graft level of about 300 percent was required to obtain an elastic fiber.

In accordance with the present invention an elastic fibrous material is provided by grafting an acrylate compound onto a cellulose-containing fibrous material using a procedure by which the elasticity can be obtained when the extent of grafting is as low as 50 percent by weight based on the weight of the fibrous material. In this process the cellulose-containing fibrous material is irradiated, there is grafted onto the irradiated material an acrylate compound of the formula



where R is hydrogen or methyl and
R_1 is alkyl of 1 to 6 carbon atoms;

and the product of the grafting step is treated with a decrystallizing agent for the cellulose-containing fibrous material.

The irradiation treatment ise carried out by exposing the cellulose-containing fibrous material to high energy irradiation such as gamma rays from cobalt-60. The dose

of irradiation given to the cellulose-containing fibrous material should be from about 0.1 to 100 megarads with a dose of 0.2 to 50 megarads being preferred. It is preferable to carry out the irradiation while maintaining the cellulose-containing fibrous material under vacuum, but irradiation can be carried out under atmospheric conditions. The irradiation decreases the degree of polymerization of the cellulose in the fibrous material with increasing irradiation dosages giving greater depolymerization and an increase in the elasticity of the final product. The dose should be limited to about 100 megarads to prevent excessive degradation of the cellulose. The irradiation forms radicals in the cellulose which are capable of initiating grafting in the subsequent grafting step.

Grafting is carried out using an aqueous emulsion of an acrylate compound of the above given formula. Preferably the emulsion contains about 1 to 60 percent by weight of the acrylate compound and 40 to 99 percent by weight of water. Other additives may be present such as up to 5 percent by weight of a dispersing or emulsifying agent. Illustrative of suitable acrylate compounds are methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, pentyl acrylate, hexyl acrylate and the corresponding methacrylates. Mixtures of these compounds can also be employed. To obtain elastic properties, the extent of grafting should be equal to at least 50 percent, preferably 100 percent, by weight based on the weight of the original cellulose-containing fibrous material.

Following the grafting step, the product is treated with a decrystallizing agent for the cellulosic material. Illustrative of decrystallizing agents are zinc chloride, cuprietylene diamine, cupritetramine hydroxide, concentrated liquid ammonia, lithium hydroxide, benzyltrimethylammonium hydroxide, ethylamine and ethylenediamine. Where the decrystallizing agent is a solid material it can be used in a concentrated solution in a solvent such as water.

In order to obtain elastic material at low levels of grafting, it is essential that the treatment with the decrystallizing agent be carried out after grafting. When the decrystallizing agent is used prior to grafting, the cellulose recrystallizes during the grafting step and little improvement in elasticity is obtained. It is believed that the large increase in elasticity obtained by treatment after grafting (post-decrystallization) is a result of the grafted material preventing or interfering with recrystallization. Although the best results are obtained with a fibrous cellulose-containing material which has been irradiated, the use of the above-described post-decrystallization is not limited to irradiated material. When a high extent of grafting is desirable or permissible, post-decrystallization can be used to give improved results where the cellulose-containing material has not been irradiated and the grafting of the acrylate compound has been initiated by other means such as chemical means, e.g., ceric ion initiation.

The cellulose-containing fibrous material can be in the form of fibers, filaments or yarns, or fabrics made therefrom. The cellulose can be from any source, including such natural sources as seed fibers such as cotton; bast fibers such as flax (linen); ramie, jute and hemp, as well as regenerated cellulose such as rayon where wood may serve as the source of cellulose.

The products obtained by the present invention possess good extensibility as measured by elongation at break and good elastic recovery. The products can be used in place of fibrous rubber in the preparation of elastic products.

The following examples are given to further illustrate the invention, but it is understood that the invention is not to be limited in any way by the details described herein.

EXAMPLE 1

Samples of various types of rayon yarn weighing 100 milligrams each were wound on three-prong glass tares and placed into glass ampoules. Subsequently, the ampoules were evacuated at 10^{-5} mm. Hg. for 16 hours at 25° C. and sealed under vacuum. The samples were then irradiated in a cobalt 60 facility at dose rates of 0.1–0.2 megarads per hour at 25° C. Following irradiation degassed emulsions of 55 millimols ethyl acrylate (EA) and 19.0 ml. of an aqueous 5% solution of an alkyl aryl polyether alcohol emulsifier were added to each sample. The samples in contact with the grafting solution were placed into a water bath maintained at 45° C. and grafting was allowed to proceed for the times indicated with slight agitation. Following the grafting period the samples were washed in at least three changes of water and then soxhlet extracted with acetone for 8 hours to assure complete removal of homopolymers.

Post-decrystallization was carried out by exposing the grafted yarn to 70% aqueous $ZnCl_2$ at 60° C. for 30 minutes followed by thorough washing with water and drying in a vacuum oven at 50° C. Cupriethylene diamine (Cuene) for 30 minutes at 25° C. followed by water washing and drying was also used in parallel postdecrystallization experiments.

The percent graft, based on initial sample weight, was calculated and the breaking extensions determined on an Instron table model tester using a crosshead speed of 2 in./mkn. at 21° C. and 65% R.H.

Rayon type	Dose (Mrads)	Dose rate (Mrads/hr.)	Grafting time (hrs.)	Percent graft	Percent breaking elongation: Before decrystallization	Cuene.	70% $ZnCl_2$
Semidull-continuous filament rayon	3.6	0.2	0.4	78	30.0	480	410
Semidull-continuous filament viscose	4.0	0.2	0.5	103	30.0	520	430
Dull-staple	11.4	0.1	0.5	177	32.0	300	450
Bright-continuous filament	14.5	0.2	5.0	690	32.0	450	400
All "core"	9.7	0.2	10.5	530	14.0	540	500
All "skin"	9.7	0.2	7.0	179	12.0	480	300

EXAMPLE 2

Cotton yarn was grafted in a similar fashion as rayon in Example 1 except using 28 millimols ethyl acrylate in 28 ml. of the 5% aqueous solution of emulsifying agent at 25° C. Also, the total dose was 4.7 Mrads at a 0.1 Mrads/hour rate. The grafting period was for 24 hours.

Sample ---------- Cotton.
Percent graft ---------- 192.
Percent breaking elongation:
Before decrystallization ---------- 18.0.
Cuene. ---------- 400.
70% $ZnCl_2$ ---------- 400.

EXAMPLE 3

A sterilized cotton gauze pad was grafted in a similar fashion as rayon in Example 1 except using 111 millimols of ethyl acrylate and 19 ml. of the 5% aqueous solution of emulsifying agent. Also, the total dose was 4.2 Mrads at a 0.1 Mrad/hour rate. Grafting was carried out for 4.0 hours at 25° C.

Sample ---------- Cotton gauze pad
Percent graft ---------- 790.
Percent breaking elongation:
Before decrystallization ---------- 35.
Cuene. ---------- 420.
70% $ZnCl_2$ ---------- 400.

EXAMPLE 4

A cellophane film (regenerated cellulose) of 1.5 mils in thickness and a Whatman Filter Paper No. 2 (cellulose fiber mat) were treated in a similar fashion as example 1 except at a total dose of 3.2 Mrads and a grafting period of one hour.

Sample	Percent graft	Percent breaking elongation: Before decrystallization	Cuene.	70% $ZnCl_2$
Cellophane film	640	14.0	500	400
Filter paper.	538	8.0	400	380

EXAMPLE 5

This example illustrates the use of postdecrystallization to improve elastic properties where the cellulose-containing material was not irradiated. Samples of a continuous filament viscose rayon yarn (150 denier, 40 filament semidull), wound without tension on a three-pronged glass bobbin, were placed in a test tube containing the specified quantity of $Ce(NH_4)_2(NO_3)_6 6H_2O$. initiator, 10 millimols HNO_3 and enough water to give 100 gms. of the final grafting solution. The system, maintained at 35° C. was purged with N_2 for 30 min. and during the last ten minutes of this time, ethyl acrylate, contained in a burette inserted in the system, was simultaneously purged. The ethyl acrylate was added to the reaction and grafting was continued for the time specified with the bubbling of nitrogen being maintained for the entire grafting time. Upon removal of the samples from the graft solution they were washed several times with tap water, then the acetone to remove the bulk of the homopolymer. Soxhlet extraction of the rewound samples with acetone was then continued until constant dry sample weights were obtained.

Post-decrystallization of grafted yarns was carried out by exposing the samples wound on glass bobbins to 60% aqueous $ZnCl_2$ solution at 60° C. for 20 min. The samples were washed with water, then with 0.1% acetic acid, and finally with water and dried under reduced pressure over a mixture of $CaSO_4/CaCl_2$.

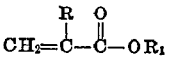
Percent graft, and physical properties were found as in Example 1.

Sample	Ce^{+4} millimols	Ethyl acrylate, millimols	Time, minutes	Percent graft	Percent ultimate elongation: Before decrystallization	Post decrystallization
B	0.5	31	90	590	47.6	79.2
A	1.0	28	90	415	30.0	57.1
Untreated					26.1	16.8

It will be apparent that many modifications and variations can be effected without departing from the scope of the novel concepts of the present invention, and the illustrative details disclosed are not to be construed as imposing undue limitations on the invention.

What is claimed is:

1. In a process for imparting elastic properties to a cellulose-containing fibrous material by subjecting said fibrous material to high energy radiation and graft copolymerizing onto said irradiated material at least one acrylate compound of the formula:



where

R is hydrogen or methyl and
R_1 is alkyl of 1 to 6 carbon atoms,

the improvement wherein the product obtained after said grafting is treated with a decrystallizing agent for cellulose selected from the group consisting of zinc chloride, cupriethylene diamine, cupritetramine hydroxide, concentrated liquid ammonia, lithium hydroxide, benzyltrimethylammonium hydroxide, ethylamine and ethylenediamine, said process requiring an irradiation dose of about 0.1 to 100 megarads and an amount of acrylate compound copolymerized onto said irradiated material equal to at least 50% by weight based on the weight of said irradiated material.

2. A process as claimed in claim 1 wherein said acrylate compound is ethyl acrylate.

3. A process as claimed in claim 1 wherein said cellulose-containing fibrous material is made of rayon.

4. A process as claimed in claim 1 wherein said cellulose-containing fibrous material is made of cotton.

5. A process as claimed in claim 1 wherein said decrystallizing agent is selected from the group consisting of zinc chloride and cupriethylene diamine.

6. A process as claimed in claim 1 wherein said cellulose-containing material is subjected to an irradiation dose of about 0.2 to 50 megarads and the amount of acrylate compound graft copolymerized onto the irradiated material is equal to at least 100% by weight based on the weight of the irradiated material.

References Cited

Nakamura el al., Cellulose Graft Copolymers, J. of Applied Polymer Science, vol. 15, pp. 391–401 (1971).

Nanamura et al, Elastomers Based on Cellulose Fibers, J. of Polymer Science, Part C, No. 23, pp. 629–645 (1968).

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U.S. Cl. X.R.

8—116 R, 129; 260—17 A, 17.4 GC