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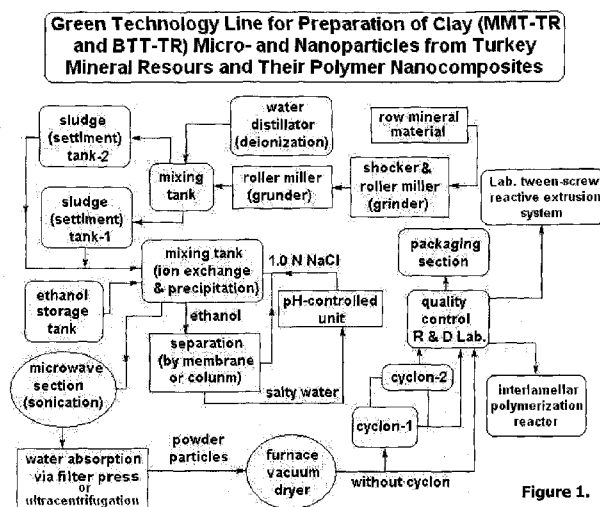


Figure 1.

(57) Abstract: Green technology method is described a combination of prototype processing for the preparation, purification and modification of micro- and nano-size scale clay particles from mineral resources of Turkey using novel functional organic intercalants as reactive nanofillers, alternating copolymers of maleic anhydride and their grafts with biopolymers as reactive compatibilizers and bioactive matrix polymers, thermoplastics, thermosets and rubbers as processible matrix polymers, which are useful for preparation of novel high performance engineering and bioengineering polymer layered silicate nanomaterials (nanofims, nanocoatings, nanofibers, nanomedicals and etc.).

**GREEN TECHNOLOGY LINE FOR PRODUCTION OF CLAY MICRO- AND  
NANOPARTICLES AND THEIR FUNCTIONAL POLYMER NANOHYBRIDS FOR  
NANOENGINEERING AND NANOMEDICINE APPLICATIONS**

### **Field of the Invention**

The present invention relates to the field of inorganic mineral micro- and nanoparticles fabrication, modification and uses. More specifically, the present invention related to green technology line for preparation of micro- and nanoparticles of clays preferably bentonite and montmorillonite like clays from mineral resources of Turkey (BTT-TR and MMT-TR) and their novel functional organic and polymeric derivatives as reactive additives-nanofillers useful for utilization *in situ* polymer/clay processing to improve the important properties (mechanical, thermal, dynamic mechanical and etc.) of thermoplastic, thermoset and elastomer-rubber polymer materials, as well as to prepare novel preintercalated functional organic clays based polymer/biopolymer layered silicate nanomaterials by interlamellar copolymerization and graft copolymerization in the presence of MMT-TR and its various derivatives as catalyst-nanofillers. Another aspect of this invention is use of nanoparticles and their organic derivatives, including reactive biopolymers, for nanoengineering and nanomedical applications.

### **Background of Invention**

It is known that many inorganic mineral micro(nano)particles, especially montmorillonite (MMT), bentonite (BTT) and their organically modified derivatives have a wide range of application areas as nanofillers in reinforced thermoplastic, thermoset and elastomer-rubber polymer nanomaterials such as nanofilms, nanosheets, nanocoatings, nanofibers, nanofoams, and the like, which exhibit suitable flexibility and excellent mechanical strength and in medicine and pharmacy as additives in drug delivery systems, and the like, as well as in food and non-food industry such as food packaging, paint-coating industry, agriculture, industrial wrapping applications, in building industry as heat transfer reducing agents-materials, electrical and electronic material industry and the like.

MMT was discovered in 1847 in Montmorillon in the Vienne prefecture of France, more than 50 years before the discovery of bentonite in the US. It is found in many locations world wide and known by other names [1]. It is used in the oil drilling industry as a component of drilling mud, making the mud slurry viscous which helps in keeping the drill bit cool and

removing drilled solids. It is also used as a soil additive to hold soil water in drought prone soils, to the construction of earthen dams and levees and to prevent the leakage of fluids. It is also used as a component of foundry sand and as a desiccant to remove moisture from air and gases [2].

Similar to many other clays, MMT swells with the addition of water. However, some MMTs expand considerably more than other clays due to water penetrating the interlayer molecular spaces and concomitant adsorption. The amount of expansion is due largely to the type of exchangeable cation contained in the sample. The presence of sodium as the predominant exchangeable cation can result in the clay swelling to several times its original volume. Hence, sodium MMT has come to be used as the major constituent in non-explosive agents for splitting rock in natural stone quarries in order to limit the amount of waste, or for the demolition of concrete structures where the use of explosive charges is unacceptable. This swelling property makes MMT-containing bentonite useful also as an annular seal or plug for water wells and as a protective liner for landfills. Other uses include as an anti-caking agent in animal feed, in paper making to minimize deposit formation and as a retention and drainage aid component. MMT has also been used in cosmetics. MMT is known for its adsorbent qualities and has been used successfully in scientific trials to eliminate atrazine from water [3]. MMT clay is widely used in medicine and pharmacology. For internal use, MMT is effective in the treatment of irritable bowel syndrome. It is also used for the prevention of aflatoxicosis, and in the treatment of constipation. Also, a modified version inhibits intestinal absorption of cholesterol (nanotechnology research), and absorbs uric acid [1]. It is used in agriculture to improve growth performance of piglets and fish [1][3].

MMT is proven to be effective in use as an adsorptive of heavy metals, toxins, and hazardous chemicals[4]. Antibacterial effects of MMT are well demonstrated [5]. It has also shown itself useful for tissue engineering [6][7].

MMT is widely used in pharmacology for a variety of application, such as stabilization of suspensions and emulsions, viscosizing, adhesion to the skin, and tablet making. It is also used as drug carrier, or as part of a drug delivery system, such as for controlled drug release; including for gene delivery, and for drug targeting to specific tissues. It is also used for stability enhancement in drug and nutrient application. There are also other similar uses [1]. MMT is also used in the production of pharmaceuticals, e.g. as a catalyst [8].

MMT and its organic derivatives are widely utilized in polymer nano- technology and nanoengineering processes as effective nano-fillers for preparation of polymer nanocomposites and nanomaterials with higher performance properties (mechanical, barrier, flame retardance, and etc.[USA Patent 2859198; USA Patents 3236802; 3328231; 3471435]. There is much interest in layered, clay-based polymer nanocomposites because of the improved properties exhibited by the nanocomposites. It is desirable to maximize delamination of the clay into individual platelet particles in order to maximize some property improvements, including barrier improvements, and to minimize deleterious effects on some properties including elongation-at-break. Ideally, the clay is exfoliated into particles with size less than about 100 nm in order to achieve clarity that is comparable to the clay-free polymer. To date, the only polymer/clay nanocomposites that meet this expectation are prepared by incorporation of organically treated clays during synthesis of the polymer from monomer.

The earliest patent on the polymerization of vinyl monomer(s) in the presence of clay belongs to Toyota [Kamigaito et al. Patent US 4384989, 1984]. The invention describes synthesis of intercalated clay composites by contacting MMT with a monomer (e.g., styrene, vinyl acetate) at room temperature, then mixing with dichlorodimethyl silane and in a few minutes effecting the polymerization. In the cited example, compositions containing 78 % intercalated clay ( $d_{(001)}$ -spacing = 1.5 nm), were hot pressed into parts that showed high heat, abrasion and flame resistance. This patent is on the borderline between highly filled clay composites and clay polymer nanocomposites.

Another patent [Kawasumi et al., US 4810734, 1989] also used bulk polymerization method, including the following steps: (a) intercalating clay to facilitate its swelling by molten monomer (at  $T > T_m$ ): when poly-methylmethacrylate (PMMA) was to be the matrix, ammonium salt having a terminal vinyl group was used as an intercalant; (b) heating the clay/ monomer mixture at the polymerization temperature 60°C for 5 h; (c) mixing organoclay (5.7%) with a monomer and radical initiator. Mechanical test showed that the modulus of composite was  $E = 568$  GPa, to be compared with  $E = 3.20$  GPa obtained for a composite with non-exfoliated clay. A XRD analysis showed that the polymerization of MMA in the presence of vinyl-terminated MMT clay resulted in exfoliation with  $d_{(001)}$ -spacing = 10.0 nm.

There are many examples in the patent literature of polymer/clay nanocomposites prepared from monomers and treated clays. For example, U.S. Pat. No. 4,739,007 discloses the preparation of Nylon-6/clay nanocomposites from caprolactam and alkyl ammonium-treated

MMT. U.S. Pat. No. 4,889,885 describes the polymerization of various vinyl monomers such as methyl methacrylate and isoprene in the presence of sodium MMT.

Some patents describe the blending of up to 60 weight percent of intercalated clay materials with a wide range of polymers including polyamides, polyesters, polyurethanes, polycarbonates, polyolefins, vinyl polymers, thermosetting resins and the like. Such high loadings with modified clays are impractical and useless with most polymers because the melt viscosity of the blends increases so much that they cannot be molded.

WO 93/04117 discloses a wide range of polymers melt blended with up to 60 weight percent of dispersed platelet particles. WO 93/04118 discloses nanocomposite materials of a melt processable polymer and up to 60 weight percent of a clay that is intercalated with organic onium salts. The use of a mixture of swellable layered clays or a clay mixture intercalated with an onium ion is not contemplated nor disclosed. U.S. Pat. No. 5,552,469 describes the preparation of intercalates derived from certain clays and water soluble polymers such as polyvinyl pyrrolidone, polyvinyl alcohol, and polyacrylic acid. The use of clay mixtures or mixtures intercalated with onium ions is specifically excluded. JP Kokai patent no. 9-176461 discloses polyester bottles wherein the polyester contains unmodified sodium MMT. Incorporation of the clay into the polyester by melt compounding is disclosed; however the use of clay mixtures or clays intercalated with onium ions was neither contemplated nor disclosed.

Clays intercalated with a mixture of onium ions are used as rheology modifiers for certain coating applications; however, their use in polymer/clay nanocomposites has been neither contemplated nor disclosed. The following references are of interest with regard to chemically modified organoclay materials: US Pat. Nos. 4,472,538; 4,546,126; 4,676,929; 4,739,007; 4,777,206; 4,810,734; 4,889,885; 4,894,411, 5,091,462, 5,102,948; 5,153,062; 5,164,440; 5,164,460; 5,248,720; 5,382,650; 5,385,776; 5,414,042; 5,552,469; WO Patent Application Nos. 93/04117; 93/04118; 93/11190; 94/11430; 95/06090; 95/14733; D. J. Greenland, J. Colloid Sci. 18, 647 (1963); Y. Sugahara et al., J. Ceramic Society of Japan 100, 413 (1992); P. B. Massersmith et al., J. Polymer Sci. Polymer Chem., 33, 1047 (1995); C. O. Sriakhi et al., J. Mater. Chem. 6, 103(1996). herefore, as shown above, a need exists for polymer nanocomposites having improved properties.

Patent US 6,391,449, 2002 invention related to polymer-clay nano- composites and methods of fabrication comprising (a) a melt-process able matrix polymer such as poly(ethylene

terephthalate) (PET), and incorporated therein (b) a mixture of at least to layered clay materials such as MMT clay and its various alkyl ammonium intercalated derivatives. This invention also related to articles produced from a nanocomposites and a process for preparing a nanocomposites. However, this invention comprises use of higher loading of clays and organoclays as well as mixtures of different clays to prepare only polyester (PET) based nanocomposites. In this systems, the mixture of micro- and nanostructures may be formed, which will be significantly decreased the engineering performance of prepared composites. In generally, these composites have a limited application areas.

Another US patent 10291141, 2002 describes preparation of clay/polymer nanocomposites by suspension polymerization of monomer(s) in the presence of hydrophobically modified clay, dispersed within the monomer phase. The applications of the resulting nanicomposite range from coatings, sealants, caulks, adhesives, binders, traffic paints, to plastics additives. Another patent from this series describes preparation of an aqueousnanocomposite dispersion [Lorah and Slone, 2002; patent US 2005580]. The goal of this invention is to protect modifications of the process with additional using a multivalent cation (Ca, Mg, Cu, Fe or Zr), which may improve the physical properties of clay/polymer nanocomposite via formation of strongly bended clay-polymer matrix.

It is also well known that the amount of clay that can be admixed in a polymer and still exhibit exfoliation of the layered clay is limited and some mechanical properties, such as elongation-at-break, are often reduced considerably upon the addition of the clay. Researchers recognized the value of inventing melt compounding processes that provide exfoliated polymer/platelet particle composites, namely more versatility of polymer choice and clay loading, and the potential for cost savings. However, with polymer/clay mixtures, the melt compounding processes explored to date do not provide sufficient exfoliation of the platelet particles. Because many academic and industrial researchers preferred use of polymer / organoclay / functionalized (co)polymer-compatibilizer ternary systems to prepare predominantly *in situ* exfoliated nanostructures [9-11] [Z.M.O. Rzayev, 2011] using industrial organic MMT clays.

Composition and formulation of the layered silicate minerals strongly depend on the origin, geographic location, country and geophysical parameters of mineral welds, and therefore, different methods of their isolation and purification were utilized by many manufacturers from various countries (USA, Kanada, France, Germany, England, China,

Japan, etc.). The results of geophysical and geochemical investigations of many Turkish researchers [12-16] were confirmed the presence of the mineral resources riched with layered smectite clay group. However, in the present time there are not global strategy for the uses of these resources for the industrial production and utilization for the nanoengineering and nanomedicine applications. Moreover, to serve a need on nanofillers, especially MMT-TR and organo-MMT-TR clays as renouncing nanoadditives for polymer nanotechnology many Turkish industrial sectors such as plastics, packaging materials, paints, coatings, foams, etc., were exported the nanofillers and organo-nanofillers from various Firms-Manufactures (Aldrich-Sigma) through foreign trade.

Early patent publications of the manufacturers from various countries (USA, Kanada, France, China, Japan, etc.) described the processing for the isolation and purification of smectite clay group, including bentonite and MMT clays, taking into consideration geophysical parameters of mineral welds locating in each country. However, prepared clays (predominantly mixtures of clays) and their properties, especially purifying degree, Zeta size and Zeta-potential parameters almost can not satisfied the requests of modern polymer nanoscience, nanoengineering and nanomedicine.

The patent invention CN1369432A relates to nanocrystalline powder material preparation method, especially relate to one kind 2:1 type stratiform montmorillonite mineral preparations of nanomaterials method .To prepare a powder nanometer MMT clay, this invention claimed a use of multicomponent system such as mixture of metatitatic acid butyl ether, alcohol (etanol, propyl alcohol or butanol), inorganic acids (hydrochloride acid or nitric acid) and powder MMT and two steps of reaction. After filtration, separation and washing processing of final product, many waste products were formed, purification of which is technologically difficult. From claim of this invention, a role of used row metatitanic acid is not explained. One the other hand, prepared MMT clay has average grain diameter 380 nm and the specific surface area of nanometer montmorillonite powder is 200-410 m<sup>2</sup>/G. These particle parameters are higher as compared with MMT-TR clay particles of present invention (Fig. 4 and 5) which shown 286.5 and 373.1 nm for BTT (bentonite)-TR and 342.2 and 229.4 nm for MMT-TR in CHCl<sub>3</sub> and water solutions, respectively. All processing in the present invention were realized at room temperature unlike above mention Chine patent invention (temperature control (20-70°C or 30-70°C at long time reactions 4-10 h, preferable 5-8 h). Moreover, this Chine invention disclosed the chemical processing for preparation of nanometer MMT clay (but no at nanoscale 0.1-100

nm) while the present invention only consisted the physical processing for preparation of MMT-TR clay. This Chine patent invention claimed a use microwave-irradiation for disinfection-activation of MMT clay while present invention disclosed a use of microwave sonication of MMT-TR particles for the reduction of size, and therefore, significantly increasing in surface area of particles which allow future prepare polymer layered silicate nanohybrids or nanocomposites with "core-shell" morphology and nanoscale (0.1-100 nm) particle size ( 85-100 nm, Fig. 8, TEM images).

### **Summary of The Invention**

As evident from the above described patent publications, many industrial MMT clays exhibit different compositions, especially different contents of Na, K, Ca, Mg, Si and Al elements and their ratios in clay,  $d$ -spacing values (distance between 1:2 silicate layers) and water content in this area, as well as different particle parameters, especially higher zeta-size (from 2000 to 6000 nm) and lower values of zeta-potential ( $>>70$  mV). Other disadvantages of these known clays are lower purification degree which essentially limited their applications, especially in medicine and bioengineering applications.

Advantages of the present invention:

1. Geographic location of mineral clays in Turkey were obtained.
2. A green technology line for production of clay (BTT-TR and MMT-TR) micro- and nanoparticles (Figures 1 and 2) and their novel organic derivatives useful for polymer nanoengineering and nanomedicine applications was disclosed.
3. This prototype technology line includes the following different physical processing steps:
  - (a) Double granulation-milling processes for raw mineral material,
  - (b) Microwave-sonication process for the preparation of micro- and nanoparticles,
  - (c) Press-filter system or ultracentrifuge for the isolation of water/ethanol mixture,
  - (d) Membrane separation (or distillation column) of ethanol from water/ethanol mixture,



- (e) Recyclic line for isolated ethanol, water and salt water with pH control unit,
- (g) Double cyclon units for preparation and selection of particles with area-size around 240-270 nm and higher Zeta-potential around 72-103 mV.

It is an object of the present invention to design green technology line and prepare micro- and nanoparticles and their organic and novel polymer layered silicate nanocomposites having advantageous properties as compared with known and commercial clays and nanocomposites. Technology line also consists (i) a reactor for preparation novel reactive and non-reactive organic derivatives of MMT-TR clay, for synthesis novel functional (co)polymers/organo-MMT-TR nanohybrids by interlamellar radical and controlled/living (co)terpolymerization, preferable radical arrangement-fragmentation and chain termination (RAFT) copolymerization of preintercalated monomer...organo-MMT-TR or terminating RAFT-agent...organo-MMT-TR complexes with various vinyl and acrylic monomers; (ii) Lab. reactive extrusion system for preparation of a wide range of new generation of the polymer (thermoplastics, thermosets, rubbers and biopolymers)/organo-MMT-TR clay nanocomposites and nanomaterials (nanofilms, nanofibers, nanocoatings by in-line nanocoating method and the like).

This invention will causes to future Turkey industrial fabrication of BTT-TR and MMT-TR clays, their novel organic derivatives and polymer/organoclay hybrids, nanocomposites and nanomaterials with high performance parameters, especially Zheta-size (around 240-350 nm) and zheta-potential ( $> 70$  mV) for a wide range of polymer nanoengineering and nanomedicine applications.

This invention discloses an utilization of mineral clay from resource of various regions in Turkey such as Niğde-Dikiltaş, Ordu-Ünye, Tokat-Reşadiye, and etc.) which provides an independence of many Turkich industrial sectors from foreign firms on the nanofillers and organo-nanofillers, as well as causes significantly development of the polymer nanotechnology, nanoengineering and nanomedicine, paint, coating, building, and other industrial sectors.

Another aspects of the present invention are: (1) use of row mineral materials from different geophysical region of Turkey riches with mixtures of smectite clays, which are marked as BTT-TR and MMT-TR and significantly differ from conventional like clays by their purification degree, particle and composition parameters; (2) production technology line comprises green and recycling processes using deionized water as a medium at room temperature; (3) production technology line contains a combination of effective milling, microwave-sonication and purification processing; (4) production technology line permits the preparation of high performance of micro- and nanoparticles useful for a wide range of utilization in modern polymer nanotechnology and nano-engineering areas; (5) this invention discloses synthetic pathways for the preparation of a new generation of organic-polymeric derivatives of clay nanoparticles and their polymer/biopolymer layered silicate nanocomposites for the polymer nano-engineering, bioengineering and nanomedicine applications.

The present invention as compared with known patent inventions consists the following new approaches and advantageous:

1. New generation of preintercalated terminating agent (RAFT)...Organo-MMT-TR clay complexes for the synthesis of functional polymer layered silicate nanocomposites and their nanoengineering and bioengineering applications.
2. Novel preintercalated functional monomer...Organo-MMT-TR complexes for the synthesis polymer/organoclay hybrids via interlamellar copolymerization in bulk and/or in aqueous medium.
3. End trithiazolecarbonate functionalized oligomers/Organo-MMT-TR nanoparticles as selective anticancer agents.
4. Smart (co)terpolymer/Organo-MMT-TR nanohybrids through microwave-assisted copolymerization for nanomedicine applicatins.
5. Novel polymer/dual functional copolymer-reactive compatibilizers/Organo-MMT-TR clay nanopcomposites as high performance of nanoengineering materials via reactive extrusion system.
6. Novel polymer/compatibilizer/O-MMT-TR nanofilms, nanocoatings and nanofibers for a wide range of industrial and specific applications.
7. Biodegradable biopolymer/thermoplastics/organoclay nanocomposites and nanomaterials.

8. Self-catalytic green process for preparation of functional copolymer-*g*-polylactic acid (PLA) nanocomposites in the presence of specific metal salts of MMT-TR clays and organo-MMT-TR clays with dual functions as catalyst-nanofillers.
9. Synthesis of a new generation of functional copolymer/organo-MMT-TR nanohybrids with 'core-shell' morphology (by TEM analysis, Fig. 8) and high performance engineering properties.

This invention disclosed a novel prototype periodical green technology processing for preparation of micro- and nanoparticles of clays titled as BTT-TR and MMT-TR and their novel organic-polymeric intercalated derivatives and new generation of polymer layered silicate nanocomposites for nano- and bioengineering applications.

### **Brief Description of Figures**

**Fig. 1.** Green Technology Line for Preparation of Clay (MMT-TR and BTT-TR) Micro and Nanoparticles from Turkey Mineral Resource and Their Polymer NANocomposites

**Fig. 2.** Detailed General Scheme

**Fig. 3.** SEM images (surface morphology with scale 1.0 and 10  $\mu\text{m}$ , x10.000 and x1000 magnification) of BTT-TR (left) and sodium MMT-TR ( $\text{Na}^+$ -MMT-TR) (right) fabricated from mineral field of Ordu-Üniye (Turkey) using above mention technology line (Figures 1 and 2)

**Fig. 4.** Particle parameters of BTT-TR and MMT-TR clays

**Fig. 5.** Particle parameters of BTT-TR and MMT-TR clays

**Fig. 6.** Particle parameters of known MMT clay (K-10)

**Fig 7.** X-Ray Diffraction Patterns of (1) bentonite (BTT-TR), (2)  $\text{Na}^+$ -MMT-TR and (3) known MMT clay (from Aldrich-Sigma, Germany)

**Fig. 8.** TEM 'core-shell' morphology images of MMT-TR clay based copolymer-*g*-biopolymer micro- and nano-nanoparticles

**Fig. 9.** Synthetic pathways of preintercalated RAFT agent (S-1-dodecyl-S-( $\alpha,\alpha'$ -dimethyl)- $\alpha''$ -acetic acid) through interlamellar complex-formation of non-reactive DMDA-MMT-TR and RAFT agent (A) and interlamellar amidization of reactive ODA-MMT-TR with RAFT agent (B) as a new generation of RAFT-agent-nanofillers

**Fig. 10.** TEM micrographs of high resolution lattice images of terpolymer/ODA-MMT clay nanocomposite

### Detailed Description of the Invention

This invention disclosed synthesis of a new generation of preintercalated radical arrangement-fragmentation chain termination (RAFT) agents (Figure 5), preferable mono- and dicarboxyl-containing trithiocarbonates such as *S*-1-dodecyl-*S*-( $\alpha, \alpha'$ -dimethyl- $\alpha''$ -acetic acid) and *S, S*-bis( $\alpha, \alpha'$ -dimethyl- $\alpha''$ -acetic acid) trithiocarbonates which are known as RAFT-1 and RAFT-2 agents, respectively, through physical (A) and chemical (B) *in situ* modification of organic derivatives of Na<sup>+</sup>-MMT-TR (dimethyldidodecyl ammonium cation, DMDA and octadecyl amine, ODA as non-reactive and reactive surfactant-intercalants, respectively). These novel RAFT agents/MMT-TR hybrids exhibit dual functions such as conventional chain terminating agents and as nanofillers useful for a widely utilization in interlamellar controlled/living RAFT (co)polymerization of vinyl, allyl, acrylic, strenic, and the like monomers for the preparation (co)polymer silicate layered nanocomposites. Another aspect of this invention is use of these RAFT-agents/MMT-TR hybrids and their (co)polymer layered silicate nanocomposites for bioengineering (novel controlled drug delivery systems, enzyme carriers, the like) and nanomedicine (antimicrobial and selective anticancer agents, and the like) applications.

This invention disclosed synthesis of a new generation of functional copolymer-*g*-biopolymer layered silicate nanocomposites through interlamellar bulk graft copolymerization of lactic acid (or lactides, oligopeptides, DNA, Chitosan, carboxyl-functionalized polysaccharides, and like) onto maleic anhydride (MA)-containing homopolymer, random and alternating copolymers, graft copolymers (Polyolefins-*g*-MA, other thermoplastics-*g*-MA, rubber-*g*-MA and the like), preferable alternating (co)terpolymer of maleic anhydride(MA) [poly(MA-*alt*- $\alpha$ -olefins<sub>C<sub>2-18</sub></sub>), poly(MA-*alt*-alkyl vinyl ether), poly(MA-*alt*-dihyropyran-co-*N*-isopropyl acrylamide), poly(MA-*alt*-2-vinyl pyrrolidone), and the like as matrix polymers in the presence of MMT-TRs (Na<sup>+</sup>-MMT-TR, Ag<sup>+</sup>-MMT-TR, ODA-MMT-TR, DMDA-MMT-TR, and the like) as nanofiller-catalyst without use of hazardous tin-containing catalysts. This disclosed method is significantly differ from known method of graft copolymerization of lactic acid which is provide the following advantages: (1) this method includes *in situ* self-catalysis process, (2) Synthesis procedure was realized at relatively lower temperature (60-80°C) and reaction time (35-50 min) as compared

with known high temperature (120°C) catalytic graft copolymerization (with 3-6 h of reaction time), (3) grafting and graft copolymerization reactions occur between silicate galleries in nano-scale, (4) the formation of nanohybrid composites produced through in situ interfacial complex-formation (physical interaction) or amidization (chemical interaction), and in situ full exfoliation processing. This invention also disclosed the preparation of biodegradable thermoplastic nanocomposites with high performance properties for a wide range of industrial and medical applications.

A novel carboxyl-trithiocarbonate functionalized polymer with super-selective antitumor activity was synthesized by a Reversible Addition-Fragmentation Chain Transfer (RAFT) controlled/living intercalated polymerization of maleic anhydride (MA) with benzoyl peroxide as an initiator and preintercalated S-1-dodecyl-S-( $\alpha,\alpha'$ -dimethyl- $\alpha''$ -acetic acid) trithiocarbonate/ODA-MMT-TR as a RAFT agent-nanofiller and with the aim to design and synthesize an effective anticancer agent with minimum or without side effects. The structure, molecular weights and composition of synthesized multifunctional polymer were investigated by  $^1\text{H}$  ( $^{13}\text{C}$ ) NMR, MTDI-TOF-MAS and GPC analyses, respectively. It was demonstrated that RAFT polymerization of MA accompanied with partially controlled decarboxylation of anhydride units and formation of conjugated double bond fragments in backbone macromolecular chains. The mechanism of interaction of pristine RAFT agent and PMA-RAFT polymer/ODA-MMT-TR nanocomposite with cancer (HeLa human cervix carcinoma) and normal (L929 Fibroblast) cells were investigated by using a combination of chemical, biochemical, statistical, spectroscopy (SEM and Fluorescence Inverted Microscope) and Real-Time Analysis (RTCA) methods. Agreeing with these results, PMA-RAFT/ODA-MMT-TR exhibits higher and selective cytotoxicity, apoptotic and necrotic effects towards HeLa cells at relatively lower concentration (around  $7.5\text{-}75\ \mu\text{g.mL}^{-1}$ ,  $\text{IC}_{50} = 11.183\ \mu\text{g.mL}^{-1}$ ) and Fibroblast cells at high concentration ( $\text{IC}_{50} > 100\ \mu\text{g.mL}^{-1}$ ). The observed higher selective antitumor activity of PMA-RAFT polymer/organoclay nanosystem useful for the future utilization in cancer chemotherapy.

Another aspect of this invention is preparation of novel smart bioengineering functional copolymer silicate layered nanocomposites by microwave-assisted (500 W) interlamellar copolymerization of *N*-isopropyl acrylamide (NIPAm,  $M_1$ ) with maleic anhydride (MA,  $M_2$ ) and terpolymerization of NIPAm with equimolar mixture of MA/dihydropyran ( $M_3$ ) comonomers in the presence of organoclay (ODA-MMT-TR).

The following Examples of the present invention for preparation of micro- and nanoparticles and their novell polymer layered silicate nanocomposites are illustrated.

### **Example 1**

Preparation of BTT-TR (bentonite-TR) and MMT-TR ( $\text{Na}^+$ -MMT-TR) clays from mineral resources of various regions in Turkey includes a combination of effective milling, isolation, purification, microwawe-sonication, centrifugation or water-absorption via filter press, drying under vacuum at  $100^\circ\text{C}$  and particle separation cyclones, as well as recycling lines to utilize water/ethanol and salt water. This prototype processing provides effective isolation of BTT-TR and its richen with Na-cation derivative ( $\text{Na}^+$ -MMT-TR) via ion exchane reactions using 0.5-1.0 M NaCl (or  $\text{NaCO}_3$ ), preferable 0.75 M water solution. Some particle parameters of BTT-TR and MMT-TR clays were presented in Tables of Figures 4-6, and SEM images and XRD patterns were illustrated in Figures 3 and 4, respectively. For the comparative analysis, these results also contained above mention analysis results for a known commercial  $\text{Na}^+$ -MMT (K-10) clay (Figure 6).

### **Example 2**

$\text{Ag}^+$ - and organic derivatives of  $\text{Na}^+$ -MMT-TR were prepared by using known intercalation via ion exchange reactions using  $\text{AgNO}_3$ , octadecyl amine or amide (ODA) as reactive intercalant and dimethydidodecyl ammonium bromide (DMDA) as non-reactive intercalant in deionized water solutions. These inorganic and organic derivatives of MMT-TR clay were isolated by evaporation and presipitation with ethanol, drying under vacuum at  $60^\circ\text{C}$ .

### **Example 3**

Intercalated RAFT agents were prepared by the following synthesis procedure:  $\text{Na}^+$ -MMT-TR, ODA-MMT-TR or DMDA-MMT-TR was dispersed in acetone (or methyl ethyl ketone (MEK) or deionized water) solution of RAFT (radical arrangement-fragmentation chain transfer) agents with intensive mixing at room temperature up to formation homogenous viscose system. Than intercalated product was isolated by evaporation or precipitation by ethanol and ultracentrifugation, draying under vacuum at  $60^\circ\text{C}$ . Physical and chemical structures of

synthesized intercalated RAFT agents were confirmed by FTIR,  $^1\text{H}$  NMR, XRD and SEM-TEM morphology analyses.

#### Example 4

Synthesis of polymer layered silicate nanocomposites were carried out by interlamellar controlled/living (co)polymerization of maleic anhydride (MA) and butyl methacrylate (BMA) in the presence of RAFT...ODA-MMT-TR (complex or amide form) or RAFT...DMDA-MMT-TR as a reactive or non-reactive nanofiller-terminating agent, respectively, and a radical initiator (AIBN) under a nitrogen atmosphere at 65°C in MEK or 1,4-dioxane solution.

#### Example 5

Partially decarboxylated oligo(maleic anhydride) OMA-RAFT-1/ODA-MMT-TR silicate layered nanocomposite was synthesized by controlled/living RAFT heterogeneous polymerization of MA monomer in toluene under a nitrogen atmosphere in the presence of BP as a radical initiator and preintercalated RAFT agent...ODA-MMT-TR. Reaction conditions:  $[\text{MA}] = 2.55 \text{ mol.L}^{-1}$ ,  $[\text{BP}] = 2.58 \cdot 10^{-2} \text{ mol.L}^{-1}$ ,  $[\text{RAFT}] = 8.34 \cdot 10^{-3} \text{ mol.L}^{-1}$ , ODA-MMT 3.5 wt % and toluene 10 mL; temperature 80°C, reaction time 24 h. Reaction mixture was cooled in liquid nitrogen and degassed in a round-bottom flask equipped with condenser and magnetically stirring, then refluxed in nitrogen atmosphere during reaction. Precipitation of polymer during reaction was observed which isolated ultracentrifugation, purified by precipitation from acetone solution with toluene and washed with hexane and drying under vacuum at 40°C for 12 h. Antitumor activity (apoptotic and necrotic effects) of the obtained nanocomposite are illustrated in Table 1.

#### Example 6

Synthesis of copolymer-*g*-biopolymer (preferable L-lactic acid (LA) and its isostructural analogs) layered silicate nanocomposites were carried out by self-catalysis interlamellar bulk graft copolymerization of LA monomer onto poly(MA-*a/t*-1-octadecene) or poly(MA-*a/t*-methyl vinyl ether) in the presence of 2.5-5.0 wt.%, preferable 3.2 wt.%) of one of each of  $\text{Na}^+$ -MMT-TR,  $\text{Ag}^+$ -MMT-TR or ODA-MMT-TR or DMDA-MMT-TR as catalyst-nanofillers using reaction mixture containing lactic acid solutions of copolymer and nanofiller at 80°C in a polymerization reactor under vacuum (600 mm/Hg) with intensive mixing up to formation homogeneous viscous liquid phase during 50-70 min, preferable 56 min (up to phase separation).  $\text{Ag}^+$ -MMT-TR clay was synthesized by ion-exchange reaction of  $\text{Na}^+$ -MMT-TR and  $\text{AgNO}_3$  in aqueous medium at 30-50°C for 3 h. Product of reaction was isolated by evaporation, drying under vacuum at

60°C. Above mention polymer/clays nanocomposites were isolated and purified by twice precipitation with ethanol (or deionized water), extraction with ethanol, centrifugation and then drying in vacuum at 60°C up to constant weight. Core-shell morphology images of nanocomposites are presented in Figure 8 (TEM images).

### Example 7

Another aspect of this invention is preparation of novel smart bioengineering functional copolymer silicate layered nanocomposites by microwave-assisted (500 W) interlamellar copolymerization of *N*-isopropyl acrylamide (NIPAm,  $M_1$ ) with maleic anhydride (MA,  $M_2$ ) and terpolymerization of NIPAm with equimolar mixture of MA/dihydropyran ( $M_3$ ) comonomers with given monomer molar ratios ( $M_1:M_2 = 95:5$  and  $M_1:M_2:M_3 = 95:2.5:2.5$ ), in the acetone solution (solvent/monomers weight ratio = 3) in the presence of different amounts of ODA-MMT-TR (around 0.5-5.0 wt %), preferable 2.0 wt %, as a reactive nanofiller and AIBN as a radical initiator (0.2 wt %) at 70°C under nitrogen atmosphere with reaction time 5 min. Yield around 88-95 %. These chosen reaction conditions provide the formation of nanostructural hybrid composition with temperature sensitivity (by DMA and DSC analysis) NIPAm fragments (~92 mol %) in (co)terpolymer chains which easily undergo to coil-globule conformational transition at 32-46°C. TEM core-shell morphology images of these nanocomposites were illustrated in Figure 10.

In Fig. 3, fine dispersed surface morphology was observed for  $\text{Na}^+$ -MMT-TR with particle size around 1.5-3.0  $\mu\text{m}$ .

As seen from this Figs. 4 and 5, average Zeta-size of BTT-TR particles to be 286 and 373 nm measuring in different solutions. These values significantly lower as compared with known industrial bentonite clay (3-10  $\mu\text{m}$ ).

As seen from these particle parameters,  $\text{Na}^+$ -MMT-TR clay exhibits essentially lower average particle size (342 and 229 nm) and narrow particle size distribution as compared with known  $\text{Na}^+$ -MMT (2535 nm) (Figure 6).

As seen from these XRD patterns in Fig. 7,  $\text{Na}^+$ -MMT-TR clay exhibits higher exchange capacity and  $d(001)$ -spacing value (distance between silicate layers) as compared with a known  $\text{Na}^+$ -MMT clay.

This patent invention firstly disclosed the preparation of functional copolymer-*g*-poly(lactic acid) / ODA-MMT organoclay (A and B) or  $\text{Na}$  (or  $\text{Ag}$ )<sup>+</sup>-MMT-TR (C and D) nanohybrid



particles with high self-organized 'core-shell' inner morphology using preferable alternating copolymer of maleic anhydride and  $\alpha$ -olefins, preferable olefin monomers with C<sub>6-18</sub> and self-catalysis interlamellar graft copolymerization method. As seen from these TEM images, polymeric nanoparticles (120-100 nm) were formed by using Na<sup>+</sup> and Ag<sup>+</sup>-MMT-TR as nanofillers-catalyst.

Synthetic pathways of preintercalated RAFT agent (*S*-1-dodecyl-*S*-( $\alpha,\alpha'$ -dimethyl)- $\alpha''$ -acetic acid) through interlamellar complex-formation of non-reactive DMDA-MMT-TR and RAFT agent (A) and interlamellar amidization of reactive ODA-MMT-TR with RAFT agent (B) as a new generation of RAFTagent-nanofillers.

TEM micrographs of high resolution lattice images of terpolymer/ODA-MMT clay nanocomposite (Figure 10) show a self-organization of particles and formation of nanostructural particles with "core-shell" morphology which are predominantly dispersed on nano-size level (around 50-100 nm for the individual particles as shown in Figure 8d).

Antitumor activities of carboxyl-trithiolecarbonate functionalized oligo(maleicanhydride) MA-RAFT/ODA-MMT nanocomposite are summarized in Table 1.

**Table 1.** Apoptotic and necrotic indexes obtained as a result of the interactions of (I) RAFT agent and (II) OMA-RAFT with different ratios in HeLa cell cultures. Statistical differences ( $P < 0.05$ ) for the apoptotic and necrotic activity between (I) and (II) samples were represented the mean  $\pm$  SD.

Amount of RAFT agent and OMA-RAFT/ODA-MMT-TR in a well ( $\mu\text{g.mL}^{-1}$ )	Apoptotic Index (%)		Necrotic Index (%)	
	I	II	I	II
0.0	2 $\pm$ 1	1 $\pm$ 1	3 $\pm$ 1	2 $\pm$ 1
7.5	12 $\pm$ 2	38 $\pm$ 3	21 $\pm$ 2	7 $\pm$ 2
15	20 $\pm$ 2	50 $\pm$ 3	43 $\pm$ 3	18 $\pm$ 3
30	30 $\pm$ 3	65 $\pm$ 3	65 $\pm$ 4	25 $\pm$ 3
50	25 $\pm$ 3	77 $\pm$ 4	74 $\pm$ 3	28 $\pm$ 4
75	13 $\pm$ 2	62 $\pm$ 5	86 $\pm$ 4	47 $\pm$ 5

The observed highly selective antitumor activity of the PMA-RAFT copolymer is related to the presence and distribution of carboxyl and trithiocarbonate groups, which are capable of physical (carboxyl-amine H-bonding) and chemical (trithiocarbonate-amine reaction and termination of free radicals and other reactive species) interactions within a biological environment, as well as its amphiphilic character. These important factors contribute to the inhibition of the cancer cell growth via destruction of supramacromolecular assemblies.

### **Methods of analysis and characterization**

The  $\zeta$ -size and  $\zeta$ -potential parameters of nanoparticles were performed by a Zetasizer 3000HSA (Malvern, UK) using 3 mL of acetone solution of polymer samples with 0.01 g/mL concentration.

Microwave sonication was performed by Lab. SONMAK Ultrasonic Clainer (Falc Instrumeny, Italy) with capacity 4 L, power 400 W, frequency 40kHz and sonication time 15 min.

The surface morphology of nanocomposites was examined using a scanning electron microscope (JSM-6400 JOEL SEM with scale: 1 and 10  $\mu\text{m}$ ,  $\times 10^4$  and an acceleration voltage 20 kV). All specimens were freeze-dried and coated with a thin layer of gold before testing.

The inner morphology of nanoparticles and nanocomposites was performed by transmission electron microscopy (TEM) JEOL JEM-2100F with an acceleration voltage of 200 kV and emission current 146 mA.

Thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses were carried out using a EXTRAR600 TG-DTA6300 and Diamond DSC Perkin Elmer Thermal Analyzers and a linear heating rate of 10°C/min under nitrogen flow. Samples were measured in a sealed alumina pan with a mass of about 10 mg.

Dynamic mechanical analysis (DMA) was performed with Dynamic Mechanic Analyzer (TA Instruments, Q800, USA). Powdered mixtures of polymer nanohybrid and  $\text{Al}_2\text{O}_3$  (50:50 wt %) were loaded into the DMA using powder-holder. The holder was clamped directly into the Analyzer dual cantilever. DMA parameters were measured at a constant frequency of 1 Hz and a heat rate of 3°C  $\text{min}^{-1}$ .

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**CLAIMS**

1. Technology line for preparation of micro- and nanoparticles of bentonite and montmorillonite clays and heir a new generation of intercalated organic derivatives and exfoliated polymer layered silicate nanocomposites characterized in comprising steps of
  - a) Double granulation-milling for raw mineral material,
  - b) Microwave-sonication for the preparation of micro- and nanoparticles,
  - c) Press-filtering or ultracentrifugeing for the isolation of water/ethanol mixture,
  - d) Membrane separation (or distillation column) of ethanol from water/ethanol mixture,
  - e) Recycling for isolated ethanol, water and salt water with pH control unit,
  - f) Double cyclonation for preparation and selection of particles with area-size around 240-270 nm and higher Zeta-potential of 72-103 mV.
2. Technology line according to Claim 1 for preparation of micro- and nanoparticles of bentonite and montmorillonite clays and heir a new generation of intercalated organic derivatives and exfoliated polymer layered silicate nanocomposites characterized in further comprising
  - a) a reactor for preparation novel reactive and non-reactive organic derivatives of montmorillonite clay, for synthesis novel functional (co)polymers/organo-montmorillonite nanohybrids
  - b) reactive extrusion system for preparation of a wide range of new generation of the polymer (thermoplastics, thermosets, rubbers and biopolymers)/organo-montmorillonite clay nanocomposites and nanomaterials
3. Technology line according to Claim 2 wherein reactor for preparation novel reactive and non-reactive organic derivatives of montmorillonite clay, for synthesis novel functional (co)polymers/organo-montmorillonite nanohybrids by interlamellar radical and controlled/living (co)terpolymerization, preferable radical arrangement-fragmentation and chain termination copolymerization of preintercalated monomer...organo-montmorillonite or terminating RAFT-agent...organo-montmorillonite complexes with various vinyl and acrylic monomers.
4. Technology line according to Claim 2 wherein the organic derivatives of montmorillonite clay is produced by using at least one trithiazolecarbonate/octadecylamine and thrithiazole

carbonate/dimethyldidodecyl ammonium cation complexes or trithiazolecarbonate/octadecyl amide as intercalants.

5. Technology line according to Claim 4 wherein the organic derivatives of montmorillonite clay, is produced by using at least one mono- and dicarboxyl-containing trithiocarbonates such as *S*-1-dodecyl-*S*-( $\alpha, \alpha'$ -dimethyl- $\alpha''$ -acetic acid) or *S, S*-bis( $\alpha, \alpha'$ -dimethyl- $\alpha''$ -acetic acid) trithiocarbonates as a terminating and end-functionalizing agent.
6. Technology line according to Claim 4 wherein preintercalated complexes between montmorillonite clay galleries, exhibit dual functions as a chain transfer arrangement-fragmentation and termination agent and a nanofiller in interlamellar radical controlled/living (co)polymerizations.
7. Technology line according to Claim 6 wherein preintercalated complexes between montmorillonite clay galleries used as effective terminating agent and nanofiller for preparation of novel polymer layered silicate nanocomposites by interlamellar controlled/living termination (co)polymerization of maleic anhydride, vinyl, styrenic and acrylic monomers.
8. Technology line according to Claim 7 wherein carboxyl-trithiocarbonate end-functionalized and partially decarboxylated oligo(maleic anhydride)/octadecyl amine-montmorillonite nanocomposite, prepared by interlamellar oligomerization of maleic anhydride in the presence of a preintercalated *S*-1-dodecyl-*S*-( $\alpha, \alpha'$ -dimethyl- $\alpha''$ -acetic acid)/octadecyl amine-montmorillonite complex and benzoyl peroxide in toluene solution at 80°C.
9. Technology line according to Claim 1 wherein intercalated/exfoliated polymer layered silicate nanocomposites exhibiting high performance particle parameters and fine dispersed surface/inner morphology.
10. Technology line according to Claim 1 wherein intercalated/exfoliated polymer layered silicate nanocomposites, are prepared by self-catalysis interlamellar graft copolymerization of lactic acid and its isostructural analogs onto at least one matrix anhydride-functionalized copolymer without use of tin-containing catalysts, in lactic acid/water solution at 80°C under vacuum (600 mm/Hg) for 35-60 min.
11. Technology line according to Claim 1, producing alternating copolymers of maleic anhydride with  $\alpha$ -olefins ( $C_{6-18}$ ), preferable poly(maleic anhydride-*alt*-1-dodecene) or poly(maleic anhydride-*alt*-1-octadecene), with vinyl-2-pyrrolydone and methyl vinyl ether, random copolymer of maleic

anhydride with *N*-isopropylacrylamide, graft copolymer of maleic anhydride with oligopropylene, terpolymers of maleic anhydride

12. Technology line according to Claim 1 producing biopolymers of poly(lactic acid) and its isostructural analogs, chitosan and carboxylated chitosan, oligopeptides, DNA, and the like proteins and polysaccharides.
13. Technology line according to Claim 1 producing montmorillonite clays as nanofillers-catalysts of Na<sup>+</sup>-montmorillonite, Ag<sup>+</sup>-montmorillonite, octadecylamine-montmorillonite, dimethyldidodecyl ammonium-montmorillonite
14. Technology line according to Claim 1 producing polymer layered silicate nanocomposites of smart (pH- and temperature-sensitivity) copolymer as matrix reactive polymer, preferable maleic anhydride-containing random (co)terpolymers such as poly(*N*-isopropyl acrylamide (NIPAm)-*co*-maleic anhydride), copolymer and poly(NIPAm-*co*-(maleic anhydride -*alt*-dihydropyran) terpolymer, poly(*N*-isopropyl acrylamide-*co*-(maleic anhydride-*alt*-dihydropyran) with *N*-isopropyl acrylamide unit contents more than 90 mol % and octadecyl amine-montmorillonite reactive organoclay with contents changed from 0.5 to 5.0 wt %, preferable 2.0 and 5.0 wt %.
15. Technology line according to Claim 1 producing polymer layered silicate nanocomposites of thermoplastics (polyolefins), preferable isotactic polypropylene, and thermo-plastic elastomers (ethylene-*co*-propylene copolymer, poly(ethylene-*co*-propylene-*co*-norbornene terpolymer with different monomer unit ratios, and the like).
16. Technology line according to Claim 1 producing polymer layered silicate nanocomposites of poly(maleic anhydride-*alt*- $\alpha$ -olefins (C<sub>6-18</sub>) and their PEO (Polyethylene oxide) grafted derivatives as reactive compatibilizer (around 5-10 wt. %), preferable using 1-dodecene and 1-octadecene as olefin comonomer in poly(maleic anhydride-*alt*- $\alpha$ -olefin) copolymer as compatibilizer.
17. Technology line according to Claim 1 producing polymer layered silicate nanocomposites of oligopropylene-*g*-maleic anhydride reactive compatibilizer (around 7-15 wt %, preferable 10 wt %).
18. Technology line according to Claim 1 producing polymer layered silicate nanocomposites of functional copolymer-*g*-biopolymer, preferable poly(maleic anhydride-*alt*-1-octadecene)-*g*-poly(lactic acid) as a biodegradable compatibilizer with contents around 3-10 wt %, preferable 5 wt. %.

- 19.** Technology line according to Claim 1 producing polymer layered silicate nanocomposites of montmorillonite clays such as octadecyl amine- montmorillonite as a reactive nanofiller and dimethyldidodecylammonium-montmorillonite as a non-reactive nanofiller loading of which is changes from 2.0 wt % to 7.0 wt %, preferable 3.5-5.0 wt %.
- 20.** Technology line according to Claim 1 producing polymer layered silicate nanocomposites, wherein process of preparation was carried out in melt compounding by a reactive extrusion system donated with milling-granulating, cooling, biaxially oriented film-forming, surface in-line coating, temperature control units.



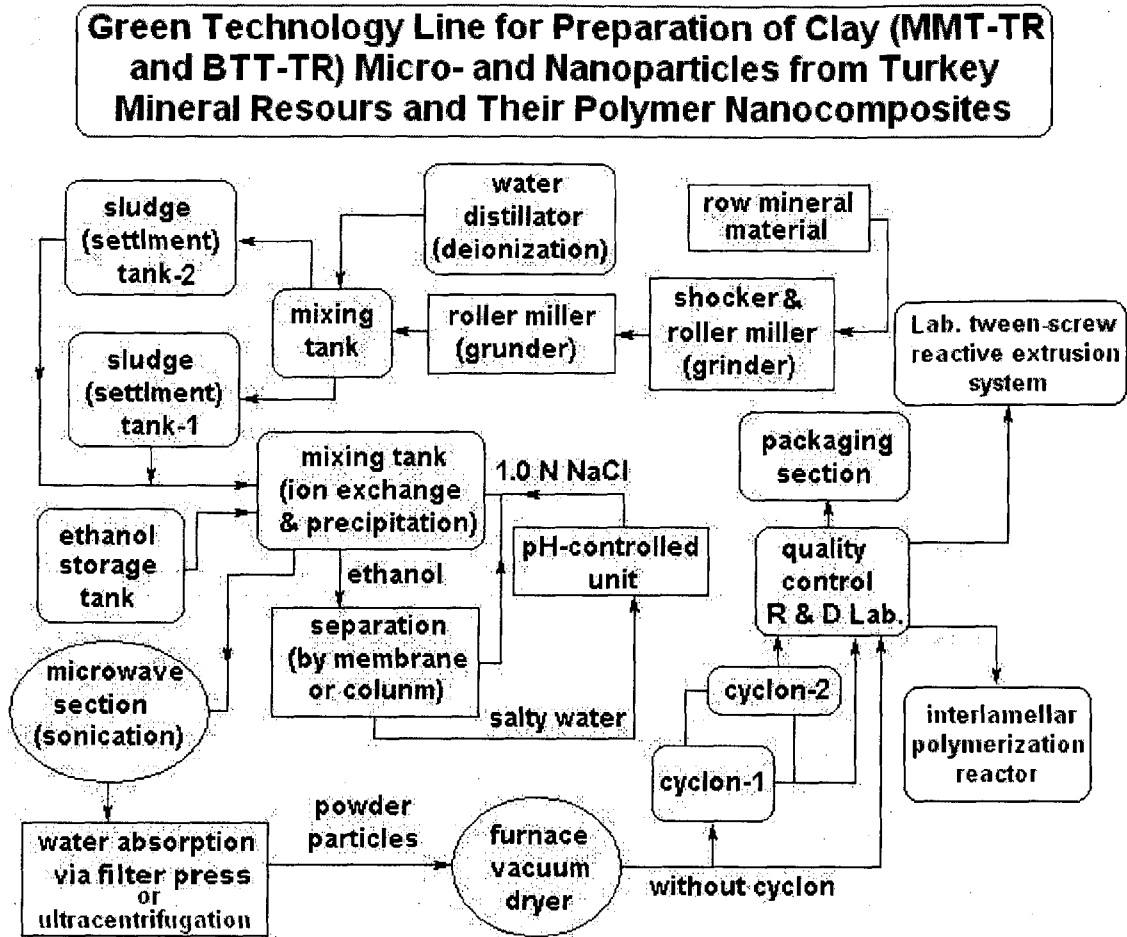
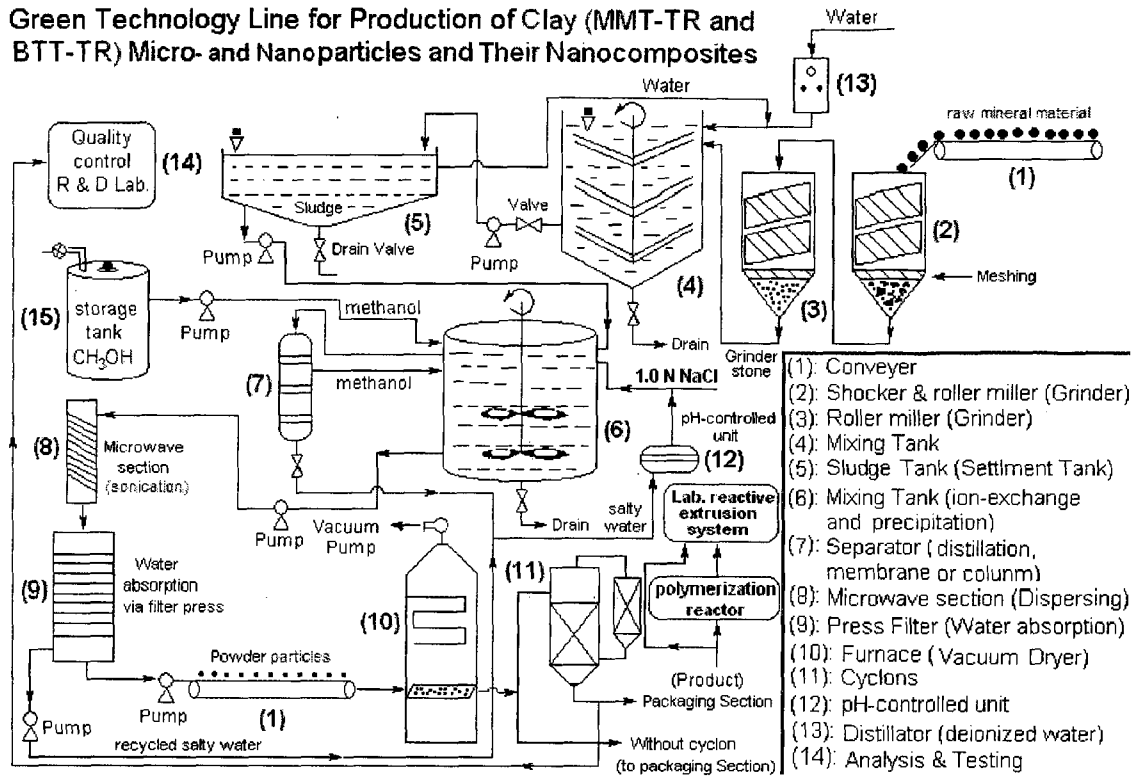
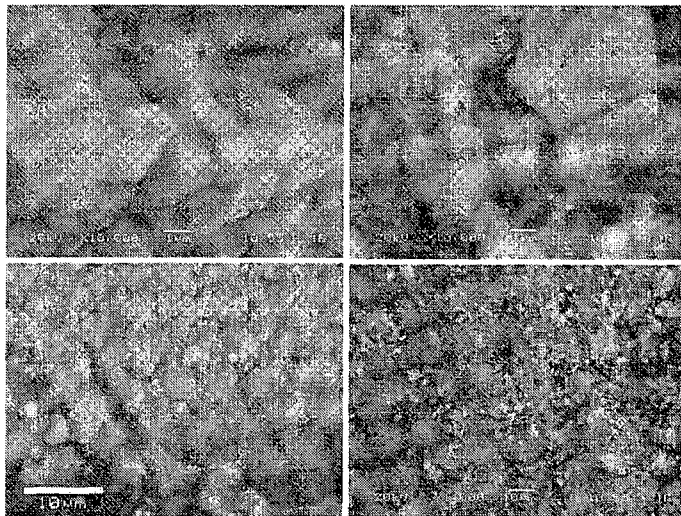


Figure 1.

**Green Technology Line for Production of Clay (MMT-TR and BTT-TR) Micro- and Nanoparticles and Their Nanocomposites**



**Figure 2.**



**Figure 3.**

**Particle parameters of BTT-TR in CHCl<sub>3</sub>**

Size (nm)	Intensity	Volume	Number
20.3	0.0	0.0	0.0
25.5	0.0	0.0	0.0
32.1	0.0	0.0	0.0
40.4	0.0	0.0	0.0
50.9	0.0	0.0	0.0
64.1	0.0	0.0	0.0
80.7	0.0	0.0	0.0
101.6	0.0	12.9	20.3
127.9	46.8	31.0	44.6
161.1	33.1	23.2	28.3
202.8	0.0	5.1	4.0
255.3	0.0	6.9	0.7
321.5	20.1	13.9	1.4
404.8	0.0	6.9	0.7
509.6	0.0	0.0	0.0
641.7	0.0	0.0	0.0
807.9	0.0	0.0	0.0
1017.2	0.0	0.0	0.0
1280.7	0.0	0.0	0.0

Peak Analysis by intensity			
Peak	Area	Mean	Width
1	79.9	141.7	58.6
2	20.1	321.5	74.7

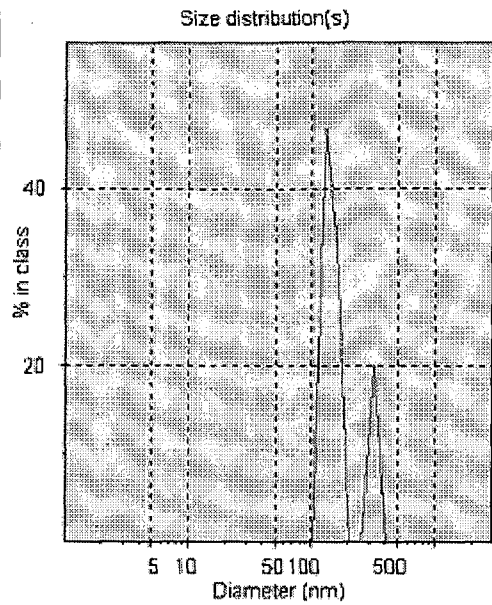
  

Peak Analysis by volume			
Peak	Area	Mean	Width
1	68.7	139.2	73.5
2	31.3	306.6	149.4

Peak Analysis by number			
Peak	Area	Mean	Width
1	97.3	136.0	67.7
2	2.7	325.8	83.3

Rec.Angle	KCounts	ZAve(nm)	Poly.Index	
2	90.0	59.6	286.5	0.945



A

**Particle parameters of BTT-TR in water solution**

Size (nm)	Intensity (Counts)	Volume (%)	Number
16.9	0.0	0.0	0.0
21.3	0.0	0.0	0.0
26.8	0.0	0.0	0.0
33.7	0.0	0.0	0.0
42.4	0.0	0.0	0.0
53.4	0.0	0.0	0.0
67.3	0.0	0.0	0.0
84.7	0.0	0.0	0.0
106.7	0.0	0.0	0.0
134.3	0.0	0.0	0.0
169.1	0.0	0.4	4.4
212.9	7.8	3.3	22.0
268.0	32.3	5.3	30.7
337.5	0.0	2.5	13.1
424.9	0.0	0.5	0.3
534.9	4.4	21.6	7.6
673.5	54.4	42.8	14.4
848.0	1.0	22.7	7.3
1067.7	0.0	1.0	0.2
1344.3	0.0	0.0	0.0
3378.0	0.0	0.0	0.0

Peak Analysis by intensity			
Peak	Area	Mean	Width
1	40.1	257.3	71.1
2	59.9	666.4	164.4

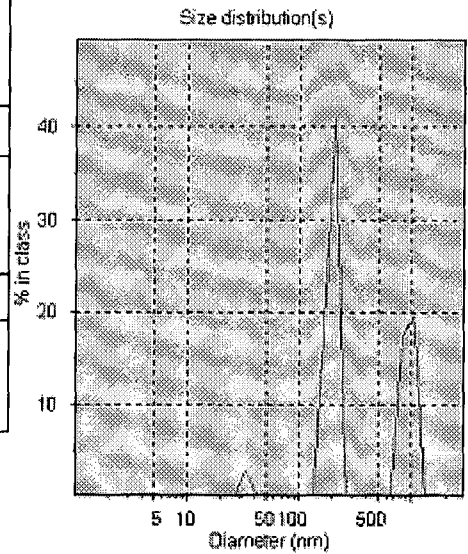
  

Peak Analysis by volume			
Peak	Area	Mean	Width
1	11.9	269.8	129.1
2	88.1	687.6	327.1

Peak Analysis by number			
Peak	Area	Mean	Width
1	70.3	258.2	132.4
2	29.7	680.6	321.9

Rec.Angle	KCounts	ZAve(nm)	Poly.Index	
6	90.0	67.3	373.1	1.000



B

**Figure 4.**

**Particle parameters of Na<sup>+</sup>-MMT-TR in CHCl<sub>3</sub>**

Size (nm)	Intensity	Volume	Number
24.2	0.0	0.0	0.0
30.5	0.0	0.0	0.0
38.4	0.0	0.0	0.0
48.3	0.0	0.0	0.0
60.8	0.0	0.0	0.0
76.6	0.0	0.0	0.0
96.4	0.0	0.0	0.0
121.4	0.0	0.0	0.0
152.8	0.0	0.0	0.0
192.4	0.0	0.0	0.0
242.3	0.0	4.7	24.2
305.0	93.9	9.4	48.3
384.0	0.0	4.7	24.2
483.5	0.0	0.0	0.0
608.8	0.0	0.0	0.0
766.5	0.0	0.0	0.0
965.0	0.0	0.5	0.0
1215.0	2.7	20.8	0.9
1529.8	3.4	40.0	1.6
1926.1	0.0	19.7	0.8
2425.0	0.0	0.0	0.0

Peak Analysis by intensity			
Peak	Area	Mean	Width
1	93.9	305.0	70.9
2	6.1	1390.2	606.0

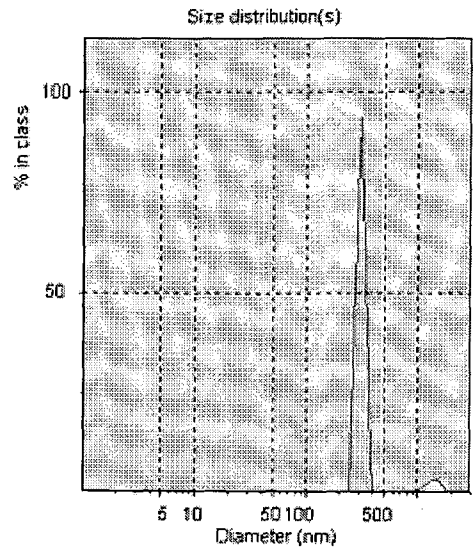
  

Peak Analysis by volume			
Peak	Area	Mean	Width
1	18.9	309.1	141.8
2	81.1	1541.7	715.7

Peak Analysis by number			
Peak	Area	Mean	Width
1	96.6	309.1	141.8
2	3.4	1533.7	720.2

Rec. Angle	KCounts	ZAve(nm)	Poly. Index	
4	90.0	43.9	342.2	1.000



A

**Particle parameters of Na<sup>+</sup>-MMT-TR in water solution**

Size (nm)	Intensity (Counts)	Volume (%)	Number
22.9	0.0	0.0	0.0
28.0	0.0	0.0	0.0
34.2	0.0	0.0	0.0
41.8	0.0	0.0	0.0
51.1	0.0	0.0	0.0
62.4	0.0	0.0	0.0
76.3	0.0	0.0	0.0
93.2	0.0	0.0	0.0
113.8	0.0	0.8	14.4
139.1	19.0	2.0	33.3
169.9	16.7	1.7	23.3
207.5	0.0	0.4	4.4
253.6	0.0	0.0	0.0
309.8	0.0	0.0	0.0
378.4	0.0	0.0	0.0
462.3	0.0	21.4	5.8
564.8	43.0	45.2	11.9
690.0	21.4	26.1	6.5
843.0	0.0	2.4	0.3
1029.8	0.0	0.0	0.0
2294.0	0.0	0.0	0.0

Peak Analysis by intensity			
Peak	Area	Mean	Width
1	35.6	153.5	59.7
2	64.4	606.4	175.7

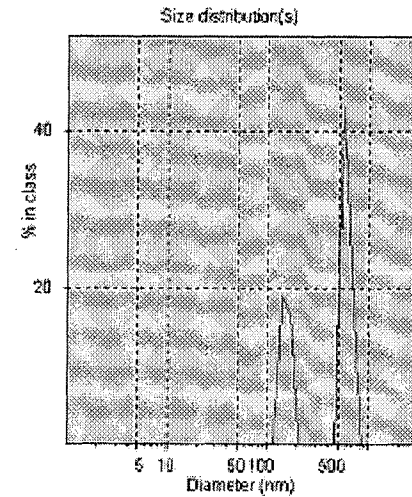
  

Peak Analysis by volume			
Peak	Area	Mean	Width
1	5.0	151.6	71.8
2	95.0	583.0	245.3

Peak Analysis by number			
Peak	Area	Mean	Width
1	75.5	147.8	66.4
2	24.5	577.7	237.8

Rec. Angle	KCounts	ZAve(nm)	Poly. Index	
7	90.0	117.6	229.4	0.766



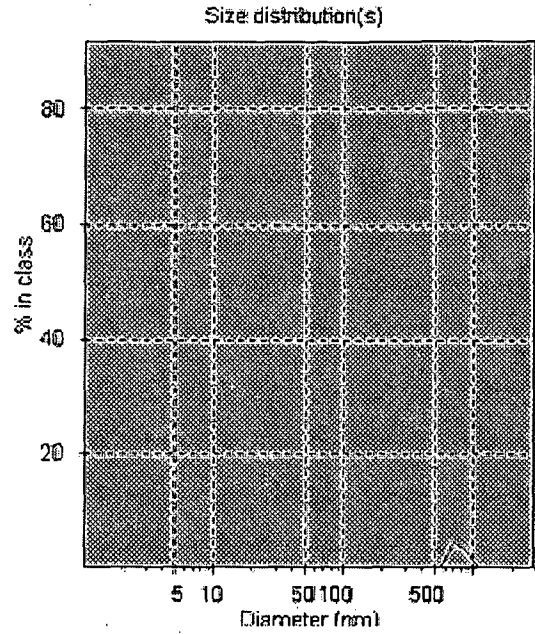
B

**Figure 5.**

**Partilce parameters of known Na<sup>+</sup>-MMT (K-10)**

Size(nm)	Intensity	Volume	Number
179.3	0.0	0.0	0.0
225.7	0.0	0.0	0.0
284.2	0.0	0.0	0.0
357.8	0.0	0.0	0.0
450.5	0.0	0.0	0.0
567.2	0.0	1.9	24.7
714.2	5.0	3.8	49.6
899.2	2.8	2.0	25.3
1132.2	0.0	0.0	0.3
1425.5	0.0	0.0	0.0
1794.7	0.0	0.0	0.0
2259.7	0.0	0.0	0.0
2845.1	0.0	0.0	0.0
3582.1	0.0	0.0	0.0
4510.1	0.0	0.0	0.0
5678.5	0.0	0.0	0.0
7149.6	0.0	0.0	0.0
9001.8	0.0	0.0	0.0
11333.8	0.0	9.6	0.0
14270.0	76.0	32.7	0.0
17966.8	16.2	36.6	0.0

Rec.Angle	KCounts	ZAve(nm)	Poly.Index
2	90.0	31.2	2335.4
			1.000

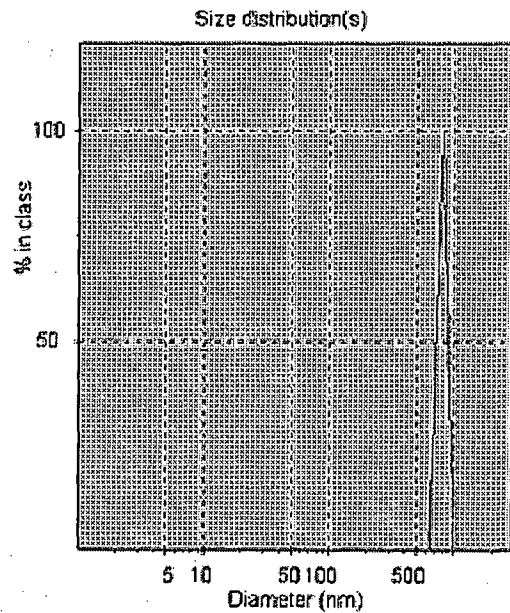


A

**Partilce parameters of known Na<sup>+</sup>-MMT (K-10) after sonication**

Size(nm)	Intensity	Volume	Number
80.1	0.0	0.0	0.0
100.9	0.0	0.0	0.0
127.0	0.0	0.0	0.0
159.9	0.0	0.0	0.0
201.3	0.0	0.0	0.0
253.5	0.0	0.0	0.0
319.2	0.0	0.0	0.0
401.9	0.0	0.0	0.0
506.0	0.0	0.0	0.0
637.0	0.0	25.0	25.0
802.1	100.0	50.0	50.0
1009.9	0.0	25.0	25.0
1271.5	0.0	0.0	0.0
1600.9	0.0	0.0	0.0

Rec.Angle	KCounts	ZAve(nm)	Poly.Index
2	90.0	214.1	1133.2
			1.000



B

Figure 6.

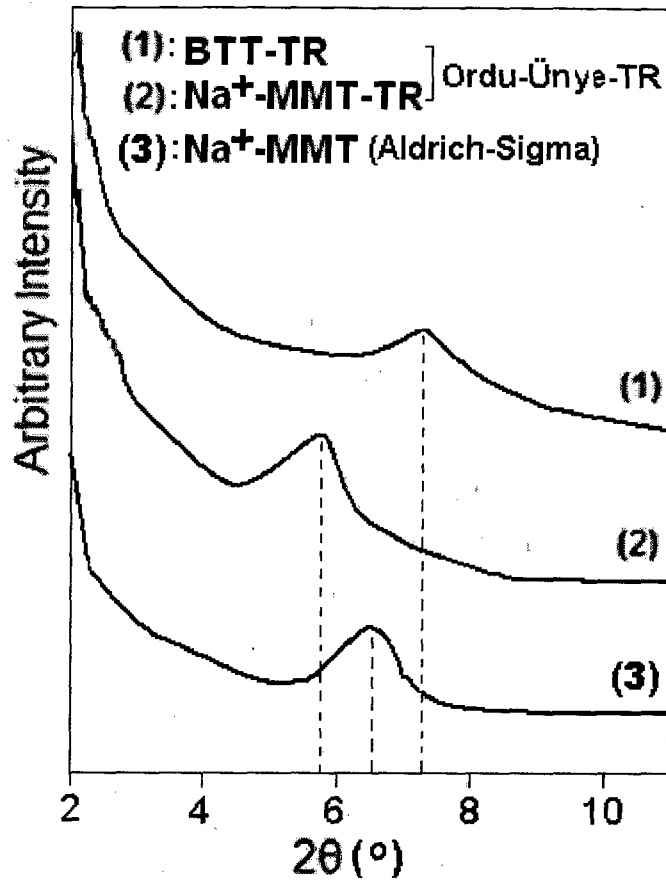
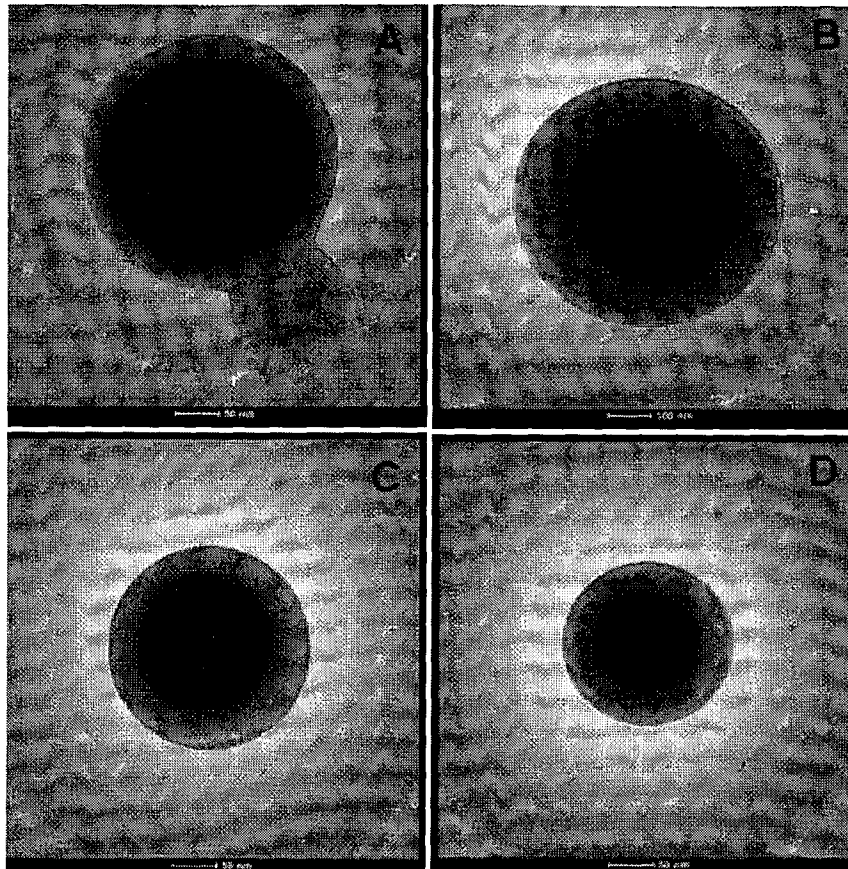


Figure 7.



**Figure 8.**

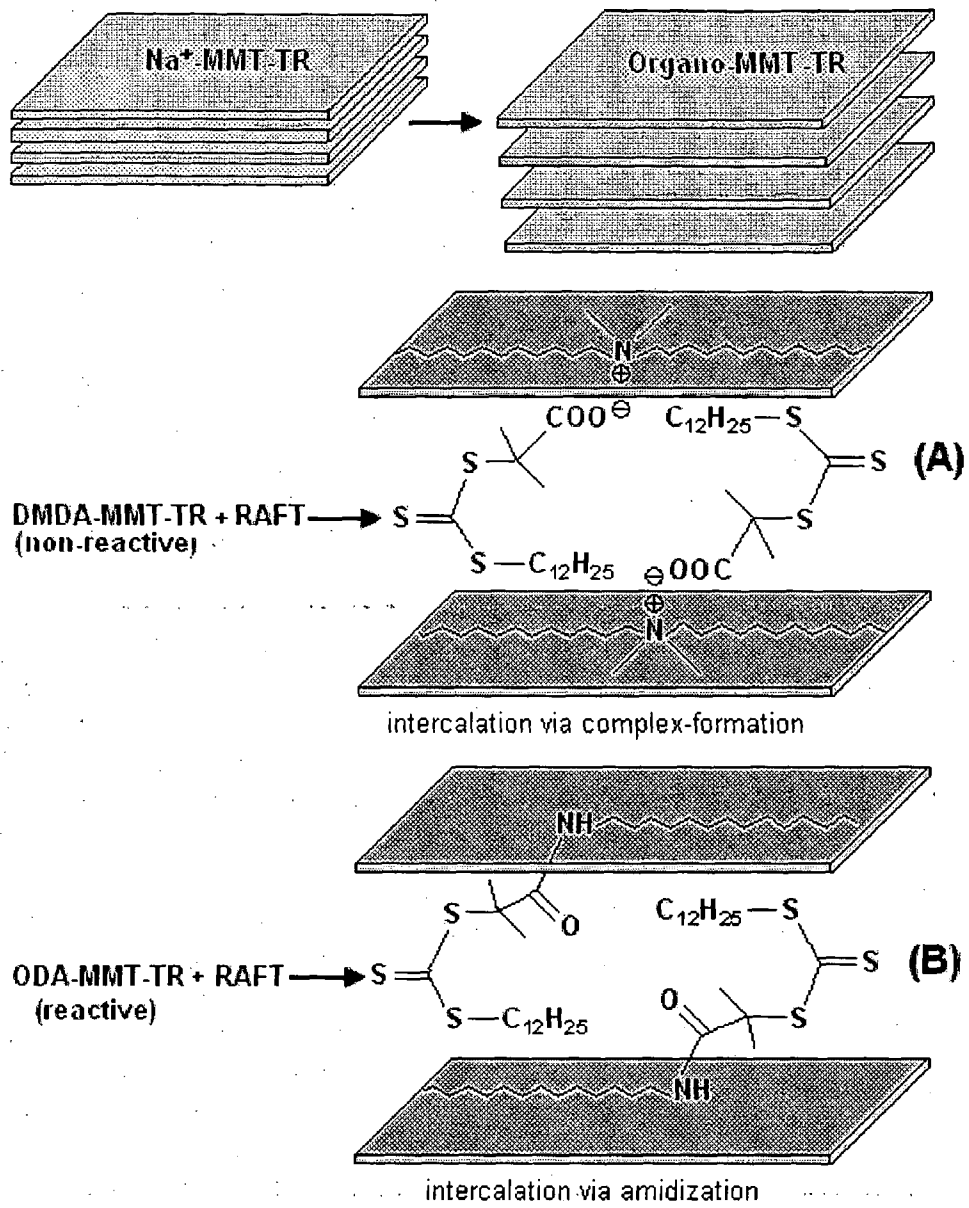
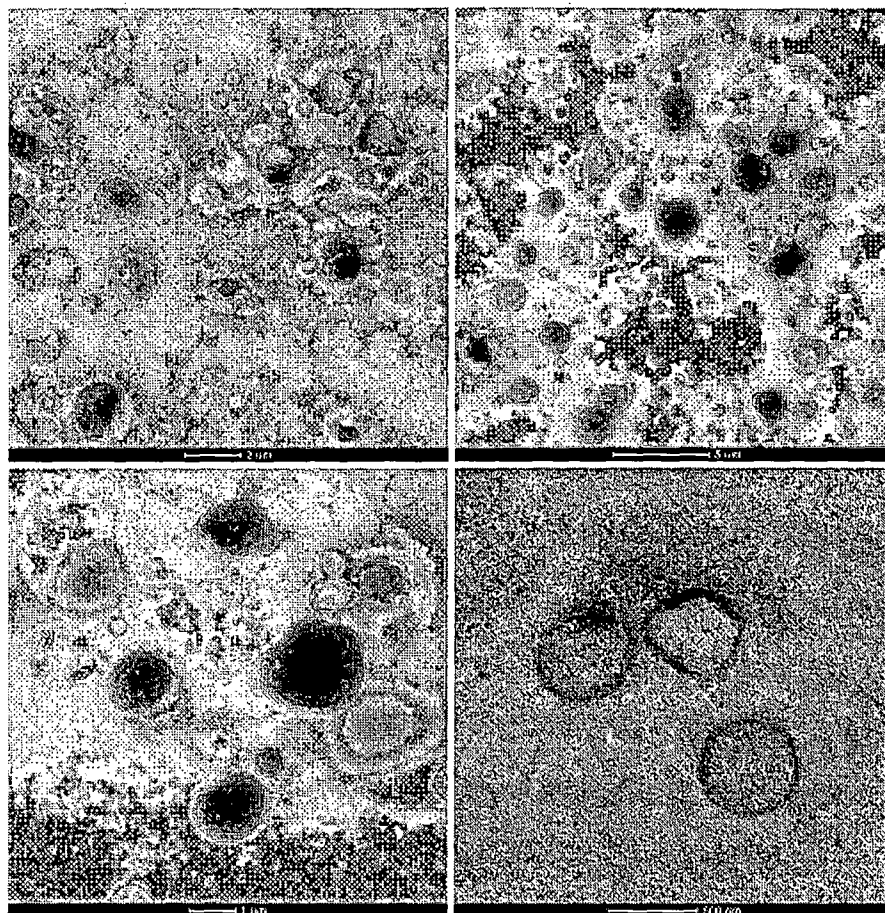


Figure 9.





**Figure 10.**