FLUOROPOLYMER COMPOSITION INCLUDING AN OLIGOMER HAVING AN ULTRAVIOLET ABSORBING GROUP

Cross Reference to Related Application

This application claims priority to U.S. Provisional Application No. 61/740,135, filed December 20, 2012, the disclosure of which is incorporated by reference in its entirety herein.

Background

Fluoropolymers are known to have a variety of useful properties, including cleanability, weather resistance, and chemical resistance. Such beneficial properties render fluoropolymers useful, for example, for a variety of outdoor applications including signage, films or coatings for architectural coverings, and protective coverings for photovoltaic modules.

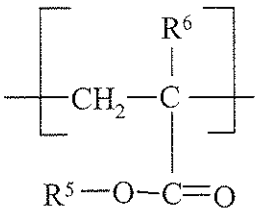
It may be desirable to incorporate ultraviolet absorbers (UVAs) into materials exposed to ultraviolet (UV) radiation, for example, to protect a topcoat or topsheet or an underlying substrate or adhesive from UV degradation. Some UVAs can be dispersed into some compositions, but sometimes they can be lost due to volatilization or migration to the surface. Covalent incorporation of UVAs into certain compositions has been proposed. See, e.g., U.S. Pat. Appl. Pub. No. 2011/0297228 (Li et al.).

It has been reported that common UVAs can be incompatible with fluoropolymers. See, e.g., U.S. Pat. No. 6,251,521 (Eian et al.). This incompatibility can lead to degradation of physical or optical properties (e.g., loss of clarity or increased fogginess) as well as increased or accelerated loss of the UVA by migration, bleeding, or blooming.

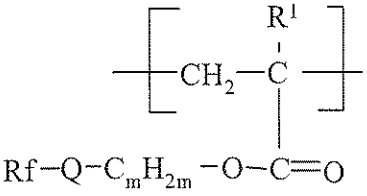
Summary

The present disclosure provides a composition that includes a fluoropolymer and an oligomer having a first divalent unit with a pendent ultraviolet absorbing group and at least one of a second divalent unit that is fluoroinated or third divalent unit that is fluorinated. The oligomers are generally quite compatible with fluoropolymers such that the oligomers and fluoropolymers are readily blended together. Compositions including the fluoropolymers and oligomers provide protection from ultraviolet light and have good transparency to visible and infrared light. These properties are typically well maintained even after accelerated UV exposure and exposure to high temperature and humidity conditions.

In one ~~aspect~~embodiment, the present disclosure provides a composition that includes a blend of a fluoropolymer and an ultraviolet light-absorbing oligomer. The ultraviolet light-absorbing oligomer includes a first divalent unit having a pendent ultraviolet absorbing group and at least one of a second divalent unit represented by formula:

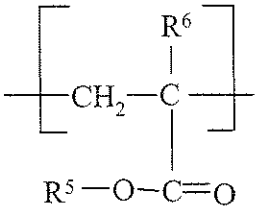


or a third divalent unit represented by formula:

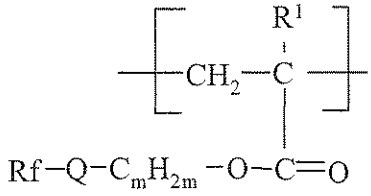


In these formulas, Rf represents a fluoroalkyl group having from 1 to 8 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoropolyether group. R^1 is hydrogen or methyl. Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen, and m is an integer from 0 to 11. R^6 is hydrogen or methyl, and R^5 is alkyl having from 1 to 4 carbon atoms. The ultraviolet light-absorbing group includes a triazine. The ultraviolet light-absorbing oligomer is in the composition in an amount ranging from 0.5 percent to 5 percent by weight, based on the total weight of the composition.

In another ~~aspect~~embodiment, the present disclosure provides a composition that includes a blend of a fluoropolymer and an ultraviolet light-absorbing oligomer. The ultraviolet light-absorbing oligomer includes a first divalent unit having a pendent ultraviolet absorbing group and at least one of a second divalent unit represented by formula:



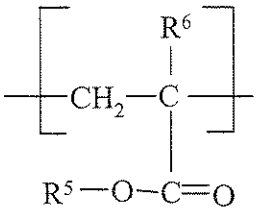
or a third divalent unit represented by formula:



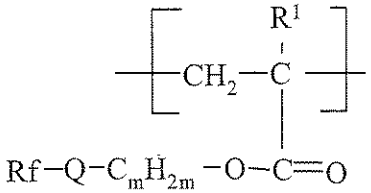
In these formulas, Rf represents a fluoroalkyl group having from 1 to 6 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoropolyether group. R^1 is hydrogen or methyl. Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen,

and m is an integer from 0 to 11. R^6 is hydrogen or methyl, and R^5 is alkyl having from 1 to 4 carbon atoms. The composition is an extruded film.

In another ~~aspect~~embodiment, the present disclosure provides a method of making a film. The method includes blending a composition including a fluoropolymer and an ultraviolet light-absorbing oligomer and extruding the composition into a film. The ultraviolet light-absorbing oligomer includes a first divalent unit having a pendent ultraviolet absorbing group and at least one of a second divalent unit represented by formula:



or a third divalent unit represented by formula:



In these formulas, Rf represents a fluoroalkyl group having from 1 to 8 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoroether group. R^1 is hydrogen or methyl. Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen, and m is an integer from 0 to 11. R^6 is hydrogen or methyl, and R^5 is alkyl having from 1 to 4 carbon atoms.

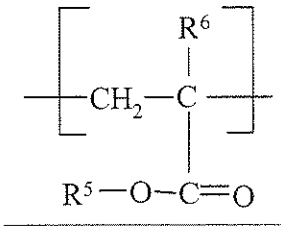
In some embodiments of the extruded film or the method of making it, the ultraviolet light-absorbing oligomer is in the composition in an amount ranging from 0.5 percent to 5 percent by weight, based on the total weight of the composition.

As described above, compositions including the fluoropolymers and oligomers typically provide protection from ultraviolet light and have good transparency to visible and infrared light. Accordingly, the present disclosure provides a photovoltaic device include the composition according to the present disclosure in any of its embodiments.

In one aspect of the present disclosure, there is provided a composition comprising a blend of a fluoropolymer and an ultraviolet light-absorbing oligomer, wherein the ultraviolet light-absorbing oligomer comprises:

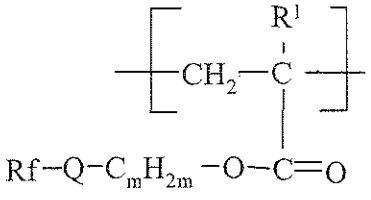
a first divalent unit comprising a pendent ultraviolet absorbing group, wherein the ultraviolet absorbing group comprises a triazine; and

at least one of a second divalent unit represented by formula:



; or

a third divalent unit represented by formula:



,

wherein

Rf represents a fluoroalkyl group having from 1 to 8 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoropolyether group;

R^1 is hydrogen or methyl;

Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen;

m is an integer from 0 to 10;

R6 is hydrogen or methyl; and

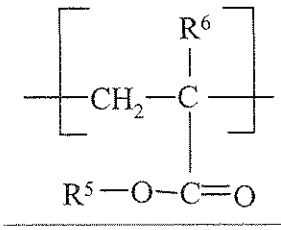
R5 is alkyl having from 1 to 4 carbon atoms,

wherein the ultraviolet light-absorbing oligomer is in the composition in an amount up to 20 percent by weight, based on the total weight of the composition.

Another aspect of the disclosure relates to a composition comprising a blend of a fluoropolymer and an ultraviolet light-absorbing oligomer, wherein the ultraviolet light-absorbing oligomer comprises:

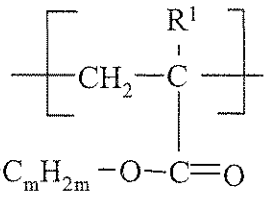
a first divalent unit comprising a pendent ultraviolet absorbing group; and

at least one of a second divalent unit represented by formula:



; or

a third divalent unit represented by formula:



wherein

Rf represents a fluoroalkyl group having from 1 to 8 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoropolyether group;

R^1 is hydrogen or methyl;

Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen;

m is an integer from 0 to 10;

R6 is hydrogen or methyl; and

R5 is alkyl having from 1 to 4 carbon atoms,

and wherein the composition is an extruded film.

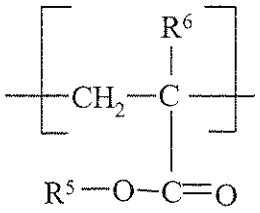
Yet another aspect relates to a photovoltaic device comprising the composition as disclosed herein.

Yet another aspect relates to a method of making the composition of any one of claims 4 to 8, the method comprising:

blending a composition comprising a fluoropolymer and an ultraviolet light-absorbing oligomer, wherein the ultraviolet light-absorbing oligomer comprises:

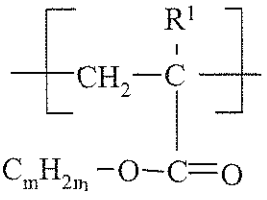
a first divalent unit comprising a pendent ultraviolet absorbing group; and

at least one of a second divalent unit represented by formula:



; or

a third divalent unit represented by formula:



wherein

Rf represents a fluoroalkyl group having from 1 to 8 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoropolyether group;

R^1 is hydrogen or methyl;

Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen;

m is an integer from 0 to 10;

R6 is hydrogen or methyl; and

R5 is alkyl having from 1 to 4 carbon atoms, and

extruding the composition into a film.

In this application:

Terms such as "a", "an" and "the" are not intended to refer to only a singular entity, but include the general class of which a specific example may be used for illustration. The terms "a", "an", and "the" are used interchangeably with the term "at least one".

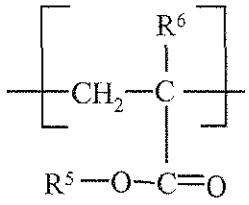
The phrase "comprises at least one of" followed by a list refers to comprising any one of the items in the list and any combination of two or more items in the list. The phrase "at least one of" followed by a list refers to any one of the items in the list or any combination of two or more items in the list.

What is claimed is:

1. A composition comprising a blend of a fluoropolymer and an ultraviolet light-absorbing oligomer, wherein the ultraviolet light-absorbing oligomer comprises:

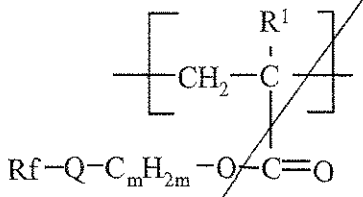
a first divalent unit comprising a pendent ultraviolet absorbing group, wherein the ultraviolet absorbing group comprises a triazine; and

at least one of a second divalent unit represented by formula:



; or

a third divalent unit represented by formula:



,

wherein

Rf represents a fluoroalkyl group having from 1 to 8 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoropolyether group;

R^1 is hydrogen or methyl;

Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen;

m is an integer from 0 to 10;

R^6 is hydrogen or methyl; and

R^5 is alkyl having from 1 to 4 carbon atoms,

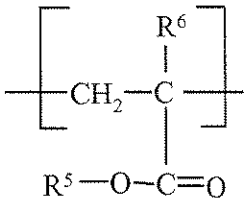
wherein the ultraviolet light-absorbing oligomer is in the composition in an amount ranging from 0.5 percent to 5 percent by weight, based on the total weight of the composition.

2. The composition of claim 1, wherein the composition is in the form of a film.

3. A composition comprising a blend of a fluoropolymer and an ultraviolet light-absorbing oligomer, wherein the ultraviolet light-absorbing oligomer comprises:

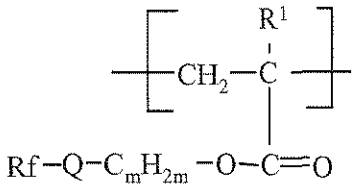
a first divalent unit comprising a pendent ultraviolet absorbing group; and

at least one of a second divalent unit represented by formula:



; or

a third divalent unit represented by formula:



,

wherein

Rf represents a fluoroalkyl group having from 1 to 8 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoropolyether group;

R^1 is hydrogen or methyl;

Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen;

m is an integer from 0 to 10;

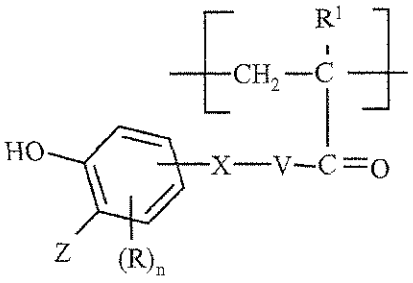
R^6 is hydrogen or methyl; and

R^5 is alkyl having from 1 to 4 carbon atoms,

and wherein the composition is an extruded film.

4. The composition of claim 3, wherein the pendent ultraviolet absorbing group comprises a triazine, a benzophenone, or a benzotriazole.

5. The composition of claim 4, wherein the first divalent unit is represented by formula:



,

wherein

R^1 is hydrogen or methyl;

V is O or NH;

X is alkylene or alkyleneoxy group having from 1 to 10 carbon atoms and optionally interrupted by one or more –O- groups and optionally substituted by a hydroxyl group;

R is alkyl having from one to four carbon atoms;

n is 0 or 1; and

Z is a benzoyl group optionally substituted by hydroxyl, alkyl, halogen, or hydroxyl; a 4,6-bisphenyl[1,3,5]triazin-2-yl group wherein each phenyl is optionally independently substituted by one or more alkyl or alkoxy groups; or a 2H-benzotriazol-2-yl group optionally substituted by one or more halogens.

6. The composition of any one of claims 3 to 5, wherein the ultraviolet light-absorbing oligomer is in the composition in an amount ranging from 0.5 percent to 5 percent by weight, based on the total weight of the composition.

7. The composition of any one of claims 1 to 5, wherein the ultraviolet light-absorbing oligomer comprises the second divalent unit, and wherein R^5 and R^6 are both methyl.

8. The composition of any one of claims 1 to 7, wherein the fluoropolymer is present in the blend in an amount of at least 90 percent by weight, based on the total weight of the blend.

9. The composition of any one of claims 1 to 8, wherein the blend further comprises poly(methyl methacrylate).

10. The composition of any one of claims 1 to 9, wherein the composition comprises a second, different ultraviolet light-absorbing oligomer in the blend, wherein the second ultraviolet light-absorbing oligomer comprises a divalent unit comprising a second pendent ultraviolet absorbing group and at least one of the second divalent unit or the third divalent unit, wherein the second pendent ultraviolet absorbing group comprises a triazine, a benzophenone, or a benzotriazole.

11. The composition of claim 10, wherein the ultraviolet light-absorbing oligomer and the second, different ultraviolet light-absorbing oligomer are present in the composition in an amount of up to ten percent by weight, based on the total weight of the composition.

12. The composition of any one of claims 1 to11, wherein the composition is essentially free of volatile organic solvent.

13. The composition of any one of claims 1 to 12, wherein the fluoropolymer is selected from the group consisting of ethylene-tetrafluoroethylene copolymer, a tetrafluoroethylene-hexafluoropropylene copolymer, a tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride copolymer, or polyvinylidene fluoride.

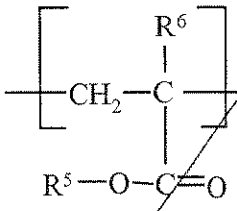
14. A photovoltaic device comprising the composition of any one of claims 1 to 13.

15. A method of making the composition of claim 3 or any one of claims 4 to 13 except as dependent on claim 1 or 2, the method comprising:

blending a composition comprising a fluoropolymer and an ultraviolet light-absorbing oligomer, wherein the ultraviolet light-absorbing oligomer comprises:

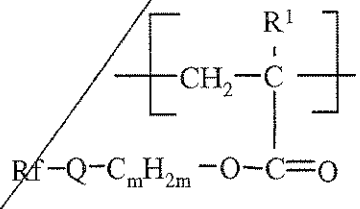
a first divalent unit comprising a pendent ultraviolet absorbing group; and

at least one of a second divalent unit represented by formula:



; or

a third divalent unit represented by formula:



wherein

Rf represents a fluoroalkyl group having from 1 to 8 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoropolyether group;

R^1 is hydrogen or methyl;

Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen;

m is an integer from 0 to 10;

R^6 is hydrogen or methyl; and

R^5 is alkyl having from 1 to 4 carbon atoms, and

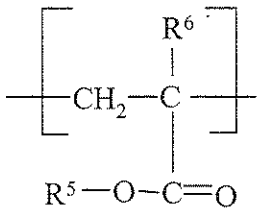
extruding the composition into a film.

What is claimed is:

1. A composition comprising a blend of a fluoropolymer and an ultraviolet light-absorbing oligomer, wherein the ultraviolet light-absorbing oligomer comprises:

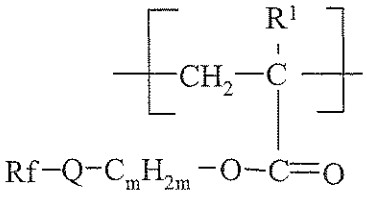
a first divalent unit comprising a pendent ultraviolet absorbing group, wherein the ultraviolet absorbing group comprises a triazine; and

at least one of a second divalent unit represented by formula:



; or

a third divalent unit represented by formula:



,

wherein

Rf represents a fluoroalkyl group having from 1 to 8 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoropolyether group;

R^1 is hydrogen or methyl;

Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen;

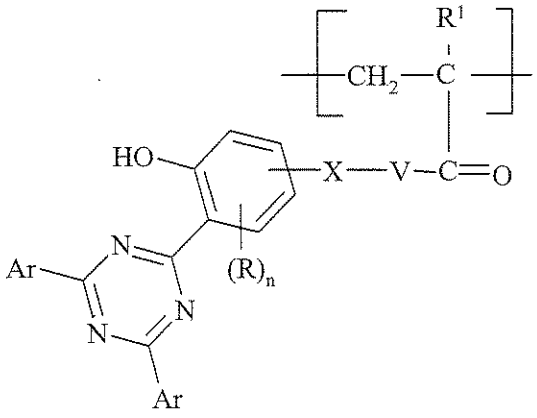
m is an integer from 0 to 10;

R^6 is hydrogen or methyl; and

R^5 is alkyl having from 1 to 4 carbon atoms,

wherein the ultraviolet light-absorbing oligomer is in the composition in an amount up to 20 percent by weight, based on the total weight of the composition.

2. The composition of claim 1, wherein the first divalent unit is represented by formula:



wherein

R^1 is hydrogen or methyl;

V is O or NH;

X is alkylene or alkyleneoxy group having from 1 to 10 carbon atoms and optionally interrupted by one or more –O- groups and optionally substituted by a hydroxyl group;

R is alkyl having from one to four carbon atoms;

n is 0 or 1; and

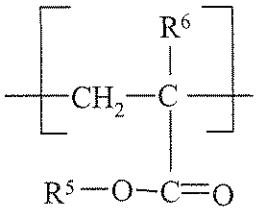
Ar is a phenyl group substituted by one or more alkyl, aryl, alkoxy, hydroxyl, or halogen substituents, or a combination of these substituents.

3. The composition of claim 1 or 2, wherein the composition is in the form of a film.

4. A composition comprising a blend of a fluoropolymer and an ultraviolet light-absorbing oligomer, wherein the ultraviolet light-absorbing oligomer comprises:

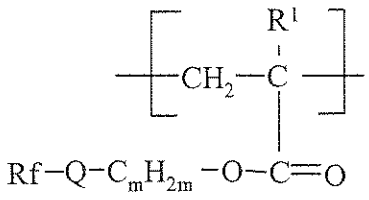
a first divalent unit comprising a pendent ultraviolet absorbing group; and

at least one of a second divalent unit represented by formula:



; or

a third divalent unit represented by formula:



wherein

Rf represents a fluoroalkyl group having from 1 to 8 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoropolyether group;

R^1 is hydrogen or methyl;

Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen;

m is an integer from 0 to 10;

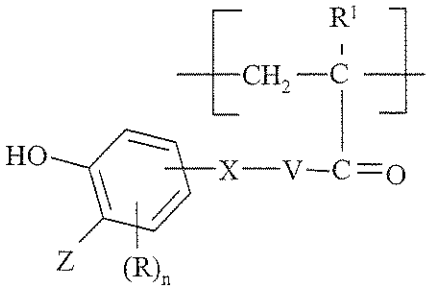
R^6 is hydrogen or methyl; and

R^5 is alkyl having from 1 to 4 carbon atoms,

and wherein the composition is an extruded film.

5. The composition of claim 4, wherein the pendent ultraviolet absorbing group comprises a triazine, a benzophenone, or a benzotriazole.

6. The composition of claim 5, wherein the first divalent unit is represented by formula:



wherein

R^1 is hydrogen or methyl;

V is O or NH;

X is alkylene or alkyleneoxy group having from 1 to 10 carbon atoms and optionally interrupted by one or more –O- groups and optionally substituted by a hydroxyl group;

R is alkyl having from one to four carbon atoms;

n is 0 or 1; and

Z is a benzoyl group optionally substituted by hydroxyl, alkyl, halogen, or hydroxyl; a 4,6-bisphenyl[1,3,5]triazin-2-yl group wherein each phenyl is optionally independently substituted by one or more alkyl or alkoxy groups; or a 2H-benzotriazol-2-yl group optionally substituted by one or more halogens.

7. The composition of any one of claims 4 to 6, wherein the ultraviolet light-absorbing oligomer is in the composition in an amount up to 20 percent by weight, based on the total weight of the composition.

8. The composition of any one of claims 3 to 7, wherein the film is a multilayer film.

9. The composition of claim 8, wherein the film is a multilayer optical film.

10. The composition of any one of claims 1 to 9, wherein the ultraviolet light-absorbing oligomer comprises the second divalent unit, and wherein R^5 and R^6 are both methyl.

11. The composition of claim 10, wherein the ultraviolet light-absorbing oligomer has a number average molecular weight of less than 20,000 grams per mole.

12. The composition of any one of claims 1 to 11, wherein the fluoropolymer is present in the blend in an amount of at least 90 percent by weight, based on the total weight of the blend.

13. The composition of any one of claims 1 to 12, wherein the blend further comprises poly(methyl methacrylate).

14. The composition of any one of claims 1 to 13, wherein the composition comprises a second, different ultraviolet light-absorbing oligomer in the blend, wherein the second ultraviolet light-absorbing oligomer comprises a divalent unit comprising a second pendent ultraviolet absorbing group and at least one of the second divalent unit or the third divalent unit, wherein the second pendent ultraviolet absorbing group comprises a triazine, a benzophenone, or a benzotriazole.

15. The composition of claim 14, wherein the ultraviolet light-absorbing oligomer and the second, different ultraviolet light-absorbing oligomer are present in the composition in an amount of up to ten percent by weight, based on the total weight of the composition.

16. The composition of any one of claims 1 to 15, wherein the composition is essentially free of volatile organic solvent.

17. The composition of any one of claims 1 to 16, wherein the fluoropolymer is selected from the group consisting of ethylene-tetrafluoroethylene copolymer, a tetrafluoroethylene-hexafluoropropylene copolymer, a tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride copolymer, or polyvinylidene fluoride.

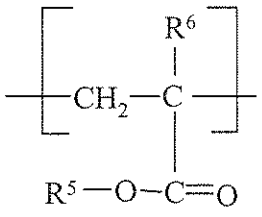
18. A photovoltaic device comprising the composition of any one of claims 1 to 17.

19. A method of making the composition of any one of claims 4 to 8, the method comprising:

blending a composition comprising a fluoropolymer and an ultraviolet light-absorbing oligomer, wherein the ultraviolet light-absorbing oligomer comprises:

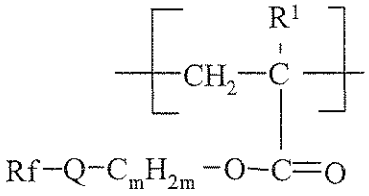
a first divalent unit comprising a pendent ultraviolet absorbing group; and

at least one of a second divalent unit represented by formula:



; or

a third divalent unit represented by formula:



,

wherein

Rf represents a fluoroalkyl group having from 1 to 8 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoropolyether group;

R^1 is hydrogen or methyl;

Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen;

m is an integer from 0 to 10;

R^6 is hydrogen or methyl; and

R^5 is alkyl having from 1 to 4 carbon atoms, and

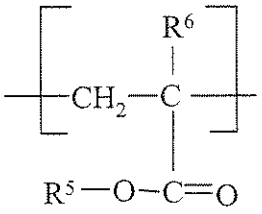
extruding the composition into a film.

20. The method of claim 19, wherein the composition is essentially free of volatile organic solvent.

21. A composition comprising a blend of polyvinylidene fluoride, poly(methyl methacrylate), and an ultraviolet light-absorbing oligomer, wherein the ultraviolet light-absorbing oligomer comprises:

a first divalent unit comprising a pendent ultraviolet absorbing group; and

at least one second divalent unit represented by formula:



wherein

R^6 is hydrogen or methyl; and

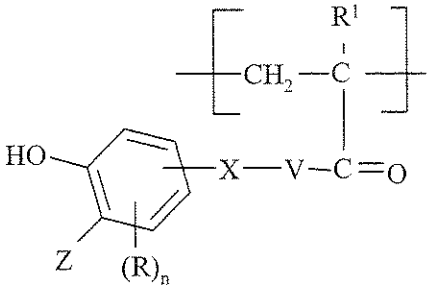
R^5 is alkyl having from 1 to 4 carbon atoms,

and wherein poly(methyl methacrylate) is present in the composition in an amount from ten percent to 25 percent by weight, based on the total weight of the polyvinylidene fluoride and poly(methyl methacrylate).

22. The composition of claim 21, wherein the pendent ultraviolet absorbing group comprises a triazine, a benzophenone, or a benzotriazole.

23. The composition of claim 22, wherein the pendent ultraviolet absorbing group comprises a triazine.

24. The composition of claim 21, wherein the first divalent unit is represented by formula:



wherein

R^1 is hydrogen or methyl;

V is O or NH;

X is alkylene or alkyleneoxy group having from 1 to 10 carbon atoms and optionally interrupted by one or more –O- groups and optionally substituted by a hydroxyl group;

R is alkyl having from one to four carbon atoms;

n is 0 or 1; and

Z is a benzoyl group, a 4,6-bisphenyl[1,3,5]triazin-2-yl group, or a 2H-benzotriazol-2-yl group, wherein the benzoyl group, 4,6-bisphenyl[1,3,5]triazin-2yl group, and 2H-benzotriazol2-yl group are optionally substituted by one or more alkyl, aryl, alkoxy, hydroxyl, or halogen substituents, or a combination of these substituents.

25. The composition of any one of claims 21 to 24, wherein the composition is in the form of a film.