ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 5, pp. 1047–1052. © Pleiades Publishing, Ltd., 2011.
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Effect of Polysulfone Modification Techniques on the Properties of Polymer–Silicate Nanocomposites

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Received December 1, 2009

Abstract—An effect of different methods of structural modification of the heat-resistant amorphous polysulfone with layered silicate montmorillonite on the properties of the resulting polymer–silicate nanocomposites has been studied. Comparative evaluation of the technological, physical, mechanical, thermal, and rheological properties of the nanocomposites has been performed.

DOI: 10.1134/S1070363211050392

INTRODUCTION

Thermoplastic polymer materials (thermoplasts) have found application in various branches of industry, including electronic, automotive, and aerospace. Foreign aviation industry applies such fire-resistant thermoplasts as polyetherketone, polyphenylene sulfide, and polyetherimide, which possess high physico-mechanical characteristics. In Russia, however, the only presently produced engineering thermally stable thermoplasts are polysulfone and polyamide. To master production of foreign materials, new costly production capacities have to be introduced.

It seems more beneficial to take a different way in the development of polymer materials, viz. to modify existing polymers. Considerable recent interest is attached to silicate nanoparticles as modifying additives. The widest application has been found by the clay mineral montmorillonite [1, 2].

A layered silicate is a "batch" of elemental nanosized layers, and the interlayer spaces are called interlayers or galleries [3–5]. Natural silicate is hydrophilic and can combine with hydrophilic polymers only. To combine silicate with hydrophobic polymers, it is modified by organic compounds [6–8].

The plane topology of silicate nanoparticles makes them a suitable material for two-dimensional reinforcement of thermoplastic matrices, which is accompanied by a lower anisotropy of properties of the resulting articles. Further condition for reinforcement is a fairly high level of adhesive interaction between nanoparticles and polymer.

Polymer–silicate composites can be divided into three groups, depending on the degree of distribution of silicate in polymer: microcomposite, intercalated nanocomposite, and exfoliated nanocomposite [9]. The properties of polymer–silicate composites depend on the degree of silicate dispersion. The composite in which silicate is present as agglomerates is called microcomposite. Layered silicates tend to agglomerate two cases: (1) unmodified silicate poorly combines with polymer or (2) organics-modified silicate is present in an excess amount. Agglomerated layered silicates exhibit properties of a usual disperse filler.

Physicomechanical properties can be considerably improved either by intercalation of the polymer matrix into layered silicate galleries or by exfoliation, i.e. complete destruction of the crystal structure of the latter. The RIAM have performed research on different methods of polymer modification composites.

Objects and Methods of Research

The objects for study were composites on the basis of an amorphous construction polymer polysulfone modified with a layered silicate of the montmorillonite family (OM-MMT). In its turn, the layered silicate was modified by a quaternary ammonium compound (dimethyldialkylammonium). Preliminary research on

samples with varied contents of layered silicate showed that the optimal properties are characteristic of the composite containing 2.5 wt % of OM-MMT. Therefore, in further studies we used just this composite.

Polysulfone was modified with layered silicate in four different ways: extrusion mixing; triple extrusion mixing; exposure to the UV field followed by extrusion mixing, and extrusion mixing with silicate super concentrate. In the first three cases we used a single-screw extruder and in the latter case, a double-screw one.

The structure of polymer–silicate composites was studied, following the "Procedure for Identication of Silicates" (X-ray Structural Diffraction Analysis of Nanosilicates and Polymer–Silicate Nanocomposites) developed at the RIAM (MM 1.595-17-330-2007).

The composite type (micro-, intercalated nano-, or exfoliated nanocomposite) was determined from the X-ray diffraction patterns of layered silicates and polymer–silicate composites.

The measurements were performed on a Rigaku D/MAX-2500 superpower diffractometer (30 kV, 100 mA, scan range $2° \le 2\theta \le 20°$). For a high-quality analysis measurements were performed until intense reflexes no longer observed.

The flexural modulus was measured according to the State Standard 9550-81. The tensile strength was measured according to the State Standard 11262-80 on an IR 5040-5 tensile testing machine (single-axis tension, temperature 22°C, rate 25 mm min^{-1}); five parallel tests were performed for each sample batch.

The Charpy impact viscosity was measured according to the State Standard 4647-80; five parallel runs were performed for each sample batch.

The DTA and DTG analyses were performed according to the State Standards 29127-91 and 21553-76, on an MOM Paulik–Paulik–Erdey Q 1500 instrument, heating rate 10°C/min.

Relaxation characteristics were measured according to the State Standard 20812-83, on a Relaksometr RM-05 instrument for testing dynamic mechanical properties of polymer materials, heating rate 2°C/min.

The rheological properties of polymer–silicate composited in the free-flowing state were studied by rotation and capillary viscometry. The melt fluidity index (MFI) was determined according to the State Standard 11645-73, viscosity was calculated by the formula $\eta = 0.5G\rho/\mathrm{MFI}$, where G is the load weight and ρ, melt density. Test conditions: temperature (for polysulfonyl–silicate composites) 325°C, capillary 2 mm, load 21.19 N.

The thermal stability coefficient was calculated from the MFI at 325°C and pressure exposure times of 10 min (first instrument channel load) (MFI_{10}) and 20 min (second instrument channel load) (MFI_{10}). The thermal stability coefficient was calculated by the formula: $K = \mathrm{MFI}_{10}/\mathrm{MFI}_{20}$.

Properties of Polymer–Silicate Nanocomposites

For research into layered silicate–polymer matrix interaction, we measured X-ray diffraction patterns of the starting polysulfone, layer silicate, and polymer–silicate composites on their basis (Fig. 1).

The intercalation of layered silicates is judged about from changes in peak intensities and positions in the X-ray diffraction pattern of the material compared to the starting components [9, 10]. The lack in the X-ray diffraction pattern of basal reflexes of the layered silicate suggests that its layers are either far distant from each other or completely exfoliated in the polymer [11]. The appearance of peaks lacking in the layered silicate suggests formation of a new polymer–silicate structure.

Figure 1a shows the X-ray diffraction patterns of the modified silicate OM-MMT, polysulfone, and polymer–silicate composite obtained by extrusion mixing. The X-ray diffraction patterns of OM-MMT contain well-defined basal reflexes (peaks), consistent with layer periodicity, the interlayer distances, nm, are as follows: d = 3.2 ($2\theta \sim 2.75°$), 2.0 ($2\theta \sim 4.4°$), and d = 1.25 ($2\theta \sim 7.0°$). Small-angle diffraction measurements revealed lack of the first and second peaks characteristic of the layered silicate in the X-ray pattern of the composite. At the same time, the peak at $2\theta \sim 7.0°$ was shifted to smaller angles ($2\theta \sim 6.1°$), and, therewith, the interlayer distance increased from 1.25 to 1.44 nm. This finding points to the presence in the polymer–silicate composite of ordered silicate layers and to polymer intercalation into the silicate interlayer space. It was thus shown that the extrusion mixing of the layered silicate with polysulfone produces an intercalated nanocomposite.

The same picture was also observed with polymer–silicate composites prepared in different ways (Figs. 1b–1d).

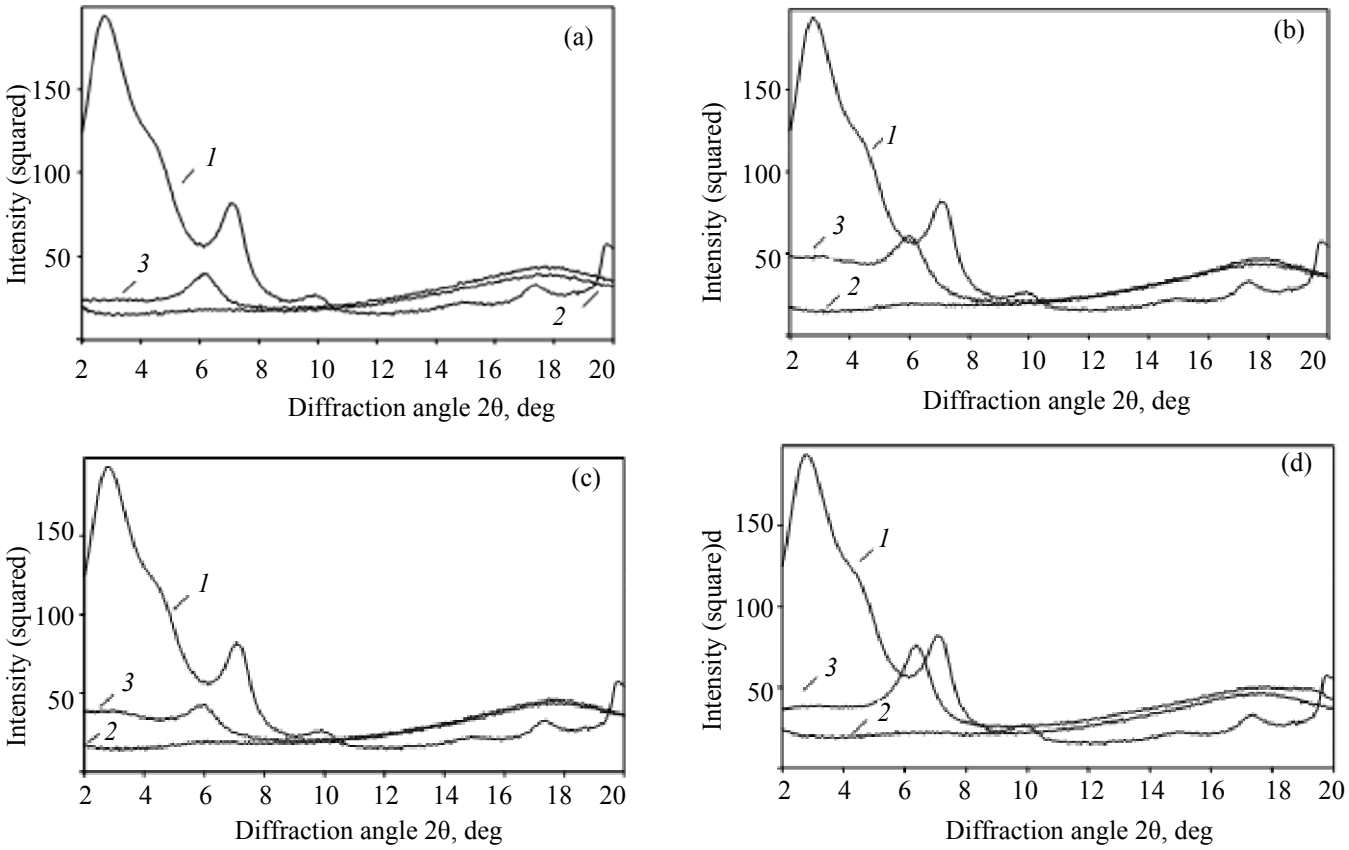

Fig. 1. X-ray diffraction patterns of (*1*) the OM-MMT layered silicate, (*2*) starting polysulfone, and (*3*) polymer–silicate composites on their basis (OM-MMT layered silicate content 2.5 wt %. Composite preparation technology: (a) extrusion mixing, (b) triple extrusion mixing; (c) ultrasonication followed by extrusion mixing, and (d) extrusion mixing with nanosilicate superconcentrate.

We studied the main properties of the polymer–silicate nanocomposites on the basis of polysulfone, modified by different procedures (see table).

As seen from the table, the properties of polysulfone can be improved by modifying it with layered silicate by different techniques. However, the nanocomposite obtained by extrusion mixing with nanosilicate superconcentrate has the best characteristics.

Analysis of tensile strength parameters showed that the tensile yield of polysulfone modified with layered silicate by extrusion mixing and extrusion mixing with nanosilicate superconcentrate increases by 5–7%. This fact suggests strengthening of the composite and a good compatibility of the matrix and modifier. As shown in [11–13], the fact that the tensile yield of a polymer composite is higher than that of the polymer itself is evidence for a strong matrix–modifier adhesive interaction which is stronger that the cohesive strength of the matrix. Obviously, the polymer–silicate nanocomposites we obtained contain just such interaction. The composites obtained by triple extrusion mixing or by ultrasonication followed by extrusion mixing exhibited no increased tensile yields. The relative elongation of polymer–silicate nanocomposites compares with that of the starting polysulfone. This is quite an important characteristic feature of nanocomposites, since any inorganic filler in a makes the latter more brittle.

The elastic modulus is an integral rigidity characteristic of a construction material. The elastic modulus of polysulfone is enhanced by its modification with layered silicate, which is associated with resistance of the latter. The elastic modulus is increased due to oriented polymer chains between silicate layers.

The impact strength relates to the ability of materials to resist to loads applied at a high speed; polymer–silicate nanocomposites it is slightly increased.

Effect of modification technology on the characteristics of polymer–silicate nanocomposites on the basis of polysulfone (OM-MMT content 2.5 wt %)

Parameter	Polysulfone	Modification technology			
		Extrusion mixing	Triple extrusion mixing	Unltrasonication followed by extrusion mixing	Extrusion mixing with nanosilicate superconcentrate
Tensile yield, MPa	76	80	75	73	81
Relative tensile elongation, %	12	12	12	12	13
Flexural elastic modulus, GPa	2.6	3.1	3.0	2.9	3.1
Impact strength, kJ m^{-2}	100	104	103	102	104
Temperature corresponding to the dynamic shear modulus of 654 MPa, °C	100	155	140	148	160
Viscosiy (log η) after exposure for 5/30 min, Pa s	3.24/3.26	2.59/2.61	2.50/2.52	2.61/2.65	2.50/2.52
Melt flow index after exposure for 5/30 min, g/10 min	6.98/7.36	8.38/8.83	8.40/8.85	8.30/8.80	8.40/8.85
Thermal stability coefficient	0.95	0.95	0.92	0.90	0.95
Glass transition point, °C	185	180	172	178	190
Decomposition initiation point, °C	460	475	470	470	480

The dynamic shear modulus characterizes the energy received and lost by unit volume over a single vibration period. The table lists the temperatures corresponding to the dynamic shear modulus of 654 MPa (100°C for the starting polysulfone). Enhanced shear strengths were found in all the polymer–silicate composites. The largest enhancement of dynamic shear modulus (by 20% with respect to the starting polysulfone) is characteristic of the composite obtained by extrusion mixing with nanosilicate superconcentrate (Fig. 2). This finding suggests the possibility to prolong the service life of the material in the working temperature range or to raise the upper working temperature.

The modification of polysulfone with layered silicate increases the glass transition point of the polymer. This is explained by a number of reasons [14–16]. At low concentration, silicate is well dispersed in the polymer free volume. Polymer penetrates into silicate galleries, which blocks mobility of the polymer chain segments situated between silicate layers. In its turn, restricted mobility of polymer chains affects their rotational and translational mobility [9]. The increased glass transition point will allow the polymer–silicate nanocomposite to be used at higher temperatures than the starting polysulfone.

Rheological measurements showed that the modification of polysulfone with layered silicate increases the melt flow index by 19–20%. The polymer–silicate nanocomposites all proved to be more thermostable.

The thermal stability of polymer–silicate nanocomposites was studied by thermal gravimetry by measuring weight loss as a function of temperature (Fig. 3). The main reference points were the decomposition initiation, and 10 and 50%-weight loss points. The maximum weight loss rates were also compared.

It was found that the decomposition initiation point of polysulfone modified with layered silicate increases by 15–20°C. The coke residues at 600 and 800°C in polymer–silicate nanocomposites are higher than in the starting polysulfone. The explanation of this finding is that the polymer chain intercalates into galleries of layered silicate and forms more intermolecular bonds with the latter. This results in weaker vibration motions on heating [16]. In its turn, nanosilicate

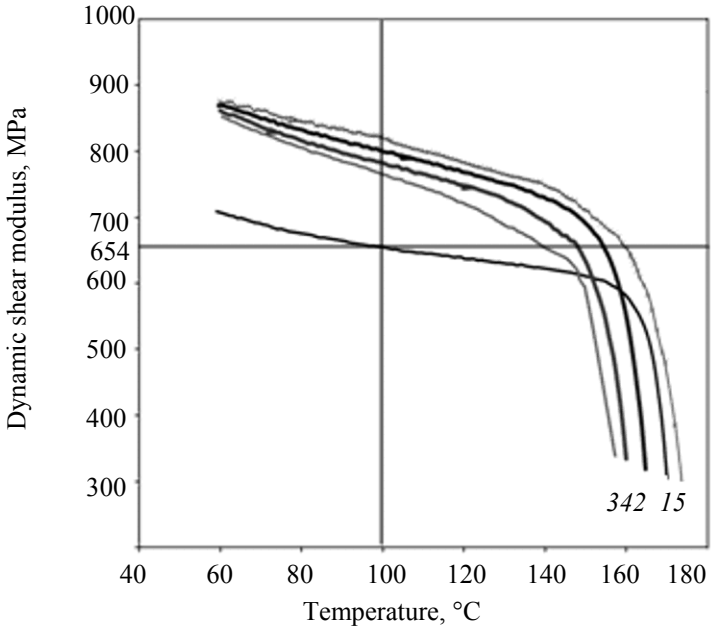

Fig. 2. Temperature dependence of dynamic shear modulus for polymer–silicate nanocomposites: (*1*) starting polysulfone; polymer–silicate nanocomposites prepared by (*2*) extrusion mixing, (*3*) triple extrusion mixing; (*4*) ultrasonication followed by extrusion mixing, and (*5*) extrusion mixing with nanosilicate superconcentrate. The OM-MMT content in layered silicate composites is 2.5 wt %.

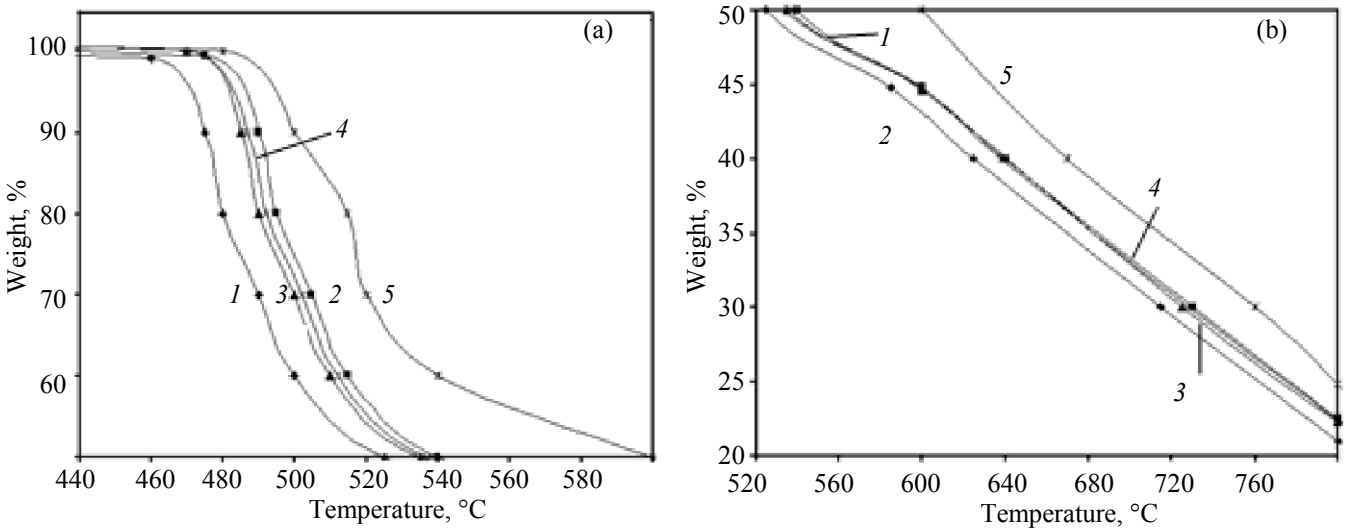

Fig. 3. Thermogravimetric weight loss curves for polysulfone and polymer–silicate nanocomposites on its basis: (*1–5*) See legend to Fig. 2. Weight loss, %: (a) ≥ 50 and (b) > 50. The OM-MMT content in layered silicate composites is 2.5 wt %.

possesses a good thermal stability, and it creates heat shield and barrier effects with respect to volatile products formed by decomposition [17–20]. The problem of the enhancement of thermal stability of polymers by their modification with layered silicates was also studied in [21, 22].

Thus, our research established that polysulfone modified with layered silicate exhibits improved strength and performance characteristics and thermal stability. The polymer–silicate nanocomposites obtained by extrusion mixing with nanosilicate superconcentrate show the best and the most stable characteristics.

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