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POLYMERIZED VINYL COMPOUNDS

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The present invention relates to film-forming thermo-plastic polymerized vinyl compounds in a condition of improved mechanical properties and a process of producing same in such condition.

When films of polymerized vinyl compounds such as polystyrene are prepared in the usual manner by pouring solutions of polystyrene or the like onto a support and allowing the solvent to evaporate, or by cutting thin leaflets from a block of polystyrene, or when threads of polystyrene are produced by extruding plastified or dissolved polystyrene through a nozzle while allowing the solvent, if such be present, to evaporate, the films and threads thus obtained are not only very brittle and fragile but they have only a small resistance to tearing and small extensibility. The methods according to which such tests are made are described for example in "J. Eggert, Filmgebilde aus Viskose, 1932", pages 216 to 218 and 236 to 238.

We have now found that the mechanical properties of film-forming thermoplastic polymerized vinyl compounds, especially of films, threads and like bodies therefrom, may be considerably improved by stretching the said substances while in a plastic state at elevated temperatures and allowing them to cool while in the stretched state. Suitable film-forming thermoplastic polymerized vinyl compounds are for example polystyrene or masses containing the same, polyvinyl esters, such as polyvinyl chloride, polyvinyl acetate or polyacrylic esters and also mixed polymerization products obtained from several of the monomeric compounds forming the basis of the said polymerized compounds, and conversion products of polymerized vinyl compounds, as for example condensation products of polymerized vinyl alcohols and aldehydes and also mixtures of polymerized vinyl compounds with each other or with softening agents or other substances. When employing mixtures of polymerized vinyl compounds, it is frequently possible to employ in these mixtures polymerized vinyl compounds which themselves have no pronounced film-forming properties, as for example ethers of polymerized vinyl alcohols and these often act as softening agents. Softening agents may be added to the materials under treatment in varying amounts, for example in amounts from 1 to 30 per cent. By heating the products to higher temperatures they become liquid.

The process according to the present invention may be carried out by extruding the polymerized vinyl compound in the said plastic state through a nozzle, for example a slit or perforation, the resulting body being stretched while still plastic and kept under tension until cooled. The temperature is preferably so chosen that the material employed has just become flexible. The stretching, for example of films or threads of pure polystyrene, is effected at temperatures of from 70° to about 200° C, preferably between 90° and 130° C. In the case of mixtures, for example of mixtures of polystyrene with other substances, such as softening agents, the temperature may sometimes be lower. The most favorable temperature depends on the nature of the treated compound and also on the tractive force, the speed of pulling and the desired thickness of the film or thread. When leaving the nozzle, films may be stretched in the direction of the pull or at right angles thereto; threads are only stretched in the direction of pull. Any overstretching of the products, as for example by too rapid pulling or working at too high or too low a temperature must be avoided. The overstretching can be avoided by controlling the clearness of the substances while stretching; overstretched products are turbid and show fractures. The conditions as to speed of pulling, pulling force and working temperature to be employed in each case differ and may be readily ascertained by simple preliminary experiments.

It may be of advantage to add to the polymerized vinyl compounds to be stretched small amounts of a volatile solvent or swelling agent, care being taken that it volatilizes during the stretching. An advantageous method of carrying out the process is by passing the polymerized vinyl compounds through hot rollers, then stretching them and allowing them to cool while in the stretched state.

The stretching, for example of polystyrene, may be carried out in air or in an inert gas or vapor or in a liquid medium which does not dissolve the polystyrene at normal or increased temperature, for example in water. The process may also be applied to foils, plates, bands and the like of polymerized vinyl compounds which have already been prepared and even the properties of poured brittle polystyrene films are improved by the said subsequent treatment.

The extension of the films may be effected for example in a stretching device with the aid of travelling bands and stretching wheels or by hand. Furthermore, polystyrene or the like may be extruded in the form of a tube, through a nozzle having a core, the still plastic tube or the tube rendered plastic again by heating being then carefully blown out with gases, such as air or nitrogen, or vapors, such as steam. After cooling the tube is cut up. Furthermore, the films may be stretched by means of a suitable device in two directions at right angles to each other.

According to the present invention products of good properties can be produced from polystyrene alone or with an addition of softening agents, as for example tricresyl phosphate, and

if desired with coloring matter and/or fillers, from polymerized vinyl chloride, vinyl acetate and the like. Mixed polymerization products, for example those from styrene and acrylic esters, vinyl esters or vinyl ethers or those from vinyl chloride and vinyl acetate may also be employed, if desired together with softening agents, coloring matters and/or fillers. Other polymerization products for example natural rubber may also be admixed with the polymerization products of one or several of the polymerizable vinyl compounds and stretched according to the present process. By suitably selecting these components of such mixtures and the additions, it is possible to adapt the mechanical properties of the products to any desired purpose.

The films, threads and the like obtained according to the present invention are no longer brittle and fragile and have substantially better strength characteristics than the unstretched material. They are clear and possess also high elasticity and excellent crease values. When heated to become plastic, for example when the polystyrene products are heated to between 90° and 100° C, they shrink to a certain degree.

The following Examples will further illustrate the nature of this invention but the invention is not restricted to these Examples.

Example 1

Pure polystyrene is rendered plastic by heating to 170° C and extruded through a slit nozzle and stretched at from 130° to 140° C. The aperture of the slit nozzle is selected so that a film of 0.1 millimeter thickness is obtained. It has the following strength characteristics:

Resistance to tearing—kilograms per square millimeter	9.2 to 10.0
Extensibility—per cent	5
Crease value	1000 to 2000

If, however, films are prepared without treatment according to the present invention products are obtained the mechanical properties of which are not so good. Thus for example films of 0.1 millimeter thickness prepared from a 10 per cent solution of polystyrene in a mixture of toluene and xylene by pouring have the following strength characteristics:

Resistance to tearing—kilograms per square millimeter	2.5 to 2.8
Extensibility—per cent	1
Crease value	0

Example 2

Polystyrene having a temperature of 170° C is extruded through a nozzle 40 millimeters in breadth and having an inner width of 2 millimeters with an extrusion speed of 25 centimeters per minute. The strip formed is stretched in all directions in a room having a temperature of 95° C with a pulling speed of 50 centimeters per minute. The strip is then allowed to cool while in the stretched state. The glass-clear film obtained has the mechanical properties given under No. 1 in the table below.

If the strip of polystyrene after extrusion is stretched with a pulling speed of 150 centimeters per minute a glass-clear film is obtained the mechanical properties of which are given under No. 2 in the table.

Other conditions (such as the temperature of the polystyrene, the temperature in the space where stretching is effected, the speed of extrusion and the speed of pulling) may also be used; over-stretching of the film, however, leads to a deterioration of the mechanical properties and usually to turbidity of the products; thus by working under the conditions stated above but by pulling with a speed of 300 centimeters per minute turbid films result with otherwise deteriorated properties as compared with the product No. 2; the test values of this product are given under No. 3 in the table below. The most suitable conditions may be easily determined by a preliminary experiment.

Table

No.	Thickness of the film	Resistance to tearing in kilograms per square millimeter		Extensibility in both directions
		Longitudinal	Transverse	
1	0.01	4.9	4.6	2
2	0.01	9.9	9.4	4–5
3	0.01	7.3	6.3	1

Example 3

A thread is prepared by slightly twisting 10 single threads which are obtained by extruding polystyrene in the plastic state for example at between 140° and 160°C through a nozzle having 10 perforations (each of which has a diameter of 0.2 millimeter) and stretching until cool. The said thread has the following properties:

Legal titer—denier	51.7
Resistance to tearing—grs. per 100 denier	82.5
Extensibility—per cent	80

A thread obtained by mere extrusion of polystyrene from the same nozzle (without stretching) has the following properties:

Legal titer—denier	500
Resistance to tearing—grs. per 100 denier	20.8
Extensibility—per cent	3.4

It may be advantageous to add to the polystyrene to be worked up slight amounts of readily volatile solvents or diluents, such as benzene, care being taken that the said addition is removed as completely as possible before cooling. In this case the working temperature may be somewhat lower.

Example 4

A plate consisting of polyvinyl chloride is passed through heated rollers, the film leaving the rollers being stretched in the longitudinal and transverse directions at 100°C, as for example in an atmosphere of steam. The resulting film has the following strength characteristics as compared with an untreated film:

Film	Thickness of film in millimeters	Resistance to tearing in kilograms per square millimeter	Extensibility, percent	Crease value
Untreated	0.08	5.5 to 6.7	10 to 25	300 to 400
Stretched by about 100 per cent	0.08	6.0 to 7.3	95 to 150	700 to 1300
Stretched by about 200 per cent	0.08	6.8 to 8.5	120 to 230	1100 to 2100

A film of polymerized vinyl chloride stretched in an analogous manner but only in one direc-

tion has the following mechanical characteristics in the direction of stretching:

Percentage stretch	Thickness of film in millimeters	Resistance to tearing in kilograms per square millimeter	Extensibility, percent
60	0.095	7.9	12.2
140	0.075	8.1	16.0
150	0.09	9.0	15.0
170	0.09	8.5	17.0

Example 5

A film obtained by rolling at 105°C from a mixed polymerization product prepared from a mixture of 68 per cent of vinyl chloride and 32 per cent acrylic acid methyl ester is stretched in one direction between heated plates in air and allowed to cool under tension. The resulting film has the following strength characteristics:

Film	Thickness of film in millimeters	Resistance to tearing in kilograms per square millimeter		Extensibility per cent		Crease value	
		Longitudinal	Transverse	*l*	*t*	*l*	*t*
Unstretched	0.28	6.9	0.0	11	5	36	175
Stretched by about 50 per cent	0.20	10.1	5.6	50	7	221	1021

In this table *l* represents the longitudinal measurement and *t* the transverse measurement.

Example 6

A foil of 85 per cent of a mixed polymerization product derived from 71 per cent of vinyl chloride and 29 per cent of acrylic acid methyl ester, and 15 per cent of para rubber obtained by rolling at 95°C is passed at 90°C through a system of pairs of rollers arranged one behind another of which the pair of rollers farther from the inlet of the film has a greater speed of rotation than that near to the said inlet, the film being allowed to cool in the stretched state. The resulting film has the following characteristics:

Film	Thickness of film in millimeters	Resistance to tearing in kilograms per square millimeter		Extensibility per cent		Crease value	
		Longitudinal	Transverse	*l*	*t*	*l*	*t*
Rolled and slightly orientated	0.28	5.8	3.4	31	1	1120	0
Stretched by about 50 per cent	0.23	7.4	4.2	19	2	3605	0

In this table *l* represents the longitudinal measurements and *t* the transverse measurements.

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