



## Research paper

# Industrially applicable methods of poly(methyl methacrylate)/organophilic montmorillonite nanocomposites preparation: Processes and cast materials characterization



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## ABSTRACT

The poly(methyl methacrylate) (PMMA)/organophilic montmorillonite cast nanocomposites were prepared via bulk free-radical polymerization of raw monomer (MMA) and PMMA/MMA syrup. Three types of commercial organophilic montmorillonites (o-Mt) (swelled in either MMA or syrup and additionally homogenized in a high-speed flow homogenizer or twin-screw extruder, respectively) have been utilized to PMMA panels manufacturing. An influence of o-Mt type and content as well as its dispersion methodology on mechanical, thermal and optical properties has been investigated. Although PMMA panels containing o-Mt exhibited similar tensile strength (in respect to unmodified PMMA samples), higher hardness (+2 HBa units) and flexural strength (+15% for PMMA prepared using raw monomer and unhomogenized o-Mt/MMA paste) have been observed. Moreover, introduction of o-Mt into polymeric matrix resulted in increased thermal stability, Vicat softening temperature (+5 °C) and glass transition temperature value determined by DMTA technique (+5 °C for PMMA/o-Mt composites prepared from syrup with non-extruded clay mineral paste). XRD and TEM analysis showed full or partial exfoliation of organophilic montmorillonites in polymer matrix, respectively.

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## 1. Introduction

Poly(methyl methacrylate) belongs to the most transparent polymeric materials for visible and UV light. That relatively expensive polymer is commonly utilized for manufacturing different kinds of protective as well as highly decorative elements (e.g. barriers, screens, shields of neon signs, motor-car accessories) by extrusion and/or injection molding. Nevertheless, the mentioned goods are mostly prepared using cast PMMA panels prefabricated via bulk free-radical polymerization of methyl methacrylate monomer (MMA) or PMMA/MMA syrup in glass molds. Various thicknesses of PMMA panels are commercially available. They could be easily processed using thermoforming and other mechanical methods.

In recent years intensive research on improving mechanical as well as thermal properties of poly(methyl methacrylate) by nanofillers addition has been conducted. There are numerous patents and scientific contributions treating of PMMA modification with organophilic montmorillonites (o-Mt). Those papers showed improved properties of PMMA/o-Mt materials prepared via emulsion (Choi et al., 2003; Essawy et al., 2004; Meneghetti and Qutubuddin, 2006; Sahoo and Samal, 2007; Wang et al., 2002), suspension (Wang et al., 2002), solution (Gao et al., 2001;

Huskić and Žigon, 2007; Tabtiang et al., 2000; Tsai et al., 2010; Wang et al., 2002) and bulk-type free-radical polymerizations (Achilias et al., 2010; Dietsche and Mühlaupt, 1999; Meneghetti and Qutubuddin, 2006; Nikolaidis et al., 2012; Okamoto et al., 2000; Oral et al., 2009; Ratnac et al., 2006; Wang et al., 2002; Zeng and Lee, 2001; Zhu et al., 2002). The incorporation of modified clay mineral ( $\geq 0.5$  wt. part of o-Mt/100 wt. parts of PMMA) into the polymeric matrix has been routinely realized through long-lasting mechanical mixing and ultrasonication and resulted in tensile strength (Nikolaidis et al., 2012), Young's modulus (Dietsche and Mühlaupt, 1999; Nikolaidis et al., 2012), thermostability (Dietsche and Mühlaupt, 1999; Meneghetti and Qutubuddin, 2006), glass transition temperature (Achilias et al., 2010; Meneghetti and Qutubuddin, 2006) as well as molecular weight of prepared materials increment (Achilias et al., 2010). However, industrial application of published results is limited due to several technical shortcomings. Basically, scaling-up of sophisticated dispersion methods of o-Mt in polymerization system seems to be too expensive and difficult to realize. Moreover, the main parameters of investigated MMA/o-Mt polymerization process usually do not correspond with these applied in industrial practice. Whereas emulsion, suspension and solution-type MMA polymerization techniques are easily controllable, the manufacturing technology of non-defected large sized PMMA panels via bulk process is generally difficult to realize and sometimes proprietary. Nevertheless, the investigation on the most important feature of poly(methyl

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methacrylate), i.e. transparency for visible light has been generally omitted in case of PMMA/o-Mt materials. The o-Mt exfoliation effect is usually analyzed without considering its effect on the optical properties of PMMA/o-Mt composites.

In this work the influence of commercially available organophilic montmorillonite on various properties of poly(methyl methacrylate) has been investigated. The PMMA/o-Mt cast materials have been prepared via bulk free-radical polymerization of either raw monomer or PMMA/MMA syrup containing nanofiller in accordance with the general industrial guidelines for PMMA panel productions. Moreover, the impact of clay mineral predispersing methods in polymerization systems on mechanical and thermal properties as well as transparency of prepared nanocomposites has been evaluated.

## 2. Experimental

### 2.1. Commercial materials

For preparation cast PMMA panels the following components were applied:

- Methyl methacrylate (MMA), purity 99%, containing  $\leq 30$  ppm of hydroquinone monomethyl ether as polymerization inhibitor (Sigma-Aldrich, Germany);
- Granular poly(methyl methacrylate) (Plexpol SC, Heko, Oświęcim, Poland);
- PMMA/MMA syrup prepared by dissolving of Plexpol SC (20 wt. parts) with MMA (80 wt. parts) at room temperature;
- 2,2'-Azobis(isobutyronitrile) (AIBN), purity 98% (Acros Organics, Belgium).

Three commercial organophilic montmorillonites as nanofillers were tested:

- NanoBent ZS1, pulverized montmorillonite modified with proprietary ammonium salt containing aliphatic and aromatic substituents with several hydroxyl groups, particle diameter 50  $\mu\text{m}$  and interlayer spacing 36 Å (Z.G.M. Zębiec S.A., Poland);
- NanoBent ZS3, pulverized montmorillonite modified with proprietary ammonium salt containing long-chain aliphatic substituents, particle diameter 50  $\mu\text{m}$  and interlayer spacing 42 Å (Zębiec, Poland);
- NanoBent ZR1, pulverized montmorillonite modified with quaternary ammonium salt, particle diameter 50  $\mu\text{m}$  and interlayer spacing 19 Å (Zębiec, Poland).

### 2.2. The o-Mt pastes preparation

#### 2.2.1. MMA/o-Mt pastes preparation

Preparation of pastes by mechanical mixing: methyl methacrylate and dry o-Mt were mechanically stirred (100 rpm, 10 min) and stored in a hermetic glass jar for 14 days at room temperature. The MMA/o-Mt pastes (80/20 m/m) have been periodically mixed with spatula.

Preparation of pastes by high-speed homogenization: the MMA/o-Mt paste was diluted with methyl methacrylate and prepared dispersion (noted as H-MMA/o-Mt) containing 2.5 wt. parts of o-Mt/100 wt. parts of MMA was homogenized for 5 min using high-speed homogenizer equipped with a flow chamber (DFK-1, ART Prozess- & Labortechnik GmbH, Germany).

#### 2.2.2. Syrup/o-Mt pastes preparation

Preparation of pastes by mechanical mixing: the PMMA/MMA syrup and dry o-Mt were mechanically stirred (100 rpm, 10 min) and stored in a hermetic glass jar for 14 days at room temperature. The syrup/o-Mt pastes (85/15 m/m; pastes noted as S/o-Mt) have been periodically mixed with spatula.

Preparation of pastes by extrusion: the syrup and dry o-Mt were mechanically premixed (100 rpm, 10 min) and stored in a hermetic

glass jar for 14 days at room temperature. Then, syrup/o-Mt paste (70/30 m/m) was homogenized using co-rotating twin-screw extruder (23 °C, 200 rpm, D = 16 mm, L/D = 40; Prism EuroLab 16, Thermo Electron Corporation, UK). Extruded pastes were noted as SE/o-Mt. In the case of composition containing NanoBent ZR1 (highly viscous system) the prepared paste was diluted with the syrup to final 20 wt.% of o-Mt concentration.

### 2.3. PMMA panels preparation

#### 2.3.1. PMMA and PMMA/o-Mt panels preparation via raw monomer polymerization

Methyl methacrylate (without purification) was prepolymerized (60 °C, 60 min) using AIBN as an initiator (0.65 wt. part/100 wt. parts of MMA) in a glass reactor with mechanical stirrer. Prepolymer has been subsequently poured into a glass mold, heated in water bath for 6 h (at increasing temperature in a range of 35–50 °C) and subsequently in a drier for 18 h (50–120 °C). Next, the glass mold was cooled and the prepared PMMA panel (150 × 220 × 4.5 mm) was released and cut using water-cooled friction saw. In the case of PMMA/o-Mt panels preparation the relevant amount of methyl methacrylate was mixed (150 rpm, 1 h, RT) with either MMA/o-Mt or H-MMA/o-Mt paste before initiator addition. The composition of PMMA/o-Mt nanocomposites prepared via monomer polymerization was presented in Table 1.

#### 2.3.2. PMMA and PMMA/o-Mt panels preparation via PMMA/MMA syrup polymerization

The syrup was prepolymerized (55 °C, 40 min) using AIBN as an initiator (0.5 wt. part/100 wt. parts of MMA) in a glass reactor with mechanical stirrer. Obtained prepolymer was subsequently poured into a glass mold and heated in water bath for 6 h (at increasing temperature in a range of 35–45 °C) and subsequently in a drier for 22 h (45–110 °C). Next, the glass mold was cooled and the prepared PMMA panel (150 × 220 × 4.5 mm) was released and cut using water-cooled friction saw. In the case of PMMA/o-Mt panels preparation the relevant amount of syrup was mixed (150 rpm, 1 h, RT) with either S/o-Mt or SE/o-Mt paste before initiator addition. The composition of PMMA/o-Mt nanocomposites prepared via PMMA/MMA syrup polymerization was presented in Table 2.

### 2.4. Test methods

The tensile and flexural tests of PMMA as well as PMMA/o-Mt samples have been carried out according to the Polish standards PN-EN ISO 527 and PN-EN ISO 178 using Instron 4206-006 apparatus (23 °C, crosshead speed 5 mm/min and 10 mm/min, respectively; Instron Corporation, USA). The hardness of the prepared materials was measured using Barcol hardness tester (23 °C, PN-EN 59). Additionally, thermal and thermochemical features of PMMA-based materials have been investigated as follows: (i) Vicat softening temperature (heating rate 50 °C/h, EN ISO 306, Vicat FWV 633.10, Fritz Heckert GmbH, Germany), (ii) glass transition temperature as a temperature of loss modulus peak (dynamic mechanical analyzer Q800 with dual cantilever clamp, heating range 45–130 °C, heating rate 3 °C/min, 1 Hz frequency, amplitude 25  $\mu\text{m}$ ; TA Instruments, USA), (iii) thermostability, i.e. temperature of 5% mass loss (thermogravimetric analyzer Q500, 45–900 °C, 10 °C/min, air atmosphere; TA Instruments, USA), (iv) oxygen index (according to ISO 4589-2). The transparency of samples was evaluated by UV-Vis spectroscopy tests (Specord M40, Medson, Germany). Efficiency of o-Mt dispersion in polymer matrix was investigated using X-ray diffractometer (Co lamp, 0–12° 2 $\theta$ ; X'Pert Pro, PANalytical) and transmission electron microscope (JEOL JEM 1200ex, Jeol, Japan).

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