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(57) Abstract

Oriented poly(chlorotrifluoroethylene) based films comprising up to 1 pourcent by weight of copolymerizable comonomers as well as oriented poly(chlorotrifluoroethylene) films formed essentially of a homopolymer comprising no copolymerizable comonomers are provided; all of the films are formed from low zero strength time film forming resin compositions which are highly amorphous in nature, and which are subjected to a process which includes the steps of: preheating the film above its glass transition temperature, stretching the film to provide a film having a stretched:unstretched ratio of between about 2:1 to about 5:1, followed by annealing the film. The films feature excellent resistance to vapor transmission, particularly water vapor, and feature good physical strength characteristics.

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HIGH BARRIER PCTFE FILM

The present invention relates to polytrichlorotrifluoroethylene films, film forming compositions, processes for making thermoplastic films featuring improved water vapor barrier properties.

Oriented films of polychlorotrifluoroethylene (hererinafter interchangeably referred to as "PCTFE") which feature useful properties such as excellent resistance to gas and vapor permeability, good film strength and other charactersitics are well known to the art.

An exemplary PCTFE film known to the art is that described in US Patent 4,544,721 to Levy for "Chlorotrifluoroethylene Polymer Oriented Films"; the film taught therein finds particular use as a heat shrinkable film. Although Levy suggests a useful PCTFE film comprising copolymerizable organic monomers, (as evidenced by his Example compositions), Levy fails to successfully teach a successful method of producing an oriented PCTFE film comprising less than the stated 3.8% of additives present in his exemplary compositions which simultaneously provide superior resistance to vapor transmission.

In accordance with the present invention, there is provided a PCTFE film formed from a polychlorotrifluoroethylene film forming composition comprising less than about 1% by weight of comonomers, such as ethylenically unsaturated copolymerizable organic monomers. Such a film may optionally be further characterized as being highly amorphous and exhibiting a very low water vapor transmission rate, within the range of less than about 0.030 grams per 100

square inches per day at 100°F for a film thickness of 1 mil. Such a film may optionally be further characterized as being highly amorphous having a degree of crystallinity of less than about 60% and exhibiting a very low water vapor transmission rate of less than about 0.03 grams per 100 square inches per day at 100°F for a film thickness of about 1 mil.

In a further aspect of the present invention, there is provided a process for forming an amorphous PCTFE film from a PCTFE film forming resin having less than about 1% by weight of one or more comonomers and having the characteristics immediately described above which comprises the process steps of:

(A) extruding the film forming composition onto a casting roll or casting rolls that are in such casting roll/rolls maintained in temperatures of below about 100°F, and preferably below about 80°F, so to effecutuate the rapid quenching of the film,

(B) stretch orienting the film in a ratio of stretched:unstretched of between about 2:1 to about 5:1. the film, and

(C) annealing the stretched film.

In an additional aspect of the invention, there is provided a process for forming a blown film from a PCTFE film forming resin as described above and which is also stretched and annealed as described above.

Optionally, the PCTFE film has a degree of crystallinity of less than about 60% and which is stretch oriented in a ratio of stretched:unstretched of between about 2:1 to about 5:1.

Figure 1 illustrates empirically evaluated percentages of crystallinity which were determined by conventional differential scanning calorimetric techniques (DSC) for films of varying compositions containing different quantities of the as a function of

the density of a film sample and as a function of the percentages of comonomer, particularly the comonomer vinylidine fluoride within a composition.

According to the present invention, there is provided a PCTFE film forming film from a PCTFE film forming resin composition of a PCTFE resin comprising up to 1 percent by weight of an additional comonomers such as ethylenically unsaturated copolymerizable organic monomers which in its final stretched and oriented form has a low degree of crystallinity, viz., less than about 60% crystalline wherein such film is also oriented in the machine direction in the ratio between about 2:1 to about 5:1; more preferably, between about 2:1 to about 5:1, most preferably between about 3:1 and about 4:1 and further wherein such film exhibits a water vapor transmission rate (hereinafter sometimes referred to as "WVTR") of less than about 0.05 grams/100 sq. in./day for a 1 mil film thickness, preferably less than 0.01 grams/100 sq. in./day for a 1 mil film thickness.

A suitable PCTFE film forming resin which may be used in conjunction with the teaching of the present invention may be any PCTFE resin which comprises up to about 1% by weight of comonomers and which may be further characterized as having a zero strength time (sometimes interchangeably referred to as "ZST") of less than about 200, preferably less than about 185 and most preferably about 160 and less. The specification of such a ZST is important to the success of the present invention as it has been found by the inventors that only such film PCTFE film forming resins having such a ZST as specified herein may be successfully oriented and formed into a film having the beneficial features as taught herein.

The determination of the ZST for the PCTFE film forming resin may be determined in accordance with the method which is more fully described in the Encyclopedia of Polymer Science and Engineering, 2nd. ed. Vol. 3 at page 476, published by John Wiley and Sons. A further method of determining the number average molecular weight of the PCTFE film forming compositions for herein may be in accordance with the specifications outlined in ASTM-D 1430-81 from which a the ZST is evaluated. Briefly ASTM-D 1430-81 utilizes a compression molded test sample formed of the PCTFE film forming having dimensions of about 1.6 mm by 4.8 mm by 5.0 mm and which has a dual "v" shaped notch in the central portion of the test sample. The sample is suspended from one end with a 7.5 gram weight suspended from the other end in an oven from 250°C. The ZST value is the time in seconds after which the sample breaks; the ZST value is known to the art to reasonably correlate to the number average molecular weight of resin used to form the tested sample.

Further suitable PCTFE film forming resins include those which have a number average molecular weight of about 1,000,000 and less, preferably about 750,000 and less. The number average molecular weight for the PCTFE film forming resin may be correlated from its intrinsic viscosity by well known techniques. Such conventional techniques, for example by determining the intrinsic viscosity of a sample of the resin in a solvent such as 2,5-dichlorobenzyltrifluoride wherein the intrinsic viscosity of the sample may be correlated to the numerical average molecular weight in accordance with the equation:

$$[\eta] = 6.15 \times 10^{-5} \text{ (Num.Avg.Mol.Wt.)}^{0.74}$$

wherein the intrinsic viscosity is the value "$[\eta]$".

Such a suitable PCTFE film forming resin may be produced in accordance with conventional processes for the production of PCTFE film forming resins by processes which include a variety of process techniques and a variety of reaction systems. Such processes include bulk polymerization via the utilization of one or more peroxides as an intiating system; aqueous suspension polymerization with redox-initiator systems which include one or more alkali metal persulfates as an oxidant, one or more alkali metal bisulfites as activators, and metal salts as accelerators; emulsion polymerization utilizing fluorocarbon and chlorofluorocarbon emulsifiers are also known. The molecular weight of the PCTFE film forming resin produced may be controlled by variance of the reactor temperature and pressure, as well as the reaction time in order to produce suitable PCTFE film forming resin.

By way of example, one suitable process, a reduction-oxidation type reaction, comprises the steps of charging a sufficient quantity of the starting reactant pctfe to a glass lined, jacketed, stirred sealable reactor which is capable of operating at least to pressures of about 200 psig. It is preferred that the reactor include a cooling jacket or other cooling means which is capable to withdraw heat from the reactor during the production process and thereby provide a means of temperature control during the reaction of the contents of the reactor.

The reaction system requires the use of an initiator/catalyst system to produce the PCTFE film forming resin from chlortrifluoroethylene monomer. Such an intitiator/catalyst system comprises reduction, oxidation and acceleration constituents wherein the oxidation constituents provide free radicals for the initiation of the polymerization of the CTFE. By way

of example, suitable reduction constituents include one or more chemicals selected from the group which includes; an alkali metal bisulfate and alkali metal persulfate. Suitable oxidation constituents include one or more chemicals selected from the group which includes: hydrogen peroxide, and various metallic persulfates, including sodium persulfate and potassium persulfate, as well as ammonium persulfite. Suitable acceleration constituents include one or more chemicals selected from the group which includes: variable valence metal sults such as ferrous sulphate, silver nitrate as well as copper sulfate. Varying ratios of these constituents may be used; i.e. the ratio of the oxidation to the reduction constituents may be varied from 1:1 to 3:1, and the activator may be included in amounts to comprise to 1000 parts per million ("ppm") as well as greater amounts.

Other processes and systems suitable for the production of PCTFE film forming and copolymer resins are described in U.S. Patent Nos. 2,705,706; 2,700,622; 2,689,241; 2,569,524; 2,783,219; 2,820,026; 3,640,985; 3,671,510; 3,642,754; 3,632,847; 3,014,01. The control of the reaction conditions leads to the producion of PCTFE film forming resins which are within the specified range of suitable ZST values.

It is contemplated that the PCTFE film forming resin may include minor amounts, i.e. generally up to 1% by weight of an ethylene compound containing fluoride, including: fluorinated α-olefins, such as hexafluoropropylene, hexafluoroisobutylene, vinylidene fluoride, tetrafluoroethylene, chlorotrifluoroethylene; fluorinated ethers such as perfluoroalkyl vinyl ethers such as perfluoropropyl vinyl ether; perfluoroalkyl ethylenes such as perfluorobutyl ethylene, and the like.

The films of the present invention may be formed by any conventional film forming technique. Such film-forming techniques include but are not limited to the following: formation of films by casting the film onto a casting roll after extrusion through a flat film-forming die, formation of films by the "blown film" technique wherein a film-forming composition is forced through a circular die and the exiting circular film profile is expanded by compressed air, casting a film-forming composition into a billet or other solid form and subsequently skiving the film from said formed billet, as well as other techniques not particularly described here. Of these techniques, preferred methods for the production of film include film casting techniques, and the production of film by blown film techniques. Of these, the most preferred is the formation of films by conventional film casting techniques.

The thicknesses of the films which are produced by any of the processes outlined above, particularly by the blown film process or by a film casting process may have thicknessess of between 0.001 and 100 mils, preferably of between about 0.05 and 60 mils thickness prior to any stretching operation which will further reduce the film thickeness.

In preferred embodiments of the invention, films may be produced by blown film techniques, as well as by extrusion forming of films wherein the film-forming composition as described above is provided to the inlet of an extruder wherein the action of heat and mechanical work performed upon the film-forming composition plastificates the film and afterwards the composition is forced through a flat film-forming die. The film exiting the film-forming die is then quickly contacted with a chilled casting roll which is

maintained at a temperature of less than about 100 °F, and preferably less than about 80 °F in order to quench the film and reduce the formation of crystallites within the film. To assure good contact of the extruded film and the chilled casting roll, the use of mechanical means (such as an idler roll, or a plurality of chilled rolls) or other inducement means (such as the use of an air knife or air blower) for inducing the contact of the film and the chilled casting roll may be used to urge and maintain the contact of the film with the chilled casting roll.

The PCTFE film removed from the chilled casting roll is an unoriented amorphous film. It may be removed and wound onto a core or spool for storage prior to subsequent processessing, or in the alternative the PCTFE film may be directly treated in the succeeding process steps.

The rapid quenching of the film as taught herein assures that the film is "substantially amorphous" which is herein defined prior to a subsequent stretching operation to be 25% or less crystalline in nature. Preferably the film prior to the subsequent stretching operation is less than or equal to about 20% crystalline in nature. The crystallinity of the film may be determined by the use of an x-ray diffraction apparatus. Alternatively a differential scanning calorimeter (DSC) may be used. Suitable films in accordance with the present teaching are those which exhibit diffusely scattered x-ray diffraction patterns, evident of a low degree of crystallinity and within the ranges described immediately above.

It has been observed by inventors that the ultimate water vapor transmission rate, a useful measure of the permitivity of the film, is reduced with reducing degree of crystallinity. Therefore, for

higher barrier properties, a more amorphous film is to be preferred and this may be accomplished by decreasing the temperature of the surface of the chilled casting roll, by decreasing the distance from the exit of the die to the chilled casting roll, or both.

Subsequent to removal from the casting roll and prior to the stretching operation, the film is preheated above its glass transition temperature (Tg) preferably at least 10 °F above its Tg, but below the film's degradation temperature. Generally, for the PCTFE films taught herein an acceptable temperature range is between about 160 °F and about 210 °F, although the use of higher temperatures may be used, particularly with thicker films. Preheating of the film may be accomplished with any effective means such as contacting the film with at least one heating rol, or with two casting rolls which contact both surfaces of the film simultaneously or in series. The film is preheated by at least partially wrapping the film about the surface of at least one heating roll for a sufficient time to elevate the temperature of the film to at least 10 degrees F above its Tg.

The preheated film is subsequently subjected to a stretching operation wherein the films of the present invention are stretched in a single direction coinciding with the length of the film (as opposed to its width) which will be referred to as the "machine direction" (MD).

The film is most desirably stretched so to have a final ratio of stretched film:unstretched film of between about 2:1 to about 5:1; preferably and most preferably the films according to the present invention have a ratio of stretch of between about 3:1 to about 4:1.

A preferred process for effectuating orientation of the film is by causing the machine direction (MD) orientation of the film by the following process steps. The film is preheated to a temperature at least about 10 deg.F above its Tg, preferably between about 160°F to 210°F, after which it is subjected to a first "slow" stretch roller at a further elevated temperature, preferably a temperature of between about 210°F to about 260°F, and subsequently to a "fast" stretch roller at a film temperature which may be same as that during the "slow" stretching, or at different, but preferably lower temperature. Both the "slow" and the "fast" stretch rollers are paralleledly rotating heatable rollers having parallel central axes which defines their axis of rotation, such as those which are conventionally used in the art for stretching films.

During the stretching operation, the film is first provided to the surface of the rotating slow stretch roller which operates at a peripheral drive speed which is approximately equal to the peripheral drive speed of the last heating roll during the heating operation. In this manner the film is preferably not subjected to any stress or stretching forces prior to the stretching operation described herein. The film contacting the surface of the rotating slow stretch roller is preferably wound at least partially upon the surface of the slow stretch roller to assure that sufficient drag is imparted upon the film to minimize slippage of the film upon the slow stretch roller prior to the stretching operation and during the stretching operation.

The film contacting the surface of the slow stretch roller and passing at least partially about its circumference is then drawn off and contacts the surface of the fast stretch roller which rotates at a

different speed so that the ratio of the circumferential speed of the slow stretch roller to the fast stretch roller is between about 1:2 and 1:5. Preferably the ratio of the circumferential speed of the slow stretch roller to the fast stretch roller is between about 1:3 and 1:4.

An important aspect of the stretching operation is the limitation of the dimensions of the "stretch zone" which is defined as the dimensions of the length of the film which is subjected to stretching between the "slow" and "fast" stretch rollers as is measureable by the tangental line which the film defines as it leaves the "slow" stretch roller and contacts the "fast" stretch roller, which is defined as the "stretch length", and, the width of the film which is subjected to stretching, which is defined as the "stretch width". It is highly desirable that the length of this stretch zone be minimized so to assure rapid stretching of the film which is believed to contribute to the improvements in the modulus of the film. In accordance with the PCTFE film taught in the instant invention, the ratio of the stretch width:stretch length should be less than 1:1, preferably less than 5:1, and most preferably less than about 7.5:1. Subsequent to the stretching operation described above, the film is subjected to an annealing operation wherein the stretched film is removed from the "fast" stretch roller and brought into contact with at least one annealling roller which is a temperature above the Tg of the stretched film and which further has a circumferential speed which is slower than that of the "fast" stretch roller. The elevated temperature of the annealling roller provides a second heat setting operation to the stretched and oriented film, which operation has been found to enhance the crystallinity

of the film and further to improve the dimensional stability of the stretched and oriented film. It is generally to be preferred that the circumferential speed of the at least one annealling roller is up to 50% slower than that of the "fast" stretch roller, and is preferably between about 5% to about 25% slower. It is also generally to be preferred that the temperature of the annealling roller is at least 10°F or more in excess of the Tg of the PCTFE film taught herein, most preferably the temperature of the annealling roller is between about 200°F and about 300°F.

Where a plurality of annealling rollers is to be utilized, it is to be understood that the circumferential speeds of each of the annealing rollers is to be maintained at a uniform speed relative to each other and within the ranges described immediately above. Examples of a plurality of annealling rollers includes but is not limited to: a "stack" of rollers as has been hereintofore described in conjunction with the description of heating rolls above.

Subsequent to the the annealling operation as performed by the annealling roll (or rollers) the film may optionally have its edges trimmed and may then be wound onto a core or spool in any manner conventionally used in the art.

The films taught in the present specification provide good physical characteristics and excellent WVTR barrier characteristics.

The physical characteristics of the film may be determined in accordance with test protocols which are known to the art and are conventionally used. These include those specified in ASTM material specifications for PCTFE plastics and resins, ASTM D-1430, including the specification for the ZST values ASTM D-1430-8. The tests included the protocols defined by the

American Society of Testing Materials, including but not limited to those designated under the protocols of ASTM D 882-83 "Standard Testing Methods for Tensile Properties of Thin Plastic Sheeting". Preferably, the samples are evaluated in both the machine direction and the transverse directions.

The density of the film forming resin compositions and/or films were determined by the use of a standard density column which utilized as reference fluids, tetrabromopropane ethylene bromide, and 1,3-dibromoethane.

The crystallinity of a film sample was determined by the equation:

$$\%cryst = 1150 \bullet (density - 2.0) + (5.56 \bullet \%VF_2) - 92$$

which equation is derived from experimentally evaluated results using conventional linear regression analytical techniques. A representation of the data is illustrated on Figure 1. Figure 1 illustrates empirically evaluated percentages of crystallinity which were determined by conventional differential scanning calorimetric techniques (DSC) for films of varying compositions containing different quantities of the as a function of the density of a film sample and as a function of the percentages of comonomer, particularly the comonomer vinylidine fluoride within a composition. As may be seen from Figure 1, the three different lines indicate the correlation for three differing film compositions comprising varying amounts of vinylidine fluoride, 3.6%, 1.0% and 0%, respectively.

Determination of the water vapor transmission rate may be evaluated in accordance with conventionally known techniques and includes the use of a Mocon

Permatran W-600 apparatus which determines the water vapor transmission rate of a sheet of film at an established temperature; the WVTR values which are provided are normalized to a 100 square inch film sample having a 1 mil thickness of film and the temperature of evaluation was established to be 122°F (50°C); values for the WVTR were also reported as normalized to the temperature of 100°F. The normalization factor was derived from empirical studies by the inventor and the normalized values of the WVTR at 100°F are provided so to produce a common denominator for comparison with other film compositions of the prior art.

Determination of other selected physical properties of the film included determination of the dimesional stability of the film; samples of the films were placed in a heated oven having a respective temperature for a set period; the shrinkange in both the machine direction and the transverse direction was then evaluated and the percent shrinkage was determined. Negative values indicated shrinkage from original dimensions. By way of example, 10 by 10 inch square film samples were placed in a 300°F oven for 10 minutes, after which the films were removed and the shrinkage in machine direction and the transverse direction was determined.

The films formed in accordance with the present teaching feature a WVTR value of less than about about 0.030 grams per 100 square inches per day; more preferably, a WVTR of less than about 0.025 grams per 100 square inches per day based on a film thickness of 1 mil.

The films taught in the present invention may also be incorporated into multi-layer film structures, which may be produced in accordance with conventional known

techniques such as by co-extrusion or lamination. By way of non-limiting example useful thermoplastic films which may be used in conjunction with the high barrier PCTFE film include:

acrylonitrile butadiene-styrene,
rubber modified acrylonitrile methyl acrylate copolymer,
cellulostic films including cellulose acetate,
cellulose triacetate,
cellulose acetate butyrate,
cellulose propionate,
ethyl cellulose,
cellophane,
fluoroplastic films including
ethylenechlorotrifluoroethylene copolymer (ECTFE),
ethylenetetrafluoroethylene copolymer (ETFE),
fluorinated ethylene-propylene copolymer (FEP),
perfluoroalkoxy (PFA),
polychlorotrifluoroethylene copolymers (PCTFE),
polytetrafluoroethylene (PTFE),
polyvinylfluoride (PVF),
polyvinylidene fluoride (PVDF),
ionomer films,
polyamide films including unoriented, monoaxially oriented, or biaxially films, including films including nylon 6, nylon 12 as well as polyamide copolymers and blends of each of the above,
polybutylene,
polycarbonate (PC),
polyethylene terephthalate (PET) as well as polyethyene terephthalate/copolymer films such as those conventionally known to the art as "PET-G" type films including KODAR® films available from the Eastman Kodak Co.,

polyethylene and polyethylene copolymer films including
low density polyethylene (LDPE),
medium density polyethylene (MDPE),
high density polyethylene (HDPE),
ultrahigh molecular weight polyethylene (UHMWPE),
ethylene-vinyl acetate copolymers (EVA),
polyimide films,
polymethylmethacrylate films, (both "standard" and "type A")
polymethylpentene,
polypropylene (PP) films including cast, unoriented, monoaxially oriented, or biaxially oriented,
polystyrene,
polyurethane,
polyvinyl chloride (PVC),
sulfone polymer films,
vinyl chloride-acetate copolymer,
vinylidene chloride-vinyl chloride films,
vinyl nitrile rubber alloy films, as well as others not particularly noted here.

It is contemplated that in such a multilayer structure, the films may formed with or without intermediate adhesive layers therebetween, such intermediate adhesive layers are also known as "tie layers" to the art and materials which are known to be useful in conjunction with PCTFE films may be used.

The high barrier PCTFE film taught herein may also be used to form a one or more layers within a multi-layer article.

The films may be used in the production or construction of a wide variety of articles which desirably feature low gas permitivity rates and low WVTR rates. By way of example but not by way of limitation these include: films, sheets, plates, bags, pouches, sealable and non-sealable articles formed

utilizing any of the above, profiled shapes, containers, flasks, bottles, jars, packing material, as well as other articles not particularly denoted here. The films of the present invention may also be incorporated into the construction of articles which require one or more layers of a high barrier film as is provided by the instant invention. Examples of such articles include but are not limited to: electroluminescent displays, electroluminescent lamps, bezels, instrument covers, and the like.

The films of the present invention are also useful as heat shrinkable films; as is well known to the art such heat shrinkable films find use in a variety of appliations, particularly packaging applications.

The film forming compositions described hereunder were formed from a plurality of PCTFE film forming resins in accordance with a redox reaction system as generally outlined above. The temperature of the reaction was controlled so to remain at a temperature level below that conventionally used for the production of PCTFE materials which have a high ZST value; for the system used the reaction temperature was maintained so as not to exceed about 90 deg.F. Particular resin compositions of the Examples included up to about 1% by weight of copolymerized vinylidine fluoride (VF_2) which

was provided as a monomer to the initial reaction. Resin compositions are outlined on Table 1.

TABLE 1

Resin:	ZST value	wt.% VF_2
Resin #1	161	0.9
Resin #2	157	0.8
Resin #3	141	0.1
Resin #4	127	0.0
Resin #5	120	3.6

Resins #1 - #4 are in accordance with the present invention's teaching. Resin #5 is provided for comparative purposes and illustrates compositions according to the prior art.

Process Example 1

The PCTFE resins were formed into films in accordance with the following general process. The constituents of a respective composition was provided to the feed inlet of a 2 1/2 inch single screw extruder equipped with a two-stage screw and having a L/D ratio of 24:1. The feed rate was 60 lbs/hr, the temperature of the feed inlet was approximately at 545 deg.F, the barrel temperature was approximately 500 deg, and the extrudate was metered at about 545 deg.F The extrudate was provided to a coathanger type film die having a width of 34 inches and a gap of about 0.045 inches. The die temperature was 610 deg.F., the die head pressure was about 2500 psi and the extruded film was extruded at a line speed of 8 ft/minute to produce a film of approximately 4 mils thickness. The film was

laid onto a casting roll at a temperature of about 50 deg.F and a diameter of 14 inches, and a lay-on roll at the same temperature and having a diameter of 8 inches. The lay-on roll was used to assure contact of the film onto the casting roll and to assure rapid quenching. The films were then wound onto a core for temporary storage.

The films were then provided to a stretching apparatus at varying rates of between 15 and 27 feet/minute. The films were first preheated to a temperature of between 180-190 deg.F, and then provided to a slow stretch roll at a temperature of about 200 deg.F, and subsequently to a fast stretch roll at a temperature of between 180-190 deg.F, and afterwards to a heat set roll at a temperature of 230 deg.F to anneal the stretched film. The annealed film was subsequently cooled by contacting the film with a cooled roll at a temperature of about 100 deg.F. The films were oriented with varying stretch ratios of between 2:1 and 3:1.

The films exiting the extruder had a thickness of approximately 4 mils prior to the stretch orientation step; subsequent to the stretch orientation the films had a thickness of between about 1.5 and 2 mils thickness.

Process Example 2

The PCTFE resins were formed into films in accordance with the following general process. The constituents of a respective film forming composition were provided to the feed inlet of a 2 1/2 inch single screw extruder equipped operating substantially in accordance with the conditions outlined above. The extrudate was provided to a coathanger type film die to produce a film having a thickness of 12 mils. The die

temperature was 610 deg.F., the die head pressure was about 2500 psi and the extruded film was extruded at a line speed of 3 ft/minute. The film was laid onto a casting roll at a temperature of about 50 deg.F and a diameter of 14 inches, and a lay-on roll at the same temperature and having a diameter of 8 inches. The lay-on roll was used to assure contact of the film onto the casting roll and to assure rapid quenching. The films were then wound onto a core for temporary storage.

The films were then provided to a stretching apparatus operating at the following parameters. The films were first preheated to a temperature of between 180-200 deg.F, and then provided at a linespeed of 20 feet/minute to a slow stretch roll having a peripheral speed of 20 feet/min. and at a temperature of about 210-260 deg.F, and subsequently to a fast stretch roll having a peripheral speed of between 60-80 feet/min. and at a temperature of between 210-250 deg.F, and then subsequently to a heat set roll at a temperature of between 240-270 deg.F and having a peripheral speed of 60-82 feet/minute so to anneal the stretched film. The annealed film was subsequently cooled by contacting the film with a cooled roll at a temperature of about 150 deg.F. and rotating at a peripheral speed of 60-82 feet per minute; the films were oriented with varying stretch ratios of 3:1, 3.5:1 and 4:1.

The final films had a thickness of about 4 mil.

Process Example 3

Film compositions were produced substantially in accordance with the method outlined above indicated as Process Example 2. Variations from that process which were used in the instant Process Example included that the casting roll temperature was controlled to be

maintained at about 60 deg.F and no lay-on roll was used.

Testing

The respective films formed were tested in accordance with standard test procedures according to ASTM guidelines, particularly those described above. Testing of the water vapor transmission were performed on a Mocon Permatron-W600 testing apparatus. Values of the WVTR values illustrated were determined and reported at 122°F (50°C) and are also reported as normalized so as to be based on a film sample having 100 square inches and a film thickness of 1 mil, under test conditions of 100°F irregardless of the actual film thickness.

Percentages of crystallinity were determined by the use of conventional differential scanning calorimetric apparatus (DSC) or alternatively were determined by correlation of the density values for the film obtained from the density column measurement described above for a film composition containing a known amount of comonomer, or absence of such a comonomer, with the graph indicated on Figure 1.

Characteristics of the films produced in accordance with the examples are outlined on Table 2 which illustrates particular barrier properties and crystallinity of the film. Particular characteristics of the film samples particularly shrinkage characteristics and tear strengths are reported on Table 3.

TABLE 2

Film Example:	F1	F2	F3	F4	F5	F6	F7	F8
Resin Example:	1	1	1	2	2	3	3	3
ZST:	161	161	161	157	157	141	141	141
Process Example:	1	1	1	1	1	1	1	2
Thickness (mil):	4	4	4	4	4	2	1.5	1.5
Draw Ratio:	2:1	3:1	3.5:1	2:1	3:1	2:1	3:1	3:1
Tensile Strength								
MD: Yield (psi):	---	---	---	---	---	---	---	---
TD: Yield (psi):	5452	5852	6374	5639	5497	5923	5183	5819
MD: Break (psi):	19399	27322	25813	17077	26569	15734	22339	21866
TD: Break (psi):	6228	6567	6437	5802	4727	4494	6013	4186
MD: Elongation,%:	44	18	15	55	23	55	18	23
TD: Elongation,%:	283	293	340	299	285	247	294	224
MD: Modulus (psi):	231226	253684	281936	223083	251991	243013	236904	232700
TD: Modulus (psi):	189765	204890	194498	178179	175971	156563	184982	204002
Density:	2.101	2.102	2.105	2.102	2.103	2.108	2.106	---
Crystallinity, %:	29.2	30.3	33.7	30.3	30.9	32.1	29.9	---
WVTR (122F)*	---	0.042	---	0.072	0.051	0.051	0.033	0.033
WVTR (100F)**	---	0.014	---	0.024	0.017	0.017	0.011	0.011

* WVTR values given as (WVTR * film thickness (grams * mils / 100 sq.inches / day) at 122 deg.F

** normalized WVTR values given as (WVTR * film thickness (grams * mils / 100 sq.inches / day) at 100 deg.F

"MD" indicates machine-direction orientation

"TD" indicates transverse-direction orientation

F14	F15	F16	F17	F18	F19	F20
5	5	4	4	4	4	4
120	120	127	127	127	127	127
1	1	4	4	4	4	4
4	4	4	6	4	4	6
2:1	2.5:1	3:1	2:1	3:1	3:1	2:1
---	---	---	---	---	---	---
5202	4885	5668	5886	6692	6725	6576
15500	20355	24779	13946	18099	23970	12101
5612	4276	3675	4446	3595	3538	3823
64	10	27	59	48	33	71
361	242	190	232	109	152	148
209716	306463	247898	218516	257077	257913	219050
177980	139203	207847	178902	194089	208992	190273
2.091	2.092	---	---	---	---	---
32.5	33.8	37.8	36.7	44.7	45.1	41.5
0.099	0.096	0.036	0.03	0.036	0.024	0.03
0.033	0.032	0.012	0.01	0.012	0.008	0.01

TABLE 3

Film Example:	F1	F2	F3	F4	F5	F6	F7	F8
Graves Tear Str.								
MD: (gm/mil):	403	291	287	398	298	423	356	392
TD: (gm/mil):	307	306	257	292	331	311	319	323
Dimensional Stab.								
at 300 deg.F:								
MD: (%)	---	---	---	---	---	---	---	-12.1
TD: (%)	---	---	---	---	---	---	---	1.1
at 257 deg.F:								
MD: (%)	---	---	---	---	---	---	---	-12.5
TD: (%)	---	---	---	---	---	---	---	0.9
at 26.6 deg.F:								
MD: (%)	---	---	---	---	---	---	---	---
TD: (%)	---	---	---	---	---	---	---	---

F14	F15	F16	F17	F18	F19	F20
387	397	--	--	--	--	--
296	307	--	--	--	--	--
--	--	-12.5	-14.1	-3.1	-6.3	-3.1
--	--	0	0	-1.6	-1.6	0
--	--	--	--	--	--	--
--	--	--	--	--	--	--
--	--	-4.7	-7.8	-1.6	-1.6	-1.6
--	--	0	0	0	0	0

As may be clearly seen from Table 2, the film compositions which included compositions of Resin #5 are exemplarly of the prior art. The films formed of Resins #1 - Resin #4 include less than 1% by weight of a copolymerizable comonomer, and particular attention is directed to Resin #4 which is seen to consist essentially of a PCTFE hompolymer resin having a ZST value of 127. As may further be seen from the results of Table 2, the films according to the invention, F1-F8, and F16-F20 feature excellent water vapor barrier transmission properties as is evidenced from the WVTR values in comparision with a conventional film according to F14-F15. It should be apparent therefore that the films according to the inventive compostiions provide improved barrier properties per mil of thickness as compared to conventional prior art film compositions.

As may be seen from Table 3, particularly from the values for films F16-F20, the films experienced good dimensional stability especially when subjected to elevated temperatures (300°F, 10 minutes) under conditions as described above.

CLAIMS

1. An amorphous polychlorotetrafluoroethylene comprising film formed from a polychlorotrifluoroethylene film forming composition comprising 0% to 1% by weight of at least one copolymerizable comonomer
c h a r a c t e r i z e d
in that the film is exhibits a water vapor transmission rate, within the range of less than about 0.030 grams per 100 square inches per day at 100°F for a film thickness of 1 mil.

2. The film according to claim 1 wherein said film is formed of a PCTFE film forming composition having a ZST of 200 and less.

3. The film according to claim 1 wherein the said film has a degree of crystallinity of less than 60%.

4. The film according to claim 1 wherein the said film is stretched in either the machine direction or the transverse direction, or in both the machine direction and the transverse direction.

5. A film according to claim 4 wherein the film is stretched in the machine direction in to have a final unstretched:stretched film ratio of between 2:1 and 5:1.

6. A process for forming an amorphous PCTFE film according to claim 1 from a PCTFE film forming composition by:

(A) extruding the film forming composition onto a casting roll or casting rolls that are in such

casting roll/rolls maintained in temperatures of below about 100°F,

(B) stretching the film in the machine direction to have a final unstretched:stretched film ratio of between 2:1 and 5:1., and

(C) annealing the stretched film.

7. A process for forming an amorphous PCTFE film according to claim 1 from a PCTFE film forming composition by:

(A) blowing the film forming composition and rapidly quenching the film so to effecutuate the rapid quenching of the film,

(B) subsequently stretching the film to have a final unstretched:stretched film ratio of between 2:1 and 5:1, and

(C) annealing the stretched film.

8. The process according to either claim 6 or 7 wherein the film has a degree of crystallinity of 60% and less.

9. A multilayer film structure or an article comprising at least one layer of a film which consists of the film according to claim 1.

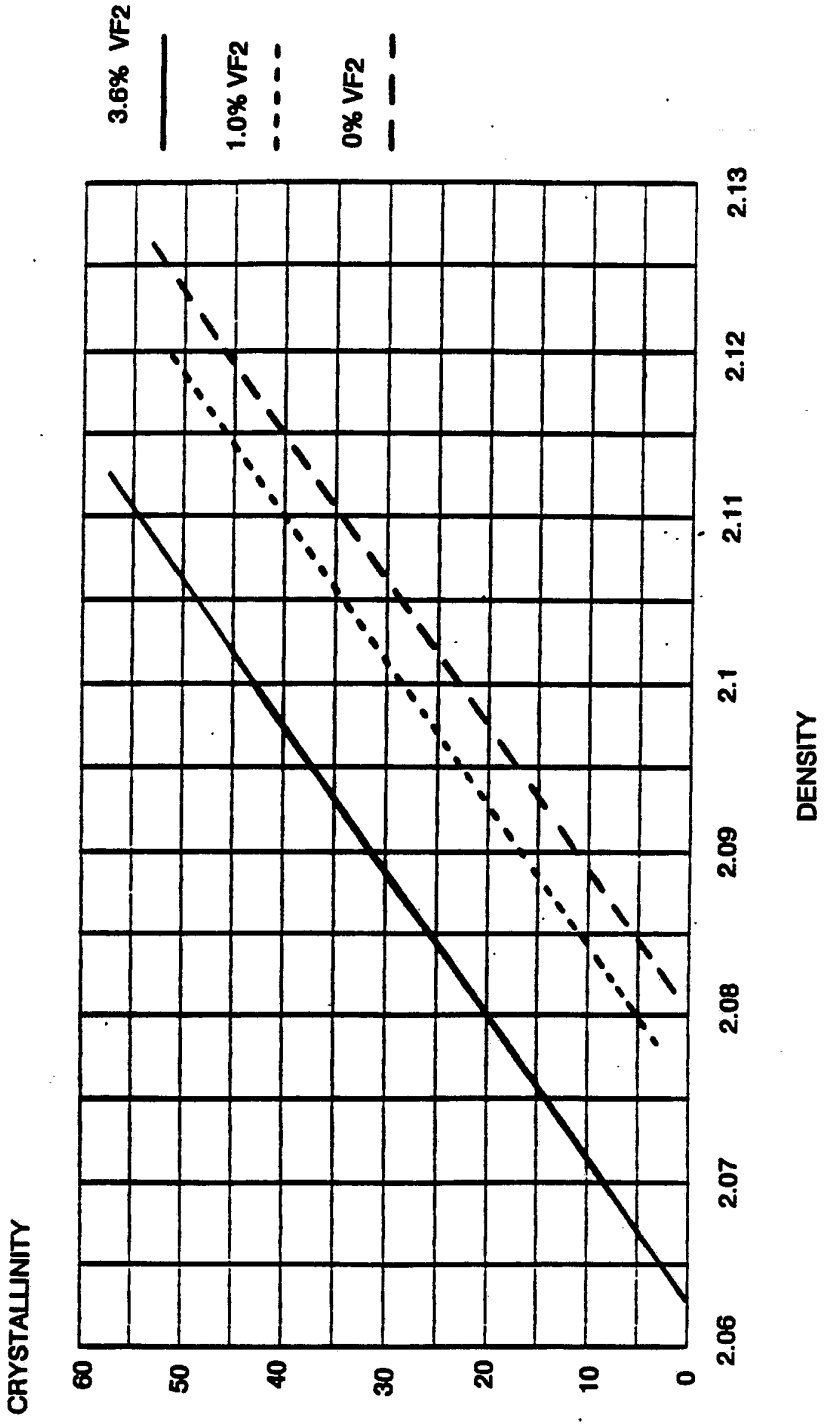

3.6% VF2
1.0% VF2
0% VF2
CRYSTALLINITY
60
50
40
30
20
10
0
2.06
2.07
2.08
2.09
2.1
2.11
2.12
2.13
DENSITY

FIGURE 1

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/08062

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08J5/18; B32B27/08

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08J ; C08F ; B32B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	EP,A,0 136 922 (E.I. DU PONT DE NEMOURS AND COMPANY)	1-5,9
A	see the whole document & US,A,4 544 721 cited in the application	6-8
P,X	EP,A,0 450 613 (DAIKIN INDUSTRIES, LIMITED) see the whole document	1-3
A	US,A,2 774 109 (H.S. KAUFMAN) 18 December 1956 see claims	1-3

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° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
26 NOVEMBER 1992	- 4. 12. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	DE JONGE S.J.P.

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	DATABASE WPIL Week 2890, Derwent Publications Ltd., London, GB; AN 90-212373 & JP,A,2 141 224 (SHINETSU CHEM IND KK) 30 May 1990 see abstract	1-9

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9208062 SA 65227

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 26/11/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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		AU-A-	3362884	18-04-85
		CA-A-	1228964	10-11-87
		JP-A-	2036238	06-02-90
		JP-B-	3014620	27-02-91
		JP-C-	1575639	24-08-90
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		JP-A-	60096626	30-05-85
EP-A-0450613	09-10-91	JP-A-	3287614	18-12-91
		US-A-	5145925	08-09-92
US-A-2774109		None		