

POLYOXYMETHYLENE RESIN COMPOSITIONS HAVING IMPROVED MOLDING CHARACTERISTICS

BACKGROUND OF THE INVENTION

5 The present invention relates to polyoxymethylene (also referred to herein as polyacetal) resin compositions having improved moldability and improved physical properties of the molded article.

 Polyacetal resin is manufactured by polymerizing a mostly formaldehyde monomer or a formaldehyde trimer (trioxane). Acetal homopolymer is a
10 homopolymer of formaldehyde (for example, Delrin® acetal resin, manufactured by E.I. du Pont de Nemours and Company). Acetal copolymer is obtained, for example, by copolymerizing alkylene oxide with for example, trioxane.

 Polyoxymethylene resin, because of its high mechanical strength, excellent abrasion resistance, fatigue resistance, moldability, and the like, is extensively used,
15 for example, in electrical and electronic applications, automotive applications, and precision machine applications.

 Polyoxymethylene resins are the most crystalline of the engineering polymers and as a consequence, freeze quickly in a mold. However, these resins also have a high shrinkage. Recently, nucleated polyoxymethylene resins have
20 been introduced to improve set-up time and reduce shrinkage. But, further improvements are desirable, especially if toughness can be improved. Additionally, it is desirable to eliminate or substantially eliminate voids in molded articles.

SUMMARY OF THE INVENTION

25 The present invention comprises a blend of a polyoxymethylene resin with a combination of a polyalkylene/unsaturated carboxylic acid lower alkyl ester nucleating material, a waxy de-nucleating material and a nucleant. Such compositions have improved set-up time and reduced shrinkage and improved elongation. Warpage is also reduced in asymmetrical parts. Voids are eliminated or
30 substantially avoided in molded articles using the present combination. Statistically designed experiments have demonstrated a previously unrecognized synergy

between the additives, i.e., an alkylene (meth) acrylate polymeric nucleating material such as polyethylene methacrylate (EMA), a waxy de-nucleating material such as polyethylene wax and a nucleant such as talc.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1a and 1b show crystallization 1/2 time plots for various polyoxymethylene resin compositions.

Figs. 2a, 2b and 2c show photocopy reproductions of cut sections of bars molded from polyoxymethylene resins containing various additives.

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Figs. 3a and 3b show photocopy reproductions of cut sections of bars molded from polyoxymethylene resins containing various additives.

Figs. 4a and 4b show photocopy reproductions of cut sections of bars molded from polyoxymethylene resins containing various additives.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a composition containing a polyoxymethylene resin and a combination comprising:

- a) a polyalkylene/unsaturated carboxylic acid lower alkyl ester nucleating material;
- 20 b) a waxy denucleating material; and
- c) a nucleant.

More particularly, the instant composition contains a polyoxymethylene resin and a combination comprising:

- 25 a) 0.5-3% by wt. of a polyalkylene/unsaturated carboxylic acid lower alkyl ester nucleating material;
- b) .1-1% by wt. of a waxy denucleating material; and
- c) .01-3% by wt. of a nucleant.

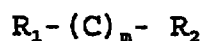
A preferred composition contains the polyoxymethylene resin and a combination comprising:

- 30 a) 1-3% by wt. of the ester nucleating material;
- b) 0.1-1% by wt. of the waxy denucleating material; and

c) 0.01-3% by wt. of the nucleant.

It should be understood that the percents by weight are based on the entire composition. The remainder of the composition is comprised of the polyoxymethylene resin and other additives.

5 The polyoxymethylene resins which can be used in the instant invention include a wide variety of homopolymers and copolymers which are known in the art. These polymers are generally polymers of formaldehyde in which the polymer chain, exclusive of the terminal portions of the chain, is a series of methylene to oxygen linkages. The polymer chain can also include moieties of the general
10 formula:



wherein m is an integer of 1 to 5 and R₁ and R₂ are inert substituents which will not cause undesirable reactions in the polymer. Such additional components of
15 the polymer chain are present as a minor proportion of the repeating units.

More specifically, the "polyoxymethylene resin" component as used herein includes homopolymers of formaldehyde or a cyclic oligomer of formaldehyde, the terminal groups of which are end capped by esterification or etherification, and
20 copolymers of formaldehyde or of a cyclic oligomer of formaldehyde and other monomers that yield oxyalkylene groups with at least two adjacent carbon atoms in the main chain, the terminal groups of which copolymers can be hydroxyl terminated or can be end capped by esterification or etherification.

The polyoxymethylene resin used in this invention can be linear or substantially linear with only minor amounts of branching and will generally have a
25 weight average molecular weight in the range of 40,000 to 175,000, preferably 50,000 to 150,000. It is preferred that the polyoxymethylene resin does not contain a measurable amount of branching. The molecular weight can conveniently be measured by gel permeation chromatography in m-cresol at 160°C or alternatively, hexafluoroisopropanol at room temperature. Although polyoxymethylene resins of
30 higher or lower weight average molecular weights can be used, depending on the physical and processing properties desired, the polyoxymethylene resins with the

above mentioned weight average molecular weight are preferred to provide optimum balance of good mixing of various ingredients to be melt blended into the composition with the desired combination of physical properties in the components made from such compositions.

5 As indicated above, the polyoxymethylene resin can be either homopolymer with different weight average molecular weights, copolymers of different weight average molecular weights or mixtures thereof. Copolymers can contain one or more comonomers, such as those generally used in preparing polyoxymethylene compositions. Comonomers more commonly used include alkylene oxides of 2-12
10 carbon atoms and their cyclic addition products with formaldehyde. The quantity of comonomer will not be more than 20 weight percent, preferably not more than 15 percent, and most preferably about 2 weight percent. The commonly used comonomers include ethylene oxide, dioxalane, and butylene oxide. Generally, polyoxymethylene homopolymer is preferred over copolymer because of its greater
15 tensile strength and stiffness. Preferred polyoxymethylene homopolymers include those whose terminal hydroxyl groups have been end capped by a chemical reaction to form ester or ether groups, preferably acetate or methoxy groups, respectively.

The polyalkylene/unsaturated carboxylic acid lower alkyl ester polymeric nucleating materials in general are copolymers or terpolymers of a lower alkene (C_2 -
20 C_4) and a lower alkyl ester of an unsaturated acid. An example of polymeric nucleating materials useful in this invention are ethylene-based polymers of the formula E/X/Y, preferably E/X. In the formula E/X, X is ethylene and Y is an unsaturated carboxylic acid ester.

The unsaturated carboxylic acid esters include alkyl (C_1 to C_8 , pref. C_1 to C_4)
25 esters of unsaturated carboxylic acids having 3 to 8 carbon atoms. Illustrative unsaturated acids include acrylic and methacrylic acids. Particular examples of esters are methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate and isobutyl
30 methacrylate, among which ethyl acrylate and methyl methacrylate are preferred.

The preferred ethylene methyl acrylate copolymer ("EMA") component is, in

general, a commercially available material and can be prepared by known means. The amount of methyl acrylate in the EMA is generally 3-40 weight percent, preferably 15-25 weight percent, of the EMA.

5 The polyalkylene/unsaturated carboxylic lower alkyl ester nucleating additive can also be an ethylene-based random polymer of the formula E/X/Y wherein E is ethylene, X is selected from methylmethacrylate, ethyl acrylate, and butyl acrylate, and Y is selected from glycidyl methacrylate and glycidyl acrylate, and glycidyl methacrylate is preferred for Y. E/X/Y consists essentially of 5-99% E, 0-35% X, and 0.5-10% Y.

10 An example of the ethylene-based random polymer consists essentially of 90%-99% by weight ethylene and 1%-10% by weight glycidylmethacrylate. Preferably, this ethylene/glycidyl methacrylate ("EGMA") random polymer consists essentially of 90%-97% by weight ethylene and 3%-10% by weight glycidyl methacrylate ("GMA").

15 Another preferred ethylene-based random polymer consists essentially of 60%-98.5% by weight ethylene, 0.5-35% by weight butyl acrylate ("BA"), and 1%-10% by weight glycidyl methacrylate ("GMA"). Preferably, this ethylene/butyl acrylate/glycidyl methacrylate ("EBAGMA") random polymer consists essentially of 55%-84% by weight ethylene, 15%-35% by weight BA, and 1%-10% by weight
20 GMA. Most preferably, this EBAGMA random polymer consists essentially of 57.5%-74% by weight ethylene, 25%-35% by weight BA, and 1%-7.5% GMA.

The ethylene-based random polymer component can be prepared by techniques readily available to those in the art. An example of the EBAGMA random polymer is provided in U.S. Pat. No. 4,753,980.

25 The waxy denucleating component is a material that is capable of being dispersed in the polyacetal resin and may be a liquid at normal room temperatures. Alternatively, if this material is a solid at normal room temperatures, it must become fluidized at a temperature lower than the temperature at which the polyacetal is being processed or molded. Examples of useful wax denucleating components are
30 natural or synthetic waxes, for example hydrocarbon and polymeric waxes. Hydrocarbon waxes include mineral, petroleum, paraffin or microcrystalline waxes

and synthetic waxes, such as, for example ethylenic polymers or chlorinated maphthalenes. The polymeric waxes include polyethylenes, polypropylenes and ethylene/propylene copolymers. Preferred materials include paraffin wax, and polyethylene wax. Good blending is obtained if the components are mixed together
5 in a twin-screw extruder, which is the preferred mixing device.

The nucleant useful in the present invention is any finely divided solid, such as boron nitride, talc, silica, polyimides, branched or crosslinked acetal copolymer or terpolymer, a melamine-formaldehyde resin, calcium carbonate, diatomite, dolomite, or other commonly known nucleants for polyoxymethylene. Boron
10 nitride, terpolymers or talc are preferred, with the branched terpolymer being most preferred. The nucleant can optionally be surface treated by standard processes.

The branched or crosslinked poly(oxymethylenes) useful as nucleants in the invention may be obtained.

- a. by copolymerization of trioxane with at least one compound reacting
15 multifunctionally and being copolymerizable with trioxane and, optionally, with at least one compound monofunctionally reacting and copolymerizable with trioxane, or
- b. by branching or crosslinking reactions performed subsequently with a linear poly(oxymethylene) having lateral or chainlinked functional groups, or
- 20 c. by copolymerization of trioxane with at least one compound reacting monofunctionally and being copolymerizable with trioxane and a branched or crosslinked polyether or by reaction of a linear poly(oxymethylene) with a branched or crosslinked polyether.

Small average particle size is preferred for the nucleant. The average
25 particle size of the nucleant should be less than 20 microns, preferably less than 10 microns, and most preferably less than 5 microns.

The nucleant may be an encapsulated nucleant. The encapsulated nucleant as used herein consists essentially of an encapsulant polymer and a nucleant.

The encapsulant polymer can be any moderate melting polymer, i.e., any
30 polymer which melts at the processing temperatures of the polyoxymethylene resin of the encapsulated nucleant. Illustrative encapsulant polymers include linear low

density polyethylene ("LLDPE"), high density polyethylene ("HDPE"), and polypropylene, each of which have a solid density of less than or equal to 1 gram per cubic centimeter, as measured by ASTM D1505. Preferably, the encapsulant polymer is either LLDPE or HDPE. The encapsulant polymer either lacks long chain polymer branching in its molecular structure or it is predominantly linear. The lack of long chain branching is due to the method by which the encapsulant polymer is produced.

The encapsulant polymer is selected from a group of polymers well known in the art. The encapsulant polymers are commercially available or, alternatively, can be prepared by techniques readily available to those skilled in the art. Generally, the encapsulant polymers are prepared by polymerizing ethylene or ethylene and alpha-olefin comonomers in solution phase or gas phase reactors using coordination catalysts, particularly Ziegler or Phillips type catalysts.

It is preferred that the LLDPE encapsulant polymer have a melt index, as measured by ASTM D1238 method, condition E, in the range of 5 to 55 grams per 10 min. It is preferred that the HDPE encapsulant polymer have a melt index, as measured by ASTM D1238 method, condition E, of about 0.5-7 grams per 10 min. Compositions containing LLDPE or HDPE having melt indices outside the range given above may yield stock shapes with good porosity values, but can give rise to compounded resin and extruded stock shapes having other undesirable characteristics, such as decreased stability or separation of the polyoxymethylene and LLDPE or HDPE (i.e., de-lamination).

Additives or ingredients that can have an adverse effect on the oxidative or thermal stability of polyoxymethylene should be avoided.

The composition useful in the present invention may optionally include, in addition to the components described above, other ingredients, modifiers, and additives as are generally used in polyacetal compositions, including thermal stabilizers and co-stabilizers, antioxidants, colorants (including pigments), toughening agents (such as thermoplastic polyurethanes), reinforcing agents, ultraviolet stabilizers (such as benzotriazoles or benzophenones), including hindered amine light stabilizers (especially those wherein the hindered nitrogen is of tertiary

amine functionality or wherein the hindered amine light stabilizer contains both a piperidine, or piperazinone ring, and a triazine ring), glass, and fillers. Suitable thermal stabilizers include polyamides (including a nylon terpolymer of nylon 66, nylon 6/10, and nylon 6 and the polyamide stabilizer of U.S. Pat. No. 3,960,984);
5 meltable hydroxy-containing polymers and copolymers, including ethylene vinyl alcohol copolymer and the stabilizers described in U.S. Pat. No. 4,814,397 and U.S. Pat. No. 4,766,168; non-meltable hydroxy-containing or nitrogen-containing polymers as described in U.S. Pat. No. 5,011,890 and in particular, polyacrylamide; and microcrystalline cellulose; polybeta-alanine (as described in German published
10 application 3715117); polyacrylamide; or stabilizers disclosed in U.S. Pat. Nos. 4,814,397, 4,766,168, 4,640,949, and 4,098,984; and mixtures of any of the above. Typical antioxidants include hindered phenols such as triethyleneglycolbis(3-(3'-tertbutyl-4'-hydroxy-5'-methylphenyl)propionate, N,N'-hexamethylenebis(3,5-di-tert-butyl-4'-hydroxy-hydrocinnamide), and mixtures thereof as well as antioxidants,
15 including those described in U.S. Pat. No. 4,972,014.

The compositions described herein may be prepared by mixing all components with the acetal polymer at a temperature above the melting point of the acetal polymer by methods known in the art. It is known to use intensive mixing devices, such as rubber mills, internal mixers such as "Banbury" and "Brabender"
20 mixers, single or multiblade internal mixers with a cavity heated externally or by friction, "Ko-kneaders", multibarrel mixers such as "Farrel Continuous Mixers", injection molding machines, and extruders, both single screw and twin screw, both co-rotating and counter rotating, in preparing thermoplastic polyacetal compositions.

These devices may be used alone or in combination with static mixers, mixing
25 torpedoes and/or various devices to increase internal pressure and/or the intensity of mixing, such as valves, gates, or screw designed for this purpose. Extruders are preferred, with twin screw extruders being most preferred. Of course, such mixing should be conducted at a temperature below which significant degradation of the polyacetal component will occur. Generally, polyacetal compositions are melt
30 processed at between 170°C and 290°C, preferably between 185°C and 240°C and most preferably 195°C and 225°C.

Shaped articles may be made from the compositions of the present invention using methods known in the art, including compression molding, injection molding, extrusion, blow molding, rotational molding, melt spinning, and thermoforming. Injection molding is preferred.

5 Examples of shaped articles include sheet, profiles, rod stock, film, filaments, fibers, strapping, tape, tubing, and pipe. Such shaped articles can be post treated by orientation, stretching, coating, annealing, painting, laminating, and plating. Such shaped articles and scrap therefrom can be ground and remolded.

10 It will be understood by those skilled in the art that various modifications and substitutions may be made to the invention as described above without departing from the spirit and scope of the invention. Accordingly, it is understood that the present invention has been described by way of illustration and not limitation.

Experiments

15 The following experiment was devised using experimental design software known as "EChip", available from ECHIP inc., Hockessin Delaware. The designed experiment includes duplicates which allows the statistician to estimate experimental error. Because this was a designed experiment, it is not always possible to compare pairs of experiments with just one variable changing. Instead,
20 one must rely on the statistical analysis for interpretation of the results. The samples were prepared using acetate capped polyoxymethylene (POM) having a weight average molecular weight of nominally 72,000. The examples listed in the table were produced using a Werner and Pfleiderer 40 mm twin screw extruder. Fifty-pound samples were prepared at 200 pounds per hour. The machine was run at 225-
25 400 rpm with barrel temperature settings of 200-225C. Samples containing P561 wax and no EMA were difficult to run because the wax interfered with melting of the POM so the higher temperatures and machine RPM were used for these. EMA is EMAC® SP2205 from Chevron Chemical which is a copolymer of 80% ethylene, 20% methyl acrylate with a melt index of 2g/10 min. P561 is a non-polar
30 hydrocarbon wax sold by Moore and Munger. Celcon® U-10 is a branched acetal terpolymer manufactured by Hoeschst-Celanese (now Ticona). Ultratalc® 609 is a

talc supplied by Barretts Minerals, Inc. Zemid® 641 is 40% talc in polyethylene supplied by DuPont. U-Talc 609/EMA is a 40% dispersion of the Ultratalc in the EMA. U-Talc 609/P561 is a 40% dispersion of the Ultratalc in the P561.

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TABLE 1

Composition Number	EMA %	P561%	Percent U-Talc	U-Talc Source	DSC Cryst T1/2 158C (min)	In Mold Cryst Time (sec)
1	0	0	0	ZEMID 641	2.9	6.7
2	3	1.5	0	ZEMID 641	3.28	7.3
3	0	1.5	0.08	ZEMID 641	2.18	6.5
4	3	1.5	0	U-TALC 609	3.31	6.9
5	3	0	0.08	U-TALC 609/P561	2.39	5.6
6	0	1.5	0.08	U-TALC 609/P561	2.12	6.8
7	0	0	0.08	U-TALC 609	1.96	5.9
8	3	0	0	U-TALC 609/EMA	7.2	7
9	0	1.5	0.08	U-TALC 609/EMA	2.03	6.3
10	3	1.5	0	U-TALC 609/P561	13.43	7.2
11	3	0	0.08	U-TALC 609	2.14	5.8
12	3	0	0.08	ZEMID 641	2.74	5.6
13	0	1.5	0	U-TALC 609	8.42	6.4
14	0	0	0	U-TALC 609/P561	3.26	7
15	3	1.5	0.08	U-TALC 609/EMA	2.26	6.1
16	0	0	0	U-TALC 609/EMA	10.47	6.8
17	1.5	0.75	0.04	ZEMID 641	2.87	6.6
18	1.5	0.75	0.04	U-TALC 609	1.75	5.5
19	1.5	0.75	0.04	U-TALC 609/P561	6.24	5.7
20	1.5	0.75	0.04	U-TALC 609/EMA	5.74	5.8
21	0	0	0	ZEMID 641	3.69	6.3
22	3	1.5	0	U-TALC 609	3.25	6.9
23	3	0	0.08	U-TALC 609/P561	2.43	5.5
24	3	0	0	U-TALC 609/EMA	7.94	6.6

The crystallization half times were determined using a differential scanning calorimeter (DSC). Ten mg of resin was heated in a Perkin-Elmer DSC 7 at 50C/min. to 210°C, held for 3 minutes, then rapidly cooled at 200°C/min. to a

crystallization temperature of 158°C, and held there until completion. The half times are taken from the peak positions of crystallization exotherms.

The in-mold crystallization times were obtained from plots of the melt pressure curves during injection molding of the samples into 1X8X.070 inch bars.

5 The DSC and in-mold crystallization data measured for these materials was then statistically analyzed using the "EChip" DOE software to provide the graphical illustration of the effect of EMA and P561 wax. Note in the presence of a talc-based nucleating agent, "Zemid", the wax which normally has the effect of slowing crystallization (DSC half time increases) now has the opposite effect, it increases
10 crystallization rate (the time for half the DSC sample to crystallize at 158°C decreases).

Note also inspection of the data in Table 2, below shows that EMA and wax individually or in combination have little
effect on in-mold crystallization time, the combination with just 0.04% talc nucleant
15 has a greater effect than 0.08% nucleant by itself.

TABLE 2 - AVERAGE DATA

EXAMPLE	EMA %	P561%	Percent TALC	Cryst Time (S) avg.
1	0	0	0	6.7
2	3	0	0	6.8
3	0	1.5	0	6.4
4	3	1.5	0	7.1
5	0	0	0.08	5.9
6	3	0	0.08	5.8
7	0	1.5	0.08	6.8
8	1.5	0.75	0.04	5.7
9	1.5	0.75	1% Celcon U10	5.6

A plot of crystallization half time in a composition containing varying amounts of EMA and P561 in a polyoxymethylene resin is shown in Fig. 1a. Fig.
20 1b shows a plot of crystallization half time for a polyoxymethylene composition containing 0.080% nucleant (Zemid) and varying amounts of EMA and P561.

Samples containing polyoxymethylene resins and the additives as shown in Table 3 below were formed by injection molding to form bars on a cycle that is too short for an unnucleated resin to produce void-free parts. The bars were cut lengthwise to reveal their internal structure. Photocopy reproductions of the cut bars are shown in Figs. 2a, 2b and 2c. It can be seen that sample 1 (Fig. 2a), an example of the present invention is substantially void free as compared to the bars shown in Figs. 2b and 2c which do not contain the three additives used in the present invention.

TABLE 3

	nucleant/%	EMA	{PE Wax
1.	Celcon U-10*/2%	1.5%	.75%
2.	0.17% Zemid® contains 0.08% Talc	0	0
3.	0	0	0

*branched terpolymer of mw = 109,000

The additives shown in Table 4, below were compounded together on a 40mm W&P twin screw extruder and then molded into 1/4 inch thick tensile bars on a molding cycle which is too short for the unmodified control resin, #3. The bars were then machined to 1/8" thickness to reveal the internal porosity. Note the control, sample #3 has many voids while the sample 14, which is the object of this invention has very few. The latter is the more desirable for molding applications.

TABLE 4

Run No.	Acetal MW	Additive	Branched terpolymer MW=109,000
3	85000	NONE	NONE
6	85000	EMA/2,P561/.4	NONE
12	85000	NONE	1
14	85000	EMA/2,P561/.4	1

Photocopy reproductions of the bars machined to show the internal porosity are shown in Figs. 3a, 3b and Figs. 4a and 4b. Fig. 3a corresponds to sample 3 of Table 4; Fig. 3b corresponds to sample 6 of Table 4; Fig. 4a corresponds to sample 12 of Table 4; and Fig. 4b corresponds to sample 14 of Table 4.

**WHAT IS CLAIMED IS:**

1. A composition comprising:
 - a) a polyoxymethylene polymer;
 - 5 b) a polyalkylene/unsaturated carboxylic acid lower alkyl ester polymeric nucleating material;
 - c) a waxy denucleating material; and
 - d) a nucleant.
- 10 2. The composition according to claim 1, which comprises:
 - a) 0.5-3% by wt. of the ester polymeric nucleating material;
 - b) 0.1-1% by wt. of the waxy denucleating material; and
 - c) 0.01-3% by wt. of the nucleant.
- 15 3. The composition according to claim 1, wherein the polyoxymethylene is a homopolymer of formaldehyde or a cyclic oligomer of formaldehyde, the terminal groups of which are end capped by esterification or etherification, or a copolymer of formaldehyde or of a cyclic oligomer of formaldehyde and other monomers that yield oxyalkylene groups with at least two adjacent carbon atoms in the main chain,
20 the terminal groups of which copolymers can be hydroxyl terminated or can be end capped by esterification or etherification.
4. The composition according to claim 1, wherein the polyalkylene/unsaturated carboxylic acid lower alkyl ester polymeric nucleating material is a copolymer or
25 terpolymer of a lower alkene (C_2-C_4) and a lower alkyl ester of an unsaturated acid.
5. The composition of claim 4, wherein the unsaturated carboxylic acid lower alkyl ester is an alkyl ester of unsaturated carboxylic acids having 3 to 8 carbon atoms.



6. The composition according to claim 4, wherein the unsaturated carboxylic acid lower alkyl ester is methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate and isobutyl methacrylate.
7. The composition according to claim 1, wherein the nucleant is a finely divided solid.
8. The composition according to claim 7, wherein the nucleant is boron nitride, talc, silica, polyimides, a branched or crosslinked acetal copolymer or terpolymer, a melamine-formaldehyde resin, calcium carbonate, diatomite, dolomite, or is an encapsulated nucleant comprising an encapsulant polymer and the nucleant.
9. A molded article, comprising:
- a) a polyoxymethylene polymer;
 - b) a polyalkylene/unsaturated carboxylic acid lower alkyl ester polymeric nucleating material;
 - c) a waxy denucleating material; and
 - d) a nucleant.
10. A method for making a polyoxymethylene composition with improved set-up time and reduce shrinkage, comprising the steps of:
- a) preparing polyoxymethylene polymer component
 - b) melt blending the polyoxymethylene polymer produced in step a) with a combination of: i) a polyalkylene/unsaturated carboxylic acid lower alkyl ester polymeric nucleating material; ii) a waxy denucleating material; and iii) a nucleant.