ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 5, pp. 1036–1041. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © Yu.P. Gorelov, I.V. Mekalina, T.S. Trigub, I.A. Shalaginova, E.G. Sentyurin, V.A. Bogatov, M.K. Aizatulina, 2010, published in Rossiiskii Khimicheskii Zhurnal, 2010, Vol. 54, No. 1, pp. 79–84.

Chemical Modification of Transparent Acrylate Polymers for Enhancing the Resource of Aircraft Glazing Parts

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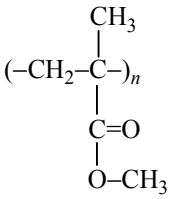
Received December 1, 2009

Abstract—Organic glasses for the production of aircraft glazing parts have been designed. Results of chemical modification of transparent acrylic polymers for enhancing the resource of organic glasses in planes are described. New polymer-based organic structured glasses VOS-1 and VOS-2 are able to operate under short-term one-side heating up to temperatures of 160–200ºC, due to a high polymer thermal resistance.

DOI: 10.1134/S1070363211050379

The problem of development of organic glasses for modern high-speed aircrafts and their perspective analogs has arisen because of the discontinuation of production of the most heat-resistant domestic fluorinated acrylate polymer glasses with operating temperatures of 200°C and above. At present organic glasses are fabricated from poly(methyl methacrylate) (PMMA):



However, we would like to note that the widely applied commercial PMMA organic glasses SO-120 and AO-120 are unable to meet increased demands to operating temperatures.

The principal characteristics of polymer construction materials, relating to their performance at elevated temperatures, are thermal stability and thermal resistance. Even though these characteristics of methacrylic polymers can be enhanced in a great number of ways, many of them are impractical in view of some technological features of the production of organic glasses and requirements to physicochemical, optical, and other properties. Technical feasibility of one or another solution at minimum economic expenses not exceeding, in particular, the expenses for recovering the production of fluorinated acrylate glasses should be taken into account.

The following ways to enhance the thermal stability of PMMAs are known: decreasing the content in the polymer of unsaturated end groups initiating depolymerization, introduction into the co-monomer of units inhibiting depolymerization, and introduction into the co-polymer at the polymerization stage of thermostabilizers, antioxidants, etc.

The molecular weight of PMMA in organic glasses is 10^6–10^7, and, consequently, the content of unsaturated end groups formed via disproportionation chain termination during polymerization is not too high, and these groups do not decrease much the thermal stability of the polymer. To change the character of chain termination during polymerization one should introduce into the composition chain propagation regulators or weak inhibitors. Inhibitors prolong the time of glass formation and thus decrease their molecular weight, which is undesirable. Therefore, this

way to enhance the thermal stability of PMMA as applied to block organic glass has not been explored in sufficient detail, but should be taken account in the research into the synthesis of organic glasses using a forepolymer.

The introduction in the PMMA macromolecules of "foreign" units for kinetic chain termination in depolymerization was used in the development of the organic glass SO-120T. The role of such units belongs to acrylic acid (AA). The choice of this acid is explained by the fact that it smaller, compared to its esters, decreases the glass-transition temperature (T_g) of the copolymer. At the same time, acrylic acid is not an optimal choice. The suitable units are also maleic anhydride $(C_2H_2CO)_2O$, maleimides $(C_2H_2CO)_2NH$, and cross-linking agents like di- and triacrylates and allyl derivatives which, enhancing the thermal stability, can enhance, to some extent, thermal resistance of the copolymer and also improve the resistance of glass to certain atmospheric exposures, which is characteristic of, say, cross-linked PMMA.

Cross-linked glasses occupy a considerable place in the range of foreign organic glasses for aircraft engineering. Thus, for example, Rohm applies diacrylate esters as cross-linking agents, which ensures stable T_g values of the copolymer under its exposure to thermal loads characteristics of the orientation modes.

There have been numerous attempts to introduce into the formulations of organic glasses potential thermostabilizing agents, but they all failed. The most widely used polymer thermostabilizers are sterically congested phenols and aromatic amines, which are efficient free-radical inhibitors. Therefore, such stabilizers are impossible to introduce at the methyl methacrylate polymerization stage; otherwise, they much prolong the polymerization time.

In the research on stabilization of organic glasses [1, 2], we studied more than 10 potential thermostabilizers. specifically phosphoric acid anilides, derivatives of substituted hydroxybenzylamines, phenylaminophosphates, etc. Certain known stabilizers did not dissolve in methyl methacrylate and others were sparingly soluble, inhibited polymerization, or colored either initial or heated glasses. As a result, only one thermostabilizer was selected (S-757) to obtain an SO-120(O) glass, and its thermal and climatic aging was tested. The tests showed that SO-120(O) does not surpass in thermal resistance the SO-120T organic glass.

The introduction of an antioxidant into organic glasses at the polymerization stage proved possible, when a redox system was used as initiator. In this way, a series of highly thermostable organic glasses T2-55 were prepared. However, these glasses tended to acquire an intense yellow color on exposure to high temperatures, on account of the presence of the initiating system peroxide–aromatic amine.

The principal approach to enhancing the thermal resistance of polymers, methacrylic inclusive, is to reduce mobility of macromolecules and their fragments (i.e. to reduce chain flexibility) at elevated temperatures. The rigidity of macromolecules and, as a consequence, thermal resistance can be increased in the following ways.

(1) Introduction into copolymers of polar groups capable of forming intra- and intermolecular hydrogen bonds.

(2) Forming intermolecular bonds by means of polyfunctional monomers (cross-linking agents).

(3) Copolymerization with monomers containing bulky cyclic fragments which restrict mobility of side groups and the whole macromolecules.

The above approaches are fairly well documented in the patent and scientific and technical literature, their use in the production of organic glass for aircraft engineering has scarcely been reported.

The approach involving introduction into organic glass of polar carboxy groups for enhancing its thermal stability was used in the development of the copolymeric organic glasses SO-140 (analogs 2-55, SO-133) and T2-55. It is known that polar groups are introduced in the formulations of certain foreign organic glasses for aircraft engineering [3]. Thus, the organic glass Plexiglass 55 (Rohm, Germany) contains *N*-(methoxymethyl)methacrylamide units, Poly 76 (Polycast Technology Division, USA) contains carboxy and amide groups, and S-350 (Swedlow, now Pilkington Aerospace, Great Brotain) contains methacrylamide derivatives.

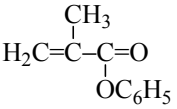
The thermal resistance of PMMAs is most commonly enhanced by introducing maleic anhydride [4, 5] and maleimide [6, 7] units. The introduction of up to 30 wt % of maleic anhydride increases the thermal resistance by 10–13°C. Ternary methyl methacrylate copolymers with Vicat softening points of 145–155°C were reported [8], but these compositions require prolonged polymerization at elevated temperatures.

The above-mentioned polar groups (carboxy, amide, anhydride, etc.) all are hydrophilic, and their intro-duction increases the water uptake of the resulting copolymers. Nevertheless, further indirect evidence for the wide use of copolymeric organic glasses in aircraft engineering is provided by the fact that the US Ministry of Defense has issued specifications for ranking organic glasses in terms of their water uptake level [9].

The formation of intermolecular chemical bonds as an approach to enhancing the thermal resistance of organic glasses is of limited application, since aircraft glazing parts are generally fabricated by molding and alignment of acrylic sheets. At a certain cross-linking degree which generally provides no considerable gain in thermal resistance, glasses are no longer feasible for processing by these technologies, having low relative creep values. The maximum allowable concentration of a dimethacrylate cross-linking agent, ensuring the subsequent glass drawing degree of 70% degree and increasing the T_g of PMMA to about 135°C is reported in the patent [10].

In this connection of interest are allylic cross-linking agents. Allyl groups are inactive in copolymerization with methyl methacrylate, thus making possible to obtain a loosely cross-linked copolymer at an almost complete conversion of methyl methacrylate which can be further cross linked at elevated temperatures.

The copymerization of methyl methacrylate with methacrylate esters with bulky cyclic groups as an approach to prepare copolymers with enhanced thermal resistance is widely presented in the literature. Methyl methacrylate has been copolymerized with cyclopentyl- [11], cyclohexyl- [12–17], and (iso)-bornyl-substituted [15, 17–19] phenyl methacrylates [20–23]:



Methyl methacrylate copolymerizes with bi- and tricyclic methacrylates of various structure [24–28]. Such copolymers characteristically exhibit a lower water uptake compared with PMMA. Therewith, monocyclic methacrylates weaker affect the strength characteristics of the copolymer compared with polycyclic.

As mentioned above, maleimides can also increase the thermal resistance of PMMA, since they comprise polar groups and have a cyclic structure. Maleimides with *N*-alkyl [29–34], *N*-cycloalkyl [31, 35–38], or *N*-phenyl substituents [30, 32, 37, 39–47] have been reported. The phenyl radical in *N*-substituted maleimides can, in its turn, contain various substituents. Copolymers with maleimides possess a high thermal stability. The strength parameters of with *N*-alkylmaleimide copolymers are higher compared with those of *N*-phenylmaleimide copolymers.

Thus, even though no direct evidence for the use of methyl methacrylate copolymers with cycle-containing monomers as organic glasses for aircraft engineering has been reported, this approach to enhancing the thermal stability of PMMA is still of interest, since it allows one to simultaneously impart, by using appropriate monomers, decreased water uptake to the resulting copolymers.

The above analysis reveals the following possible directions for the development of organic glasses with increased working temperatures:

– copolymerization of methyl methacrylate with allylic cross-linking agents to obtain a loosely cross-linked organic glass feasible for further structuring by molding and alignment processing;

– modification of SO-133 (2-55, SO-140) glasses by introducing in them the third comonomer unit to decrease the water uptake of the glass but simultaneously preserve its thermal resistance and a complex of deformation and strength characteristics;

– modification of T2-55 glasses to attenuate their tendency for coloration at elevated temperatures and decrease the water uptake.

The T2-55 glass is one of the most thermostable organic glasses for aircraft glazing. Its high thermal stability is due to the fact that it contains an antioxidant which prevents thermooxidative destruction processes at elevated temperatures. To introduce antioxidants at the polymerization stage proved possible by using redox systems as initiators [48]. However, this entailed coloration (yellowing) of the glass on exposure to elevated temperatures. The second disadvantage of the T2-55 glass is its high water uptake due to the presence, like in SO-133, of hydrophilic groups.

Foreign companies apply UV absorbers and UV stabilizers in the formulation of organic glasses on the basis of PMMA. The presence of UV absorbers is a requirement for all types of organic glasses for aircraft engineering. Foreign technical regulations allow almost no transmission at 290–330 nm (no more than 2%). Domestic regulatory documents do not contain this parameter, but, nevertheless, all previously deve-

Comparative characteristics of thermostable organic glasses

Parameter	Glass brand							
	AO-120 oriented		VOS-1		VOS-2		E-2 fluoroacrylate glass	
Softening temperature, °C	120		133–137		150		180	
Thermal stability, °C	180		230		230		230	
Specific shock viscosity, kJ m^{-2}	32		25		23		21	
Test temperature, °C	20	100	20	100	20	100	20	100
Longitudinal:								
strength, MPa	83.0	18.5	92.0	35.0	83.0	35.0	83.0	42.0
elongation, %	20	>60	4.6	>68	5.7	10.0	3.8	26.8
elastic modulus, MPa	3100	750	4000	1400	4200	–	3380	1670
Static flexural strength, MPa	>101	>23.5	130	–	120	48	122	59.0

loped glasses for aircraft engineering contain the UV absorber phenyl salicylate which shifts the glass transmission range from 290 to 335–340 nm. In particular, Röhm introduces, along with a UV absorber, into the glass formed by 95% by methyl methacrylate units, a UV stabilizer of the class of sterically congested amines. The problem of UV stabilization of more urgent for copolymeric organic glasses with a large fraction of methacrylic acid units (2–55 and T2-55 brands and their modifications), since they are less resistant to atmospheric factors than glasses on the basis of an almost pure PMMA.

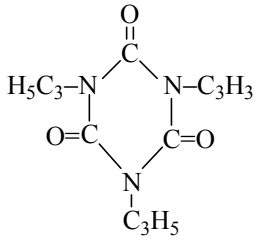
Our research showed that modification of PMMA (organic glass SO-120MT) makes it possible to increase its working temperatures and enhance the shape stability of pieces molded from this glass. The strength characteristics of the SO-120MT glass at 160°C are much higher compared to its analogs.

It was shown that the water uptake of SO-133 and T2-55 glasses, as one of the factors responsible for their low environmental resistance, can be decreased without sacrificing the thermal resistance, thermal stability, and optical and deformation strength characteristics.

The degree of coloration of the T2-55 glass can be decreased by replacing the initiating system on their polymerization.

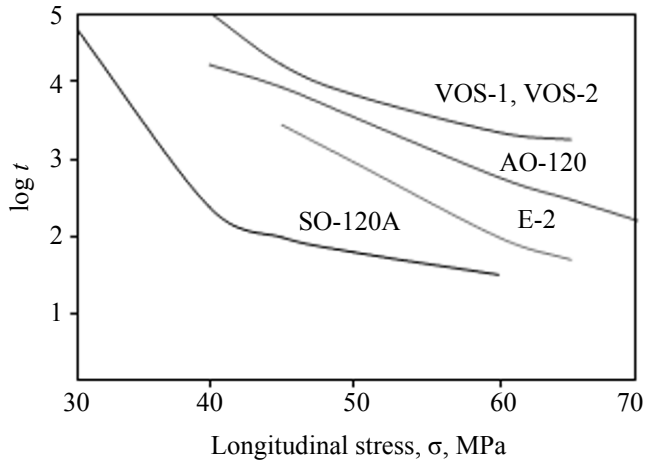
We developed and certified a new thermostable acrylic copolymer glass VOS-1 with the softening point 135°C and the working temperature on one-sided heating from –60°C to 160°C [49]. The technical specifications "Glass Organic Thermostable VOS-1 (T2-55M)" (TS 2216-396-00202947-2003) were issued. This organic glass is serially produced at the pilot plant of the PCTRI.

Further research resulted in the preparation of a number of modifications of copolymeric organic glasses with the softening points 140–150°C, stable under complete heating at 180°C for 50 h. These glasses are formed by copolymerization of methyl methacrylate (MMA) with methacrylic acid (MAA) with a triallyl cyanurate cross-linking agent:



To raise the thermal resistance to values of about 150°C, part of MMA units is the copolymer are replaced by chloroacrylate monomers containing bulky cyclic groups, and this much decreases the water uptake of the resulting organic glasses. Along with the above-mentioned monomers and cross-linking agent, these modifications contain UV stabilizers and UV absorbers in standard amounts.

These glass modifications formed the basis for the development of acrylate copolymer glasses with working temperatures of up to 200°C. Pilot formulations of acrylate copolymer glasses with the softening



Logarithmic dependence of fracture initiation time on longitudinal stress at 20°C.

point 150°C and working temperature about 200°C (SO-150-1, SO-150-2, and SO-150-3) on the basis of MMA and MAA, and an allyl cross-linking agent. The use of such cross-linking agent allowed maintaining the required thermostability parameters at 230°C for 5 h. In the SO-150-1 and SO-150-3 we introduced for the first time a phenyl methacrylic ester as the UV stabilizer, and this favored enhanced resistance of the polymers to high temperatures. The UV absorbers applied in all the formulations were Tinuvin P or Tinuvin 360. For reduced water uptake, a chloroacrylate ester with bulky cyclic groups was introduced into the SO-150-2 and SO-150-3 formulations. The breaking strength and relative elongation at 20°C of glasses of all the modifications were above 80 MPa and 4%, respectively. After complete heating at 200°C for 20 h the strength of all glass modifications decreased no more than 25%. It was shown that all formulations are thermostable under complete heating at 200°C for 20 h and at 230°C for 5 h.

To choose an optimal glass formulation, comparative tests of the developed organic glasses SO-150-1, SO-150-2, and SO-150-3. Thermal and light stability tests of the organic glasses showed that SO-150-1 has an optimal formulation for an organic glass with the working temperature 200°C. The SO-150-1 glass was certified as VOS-2 brand. The softening temperature of VOS-2 is 150°C, and the working range of this glass ranges is –60°C to 200°C [50]. The "Glass Organic Thermostable of VOS-2 Brand" Technical Specifications (TS 2216-474-00208947-2006) were developed. This glass is commercially produced at the pilot plant of the PCTRI.

The light transmission factor of the developed aviation organic glasses VOS-1 and VOS-2 is about 90% in the initial state, and is preserved at the required level of 70–75% after complete heating at 200–230°C.

The table compares the principal thermophysical and physicomechanical parameters of the aviation organic VOS-1 and VOS-2 with those of the serially produced organic glasses AO-120 and E-2.

The physicomechanical parameters of VOS-2 fit the requirements for glazing materials with the working temperature 200°C and rank only below the previously developed fluoroacrylate glass E-2 at the test temperature 100°C.

The chemical modification of acrylate glasses with cross-linking made it possible to considerably improve the most important performance characteristic: cracking resistance ("silver resistance").

The results of testing the organic glasses for resistance to long-term exposure to longitudinal stresses, shown in the figure, revealed that VOS-1 and VOS-2 are much better resistant to cracking than widely used oriented and nonoriented glasses SO-120A, AO-120, and E-2.

The chemical and formulation modification of cross-linked acrylate thermally stable organic glasses allowed production of sheet materials feasible for processing by molding and orienting, and, therefore, for fabricating real aircraft glazing parts with working temperatures of up to 160–200°C.

The following PCTRI staff members were involved in the work: L.V. Zmanovskaya, T.G. Chmykhova, N.N. Safonova, M.A. Perevaryukha, A.L. Efimov, N.K. Kobyakova, E.P. Beshenov, etc.

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