⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: 0 000 994
A1

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **78300277.7**

㉒ Date of filing: **11.08.78**

(51) Int. Cl.²: **C 08 G 81/02**, C 08 L 51/00,
C 08 F 259/04
// C08F210/12

㉚ Priority: **18.08.77 US 825758**

(43) Date of publication of application: **07.03.79**
Bulletin 79/5

(84) Designated Contracting States: **BE DE FR GB NL**

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(54) Process of preparing plasticized compositions of PVC and butyl rubber.

(57) Process of preparing plasticized compositions of PVC and butylrubber (IIR) including the steps of preparing the graft copolymer PVC-g-IIR and subsequently crosslinking the ungrafted butyl rubber with the graft copolymer. By employing the crosslinking step, substantially great amounts of butyl rubber may be incorporated with PVC.

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The present invention relates to a novel process for the compatibilization of polyvinyl chloride (PVC) and butyl rubber (IIR) to prepare useful plasticized PVC compositions. In order to impart useful, flexible properties to PVC it is necessary to incorporate a plasticizer. Butyl rubber, a random copolymer of isobutylene and a small percent isoprene can plasticize PVC, however, it has been difficult to add and maintain a relatively high content of butyl rubber in PVC either by blending or grafting.

PVC and butyl rubber can be made compatible to some extent by the preparation of a graft product PVC-g-IIR. It is presently known that polyvinyl chloride, in the presence of certain alkylaluminum compounds, will initiate polymerization of isobutylene (IB) to produce PVC-g-PIB copolymers. One such cationic grafting process is disclosed in U.S. Pat. Nos. 3,904,708 and 3,933,942, wherein a halogenated polymer serves as a backbone for the graft of cationically polymerizable monomers such as isobutylene, styrene, isoprene, butadiene and the like.

Further work with cationic graft polymerization has been reported by J.P. Kennedy and D.L. Davidson, J. Polym. Sci. Chem. Ed. 13, 153 (1976), wherein isobutylene and isoprene were copolymerized in the presence of a PVC backbone and an alkylaluminum halide compound to form PVC-g-IIR copolymers. The product obtained was generally a mixture of PVC-g-IIR and ungrafted PVC and butyl rubber. The highest amount of butyl rubber in the graft product was reported as 39.1% by weight. The grafting efficiency was 14.6%, indicating a large formation of ungrafted butyl rubber. After the copolymerization of the isobutylene and isoprene the reaction was terminated and the ungrafted butyl rubber was extracted. Tests were subsequently undertaken with solvent cast films of the graft copolymer uncured and cured with sulfur monochloride (S_2Cl_2). The uncured product failed at 160 kg/cm^2 while the cured product showed a reduction in stress properties, failing at about 130 kg/cm^2.

Thus, while the preparation of PVC-g-IIR has been described elsewhere, the product used as such has not been readily millable nor moldable, nor strong and homogeneous. In terms of processing, the extra step of extraction of ungrafted butyl rubber had been necessary and the ungrafted butyl rubber had merely become waste. Though the extracted product PVC-g-IIR possesses acceptable properties in films (solvent cast), it is still not readily millable or moldable under commonly utilized PVC processing conditions. Thus, the prior art has yielded a graft product which could not be utilized commercially except in a very limited sense, e.g., solvent cast films.

It is therefore an object of the present invention to provide a novel process for the compatibilization of PVC and butyl rubber branches are first grafted from a PVC backbone and then the graft copolymer and ungrafted butyl rubber are cured together.

It is another object of the present invention to provide a novel process for the compatibilization of PVC and butyl rubber wherein a much higher amount of butyl rubber is incorporated with the PVC, as a plasticizer, than has heretofore been possible.

It is yet another object of the present invention to provide a novel process for the compatibilization of PVC and butyl rubber wherein excess, ungrafted butyl rubber is not extracted from the total graft product, thereby eliminating waste.

It is still another object of the present invention to provide a useful composition of PVC and butyl rubber which is strong, homogeneous, millable and moldable upon curing.

These and other object of the present invention shall become apparent from the specification and claims which follow.

In accordance with the invention there is provided a process for preparing a plasticized composition of PVC and butyl rubber characterized by preparing the graft copolymer, PVC-g-IIR from a suitable PVC backbone and a quantity of isobutylene and isoprene in the presence of a suitable catalyst and a swelling agent; dissolving said graft copolymer and any ungrafted PVC and butyl rubber in a suitable solvent; and thereafter crosslinking said graft copolymer and ungrafted butyl rubber for a period of time of up to about 60 hours to form the desired product.

The PVC polymer may be suspended in a suitable solvent, a monomeric charge of isobutylene and isoprene is added, the mixture is cooled to approximately -40°C. and a catalytic amount of an alkylaluminum halide solution is added to initiate copolymerization of the isobutylene and isoprene from the PVC backbone. The polymerization reaction is terminated after a suitable time following which the graft copolymer and remaining ungrafted PVC and butyl rubber are dissolved in tetrahydrofuran (THF) and treated with S_2Cl_2 and allowed to cure for a period of time of from about 20 minutes to about 60 hours. The cured product may be readily milled and molded by mixing it with conventional processing aids and stabilizers. In this process substantially all of the butyl rubber formed is incorporated with the PVC being either grafted therefrom or crosslinked to the graft copolymer.

The polymerization reaction conditions

under which the graft copolymer, PVC-g-IIR may be prepared include polymerization times of from about 5 minutes to about 120 minutes with 20-90 minutes being preferred and a temperature of from about -70°C. to about 0°C., with -55° to -40°C. being preferred.

Selection of the polyvinyl chloride polymer is not necessarily critical. The number-average molecular weight of the polymer may range from about 5,000 to about 200,000 with 30,000 - 130,000 g/mole being preferred. Similarly, the graft butyl rubber branches may be any conventional unsaturated random copolymer of an isoolefin and a multi-olefin such as disclosed in U.S. Pat. Nos. 2,727,874 and 3,694,377, with number-average molecular weights of the graft, per branch, ranging from about 15,000 to about 1,000,000 g/mole. In terms of weight %, it is believed that the amount of polymer backbone and the butyl rubber branches in the product may each range from about 5 to 95 in any combination totalling 100. For plasticized PVC, the preferred combination is from about 25 to 65 percent by weight of butyl rubber in the total product.

Perhaps somewhat more significant than selection of the components comprising the graft branches is the percent by weight ratio of each to the other in the overall product. While in prior art techniques it has not been possible to incorporate unlimited amounts of butyl rubber by grafting, the process of the present invention permits essentially all of the butyl rubber formed to be incorporated with the PVC. Therefore, variations in the amount of butyl rubber, ranging from about 5 wt. % to about 95 wt. % are possible, and will vary the properties of the resultant graft product from hard plastic-like to soft elastomeric, respecively. Depending upon selected composition, the product may be used for flexible tubing, packaging films, pipes and protective coatings. However, raising the butyl rubber content to about 54% provides very similar hardness of the PVC as when it has been plasticized with about 30% dioctyl phthlate.

The catalyst system of the present invention comprises a compound of the type $Al(M)_2R$, where M is a branched or straight chain alkyl group having from 1 to about 12 carbons and R is selected from the group consisting of M, hydrogen or halogen. Although the compound, i.e., alkylaluminum, is referred to as the catalyst it is to be understood that the compound works with the polymeric halide as a coinitiator system which will enable the cationic polymerization of the olefins to commence and proceed from the polymeric halide. Representative compounds which may be employed are listed in U.S. Pat. No. 3,694,377, the subject matter of which is hereby incorporated by reference. A particularly useful compound is diethylaluminum chloride, Et_2AlCl.

In order to conduct the grafting efficiently, suitable solvents such as methylene chloride, ethylene chloride, 1,2-dichlorobenzene or mixtures thereof may be employed as a swelling agent.

In a typical laboratory synthesis of the graft copolymer, the procedures employed were as follows:

A commercial PVC sample (FPC 9326 or FPC 9300, Firestone Plastic Co.) was utilized for grafting. Isobutylene (Union Carbide Corporation) was dried by passage over molecular sieves and barium oxide. Isoprene (Matheson, Coleman & Bell Co.), diethylaluminum chloride (Ethyl Corp.) and methylene chloride (Matheson, Coleman & Bell Co.) were each freshly distilled prior to use. All reactions and manipulations were conducted in a stainless steel safety enclosure under dry nitrogen atmosphere (moisture content less than 50 ppm). All parts are in terms of percent by weight unless otherwise specified.

300 Mls. isobutylene and 40 mls. isoprene were charged to a suspension comprising 90.0 gms. of

PVC in 100 mls. methylene chloride at -40°C., to which was added 20 mls. of diethylaluminum chloride solution (1.5M in n-hexane) twice at intervals of 20 minutes with continuous stirring. The reaction was terminated with methanol after about 60 minutes and the product which was subsequently precipitated in excess methanol and dried, weighed 110.2 gms indicating a content of 18.3% butyl rubber. The conversion, based upon the amount of isobutylene, was 8.5%. The product from this stage of the process should be understood to consist of the graft copolymer as well as any ungrafted butyl rubber and PVC.

Six solutions were prepared for curing containing 5% wt./vol. of the product in THF. To this solution was added S_2Cl_2 to give a 1% vol./vol. solution of the latter in THF. The subsequent crosslinking reaction was allowed to proceed for various time periods ranging from about 20 minutes to 60 hours. The reaction was terminated with methanol and the product thereof was subsequently dried. Next, equal parts (1 part per 100 parts of the product) of calcium stearate, as a processing aid, and barium-cadmium laurate, as a stabilizer were added to the product. Although calcium stearate and barium-cadmium laurate were employed, it is to be understood that any conventional processing aid and stabilizer for PVC may be selected.

While the uncured product could not be milled, was very sticky and became nonhomogeneous, as cure time increased, the product became less sticky and stronger. Compression molding of the cured product routinely carried out at 148-163°C. for 3-10 minutes was also quite feasible but not for the uncured product. Generally, an increase in the tensile strength of the product was observed to be directly related to an increase in the cure time as indicated in Table I for a graft product containing 18.3% butyl rubber. Although reduction in the cure time is possible without much sacrifice in tensile strength by employing peroxides with the S_2Cl_2, it has been found that the best results were obtained by allowing the product to cure slowly.

TABLE I

Tensile Properties of PVC-g-IIR as a Function of Cure Time

Cure Time (hrs.)	3.5	5.0	7.0	24.0	31.0	55.0
Tensile Strength (Kg/cm^2)	17.58	23.20	35.15	84.37	105.46	210.90

In Table II, six graft products are presented wherein the weight percent of butyl rubber in the products ranges from 15-65%. Tensile strengths, ultimate elongation and hardness properties have been determined and are included. The curing was carried out as explained hereinabove, i.e., utilizing a 5% wt./vol. of the product in THF to which S_2Cl_2 is added to give a 1% vol./vol. solution of the latter in THF.

TABLE II

Tensile Properties of PVC-g-IIR as a Function of % IIR Present

Sample No.	%IIR	Ultimate Elongation %	Tensile Strength[a] MPa	Kg/cm^2	Hardness	
1	15	40	48.8	497	--	
		115	17.9	183[b]		
2	18	23	20.7	211	40	(R)
		125	6.6	67[b]		
3	26	17	26.2	267	72	(R)
		66	13.0	132[b]		
4	46	70	31.0	316	10	(R)
		230	6.0	61[b]		
5	55	95	21.4	218	54	(D)
		150	5.5	56[b]		
6	65	90	5.5	246	56	(D)
		140	7.6	77[b]		

(a) Cure Time 55 Hrs.

(b) Tests carried out at 100°C.

Thus, it can be seen that the disclosed invention carries out the objects of the invention set forth above. By crosslinking the ungrafted butyl rubber branches to the graft copolymer prepared not only is a costly step of extraction eliminated but also, there is no waste of butyl rubber. Furthermore, much greater amounts of butyl rubber may be incorporated with the PVC than has been heretofore possible by grafting techniques alone. As will be apparent to those skilled in the art, properties of the PVC and butyl rubber product can be varied by selection of the resultant molecular weight and percent composition of the product and, it is believed that the preparation of these can be obtained without departing from the spirit of the invention herein disclosed and described, the scope of the invention being limited solely by the scope of the attached claims.

CLAIMS

1. A process for preparing a plasticized composition of PVC and butyl rubber, characterized by preparing the graft copolymer, PVC-g-IIR from a suitable PVC backbone and a quantity of isobutylene and isoprene in the presence of a suitable catalyst and a swelling agent; dissolving said graft copolymer and any ungrafted PVC and butyl rubber in a suitable solvent; and thereafter crosslinking said graft copolymer and ungrafted butyl rubber for a period of time of up to about 60 hours to form the desired product.

2. A process according to claim 1, characterized by the fact that the graft copolymer is prepared by charging a suitably prepared reaction vessel with polyvinyl chloride and the swelling agent; charging a quantity of isobutylene and isoprene to the reaction vessel at a temperature of from -70°C. to 0°C.; adding a catalytic amount of an alkylaluminum compound with continuous mixing whereby said polyvinyl chloride and said alkylaluminum compound initiate copolymerization of said isobutylene and said isoprene; and reacting the contents of the reaction vessel for a period of time of from about 5 minutes to about 120 minutes to form a graft copolymer of PVC and butyl rubber.

3. A process according to claim 2, characterized by the fact that the alkylaluminum compound is diethylaluminum chloride.

4. A process according to any one of the preceding claims, characterized by the fact that the weight percent of the butyl rubber in the desired product is from 5.0 to 95.0.

5. A process according to any one of the preceding claims, characterized by the fact that S_2Cl_2 is added to the solution of graft copolymer and ungrafted PVC and butyl rubber in the crosslinking step.

6. A process according to any one of the preceding claims, characterized by the fact that the solvent is THF.

7. A process according to any one of the preceding claims, characterized by the fact that the swelling agent is methylene chloride, ethylene chloride, 1,2-dichlorobenzene or mixtures thereof.

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EUROPEAN SEARCH REPORT

0000994
Application number
EP 78 30 0277

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	No relevant documents have been disclosed. ----	

CLASSIFICATION OF THE APPLICATION (Int. Cl.²)

C 08 G 81/02
C 08 L 51/00
C 08 F 259/04//
C 08 F 210/12

TECHNICAL FIELDS SEARCHED (Int.Cl.²)

C 08 G 81/02
C 08 L 51/00
C 08 F 259/00
C 08 F 259/02
C 08 F 259/04
C 08 F 291/04

CATEGORY OF CITED DOCUMENTS

X:	particularly relevant
A:	technological background
O:	non-written disclosure
P:	intermediate document
T:	theory or principle underlying the invention
E:	conflicting application
D:	document cited in the application
L:	citation for other reasons
&:	member of the same patent family, corresponding document

☒ The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	24-10-1978	GIRARD

EPO Form 1503.1 06.78