DEVELOPMENT OF POLY(METHYL METHACRYLATE) PRODUCTS WITH SUPERHYDROPHOBIC SURFACES

BY

NITHIWIT SRIPRASERT

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ENGINEERING (ENGINEERING TECHNOLOGY) SIRINDHORN INTERNATIONAL INSTITUTE OF TECHNOLOGY THAMMASAT UNIVERSITY ACADEMIC YEAR 2016
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A Thesis Presented

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Abstract

DEVELOPMENT OF POLY(METHYL METHACRYLATE) PRODUCTS WITH SUPERHYDROPHOBIC SURFACES

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Bachelor of Science (Biochemistry), Chulalongkorn University, 2010
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Surface’s wettability is one of very important properties of materials, which determines their potential applications. In this regard, superhydrophobic surfaces, i.e., those possess water contact angle (CA) of greater than 150°, show many interesting properties. The materials, therefore, have attracted enormous attentions from both researchers and industries, as these can be used in various applications, for example, self-cleaning windows, containers or plastic pipes with low drag friction, and antibacterial or antifungal containers. Hydrophobicity of surface of plastic materials can be improved by using various methods. In this work, poly(methyl methacrylate) (PMMA) products is employed as substrate. Several techniques, including grafting of Alkyl Ketene Dimer (AKD) as hydrophobic agent on the surface, creating patterned surface roughness, and embedding of nano- and microspheres derived from poly(methyl methacrylate-co-ethylene glycol dimethylacrylate), P(MMA-co-EGDMA) on the surface are investigated. It was found that the introduction of the nanospheres by a spin-coating technique gives superhydrophobic PMMA films with the highest water contact angle of 165°. Properties and performance of the materials and mechanisms of the treatments are examined.

Keywords: Superhydrophobic surface, Alkyl Ketene Dimer (AKD), Nanospheres, P(MMA-co-EGDMA), Poly(methyl methacrylate), Water Contact Angle (CA)
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Chapter 1
Introduction

1.1 Statement of purpose

Over 50 years, global plastic production has increased steadily. In 2013 some of plastic were produced up to 299 million tons, leading to an increase of 4% over 2012. Although plastics are reused and recycled, however, remain insufficient, and millions of tons of plastics end up in landfills and oceans each year (Gaëlle Gourmelon, 2013).

Worldwide plastic production is growing continuously, as its durable, primarily petroleum-based material, and it can replace some materials such as glass and metal. Nowadays, person living in Western Europe or North America consumes 100 kilograms of plastic each year (in average), especially in the form of food or product packaging. While Asia uses just 20 kilograms per person, however this number is forecasted to increase rapidly due to an expansion of economies in the region.

The United Nations Environmental Program shows 22 – 43% of the plastic are used worldwide is discarded in landfill. This waste takes up many valuable spaces, and it disgraces communities. Recovering waste plastic for recycling or for combustion in order to generate power could be alternatives to manage these problems. However, large quantity of the plastic is collected for recycling is transported to countries because their lower environmental regulation or concern. Furthermore, combustion plastic for energy requires controlling of air emission and production of hazardous ash, etc. which are relatively inefficient.

Lots of plastic scraps generate by the United States, Europe, and other countries with the establishment of a collection system are shipped to China, which receives around 56 wt% of total plastic waste imports worldwide. Indirect evidence indicates that most imported plastic will be re-manufactured using the minimum technology, uncontrolled family facilities in the Environment, such as proper disposal of contaminants or waste water. There are also concerns that low-quality plastics can not be reused but disposed or burned for energy in factories without air pollution control. Through its 2010 Green Fence Operation, the Chinese government has start implementing work to decrease the number of unregulated facilities.
Every year, around 10–20 million tons of plastic end at the oceans. A recent study estimated that around 268,940 tons of plastic debris are currently floating in the oceans around the world. This plastic particles results in an approximated $13 billion per year in losses from harm to ecosystems of marine life, including losses in finance with fisheries and tourism as well as waste time to clean beaches. Marine animals include seabirds, whales, and dolphins can become trapped in plastic waste, and floating plastic debris—such as scrapped nets, docks, and boats—can transport microorganisms, algae, invertebrates, and fish into non-native regions, which will affect to the local ecosystems.

The benefits to environmental and social of plastics must be weighed against the issues that the durability and high volume of plastic present to the waste mountain. Plastic is beneficial in reducing waste from food for example, fresh product can keep longer. Moreover, it can be used in the production of life-saving healthcare apparatus, or used in mass items’ packaging, improvement of transportation efficiency, and used in the renewable energy technologies. However, plastic litter in the oceans and toxin from plastic additives—such as colorants, flame resistant, and plasticizers (i.e. bisphenol A, BPA)—are dangerous to the world along with reducing unnecessary used of plastics, finding more eco-friendly alternatives packaging, and improving product and packaging design to use less plastic, many challenges associated with plastics could be addressed to improve our plastic utilization management and overall well-being to the nature and ecosystem.

In order to improve properties of plastics, the surface’s wettability of materials is one of the very important property that determine their behavior. Superhydrophobic surfaces, which have a water contact angle (CA) greater than 150° is very interesting property, this also attracts enormous interest from many researchers and industries. The superhydrophobic behaviors are valuable for our life, for example preventing the adhesion and contamination of water or dust to windows or interior and exterior parts of building, reducing of drag friction in packaging materials or containers or plastic pipes, stain resistant textiles and utensils, antibacterial or antifungal containers.

The surface of materials can be converted to hydrophobicity by using various methods. Conventionally, an introduction of a rough morphology to the surface and modification of the surface by chemicals or materials with low surface free energy are
typically conducted. A group of common chemicals used for this purpose are fluorinated compounds. Recently, other methods have been applied to control the surface topography of materials. For example, fluoroalkylsilane compounds, densely packed aligned carbon nanotubes, or gold nanoclusters have been introduced. Plasma fluorination has been applied to modify a polymer surface. Blending of incompatible polymers leads to phase separation and also hydrophobic surface. A superhydrophobic coating of polypropylene can be obtained by controlling the surface roughness using suitable solvents and temperature or adjusting time of the crystallization and rate of nucleation of the polymer.

1.2 Objectives

The main objectives of this study are as follows:

1.2.1 To develop PMMA products that display superhydrophobic property by different techniques.

1.2.2 To conduct experiments to validate hypothesis on the proposed processes.

1.3 Scope of the project

The purpose of this project is to develop appropriate technology for production of poly(methyl methacrylate) (PMMA) products with superhydrophobic surfaces. In this work, application of nano- or microbeads of poly(methyl methacrylate-co-ethylene glycol dimethylacrylate), P(MMA-co-EGDMA) embedded on the surface of plastic films will be studied.

Poly(methyl methacrylate-co-ethylene glycol dimethylacrylate), P(MMA-co-EGDMA) nano- or microparticles are prepared by micro-suspension polymerization. Effects of co-monomer composition, reaction time and temperature on structures and properties of the resulting particles are investigated. The resulting particles shows spherical structure, derived from PMMA-based copolymers. Chemical structures, size, size distribution, and surface morphology of the particles are evaluated. Heat stability and density of the beads are examined. Nanoparticles are enhanced their hydrophobicity by treating with hydrophobic agent. Embedding technologies of the dispersed beads in pure and mixed solvent are studied, such as electrospray, spin coating, and dip coating.
Chapter 2
Literature Review

2.1 Superhydrophobic

Nowadays, superhydrophobic surfaces (Lotus Effect) are attracting interest. Because of the small contact area between solid’s surfaces and water, leads to high angle value of water droplet (greater than 150°) results in low flow resistance, and self-cleaning. There are many phenomena, such as snow depositing or water resistance, are expected to be interrupted or reduced on the property. Various methods have been developed for the converting of materials’ surface to be superhydrophobicity. Generally, the superhydrophobic properties are made by controlling the surface chemistry and surface roughness of many materials, which are then applied by difference methods and several steps. In order to develop surface of variety product, there are many techniques that can be used. Erbil et al., 2003 described a simple and inexpensive method for generating a superhydrophobic coating by using of polypropylene (PP) by select a suitable solvents and temperature in order to control the rough surface. Recently, many studies focused on superhydrophobic surfaces have been carried out, for example superhydrophobic fluorocarbon coating with ribbon surface structures (Favia P et al., 2003), super-hydrophobic silica aerogels (Rao AV et al., 2003), chemical vapor deposition of trimethylmethoxysilane (Wu Y et al., 2002), superhydrophobic surface based on a steric acid selfassembled monolayer over polyethyleneimine thin films (Ren S et al., 2003). Products with the superhydrophobic properties are meaningful to human, such as windows or interior and exterior parts of building with the properties can prevent themselves from water or dust contamination, drag friction reduction in packaging materials or containers or pipes made of plastic, stain resistant textiles, and antibacterial or antifungal containers.

2.2 Poly(methyl methacrylate) (PMMA)

Poly(methyl methacrylate) (PMMA), commonly known as Acrylic, is classified as thermoplastic. Thermoplastics can be heated to the melting point, cooled, and
reheated again. The materials can be injected into a mold easily and then subsequently recycled.

On the other hand, thermoset plastics can be only one time heated. They will be set at the first heating resulting in a change of chemical that cannot be reversed. If a thermoset plastic was tried to heat up to a high temperature a second time it would be burn easily. This inferiority characteristic of thermoset plastics makes it poor candidates for recycling.

PMMA start to melt at 160 °C (their melting point). Acrylic is an amazing useful plastic for many applications that require medium impact resistance but still transparence. Acrylic shows good resistant to scratch, compared to other transparent plastics. Its weight is lighter than glass and economical replacement for polycarbonate (PC) in some applications where strength is not a key factor. PMMA can be cut into very fine shapes by the use of laser cutting technology because the plastic evaporates upon impact with the concentrated energy of laser. Another advantage over glass of PMMA is that its more transparent than glass at high thickness. When glass windows are made too thick, they become opaque, but thickness of PMMA windows can be made as much as 13 inches, while their transparency still remains. After machining, the parts are generally need to be polished in order to remove the marks making by tools and restore the optical clarity. A few examples of PMMA products include lens, glass replacement, fashion accessories, package, and roof. PMMA is another type of vinyl polymer, produce by free radical vinyl polymerization from the monomer methyl methacrylate, as shown in Figure 1.

![Figure 1. Polymerization of poly(methyl methacrylate).](image-url)
There is a potential advantage of PMMA that it does not contain or release Bisphenol A (BPA) during hydrolysis like other related plastics, polycarbonate (PC), which contains BPA. Many studies showed that BPA is hazardous risk to health (Frederick S. vom Saal et al., 2005, Beverly S.Rubin, 2011). Regardless of the conflicting studies about the negative effects of BPA, certain types of Polycarbonate have been associated with its release. This leading to the advantage of “BPA-Free” polycarbonate products (commonly produced on consumer products such as canning jars). PMMA is another “BPA-Free” polymer instead of PC that is not toxic in a solid form. Fumes from 3D printing machine with acrylic or from the melted material used during injection molding processing should not be inhaled and these manufacturing processes should be conducted in a well-ventilated area to keep away from the hazardous substances effects of gaseous polymer.

2.3 Micro-suspension polymerization

A method to produce polymer particles with sizes of between emulsion polymerization (0.05-1 micrometers) and conventional suspension polymerization (20-3000 micrometers) is called micro-suspension polymerization. The products are usually applied for low volume, high value-added materials, for example chromatographic column packing, ion-exchange resins and xerographic toners. Kinetics of micro-suspension polymerization repeatedly show characteristics of both suspension and emulsion polymerizations. The true suspension polymerization is intended process that is very correspondent to a bulk polymerization within the droplets of monomer. They are stabilized by an agent named surface-active agent, and the initiator is soluble in the monomer. Nevertheless, the presence of even small amounts of monomer and initiator in the aqueous phase can lead to emulsion particle nucleation so, emulsion polymer tends to form some scope in all suspension polymerization. While the droplet size of the monomer gets smaller, the inclination to form emulsion polymer becomes greater. The trouble is frequently cruel to the droplets that under 20 micrometers.

There are many advantages of suspension polymerization that concern with operating the reactor and economics processing, including help to release heat, low friction of the reaction mixture, higher purity level than emulsion polymerization and easily handle of the particles throughout the polymerization, isolation and drying.
process. On the other hand, disadvantages are low amount of output because of low solid content and problems with fouling of components in the reactor (Cunnungham, 1999). Moreover, a critical disadvantage of suspension polymerization process is the lower of limiting conversion than emulsion polymerization (Vivaldo-Lima et al., 1997; Arshady, 1992; Hamielec and Tobita, 1992; and Yuan et al., 1991).

The limiting conversions of suspension are often higher than bulk, which is usually attributable to the presence of emulsion polymer in addition to the suspension polymer (Adams et al., 1990). An expect yield to be a homogeneous dispersion of suspension polymer particle from the process of micro-suspension polymerization that is free of emulsion polymer, while achieving the nearly complete conversion of monomer that is characteristic of emulsion processes. The study of Cunnungham, 1999 examines the kinetics of MMA micro-suspension polymerization, including the effects of particle size and initiator solubility in the aqueous phase on conversion against time, limiting conversions and molecular weight distributions that almost achieve 100% conversion.

2.4 Paper sizing agent (Hydrophobic agent)

Alkyl Ketene Dimer (AKD) is synthesized from fatty acids. The most common form is a waxy solid material dispersed as small particles in a solution that contains a stabilizer. The stabilizer may be cationic starch or another cationic polyelectrolyte. A liquid form of AKD is slightly less efficient as a sizing agent than the waxy form, the unsaturated product does not make the paper as slippery. AKD is insoluble in water with a melting point of 50 °C. It is prepared from natural fatty acid consisting of 14 to 20 carbons. In order to reduce the hydrolysis of AKD, it is kept at pH below 4 in the form of emulsion (Sunil Kumar et al., 2012).

![Figure 2. Synthesis and chemical structure of AKD.](image-url)
AKD is mainly used as an industrial sizing agent for paper to increase the hydrophobic properties of paper, especially when made under alkaline conditions. It is widely used for liquid containers, ink-jet printing papers, and many other grades of paper and paperboard. AKD is especially favored for products require water resistance over a long period of time. Moreover, the agent helps optimizing parameters process such as absorption of liquids, writability and printability, dimensional stability and run ability of the machine.

AKD is used in a form of milky emulsion in paper mill, which is very convenient. Paper made with high levels of AKD is likely to be slippery, and it may cause problems in precision cutting and register during conversion, or in stacking during high-speed xerographic printer. These effects can be minimized by limiting the dosage (perhaps supplementing the sizing effect with surface hydrophobes added to the size-press starch), or by use of alkenyl ketene dimer (unsaturated form) in place of the more usual AKD.

There is a research that studied application method of the agent, which are 1. impregnating with an aqueous AKD-solution and cured at 130 °C for gluing, or 2. spraying with a mixture of AKD-solution and urea-formaldehyde (UF)-resin in a single step. Boards are used with and without paraffin wax as controls. They found the result of first set of particle boards that after immersion 2, 24, and 48 hours, the thickness swelling was decreased by 90, 62, and 59% and also water uptake was reduced by 91, 75, and 60% respectively, compared with untreated control boards. Moreover, they found that impregnation of AKD with subsequent curing decreased the internal bound strength by 53%, showing that AKD obstructs the adhesion. But AKD mixed with UF-glue shows inconsiderable hydrophobic property. Then, they suggested that some part of AKD formed ester bonds at the wood surface by increasing methyl/methylene and carbonyl bands in FTIR-spectra after extraction by toluene. (Ulrich Hundhausen et al., 2008)

Xi Zhang et al., 2008 have developed a simple and suitable method to provide the stability of low-surface-energy coatings on organic surfaces, by using of surface-reactive molecule of 4-azido-N-dodecylbenzamide. This molecule carries an alkyl chain as a hydrophobic tail and an azide group as the reactive surface anchor, which can pin to almost all types of the surfaces by surface photoreaction. After modification
to be hydrophobic, rough organic surfaces can change their wetting properties from superhydrophilicity to superhydrophobicity. Furthermore, the materials with low-surface-energy can be directly spin coated on rough surfaces. Liu and coworkers have obtained superhydrophobic surfaces of aluminum and its alloys by spin coating perfluorononane and vinyl terminated poly(dimethylsiloxane).

Other polymer such as LDPE shows various morphologies. They depend on the processing conditions. When LDPE was melted at 150 °C between two glass slides and then crystallization at 60 °C, a smooth surface was presented. Leading to the surface had a contact angle of 101.5° ± 2.9°. In order to increase the value of contact angle, a series of LDPE films was prepared by Xiaoying Lu et al., they controlled the crystallization behavior of LDPE by adjust the temperature of crystallization and rate of nucleation. After LDPE was dissolved in xylene at 90 °C, a few drops of the LDPE

![Figure 3. FE-SEM images of LDPE films from a solution (10 mg/ml) in xylene when solvent was evaporated in a vacuum oven at different temperatures: a) 90 °C, b) 70 °C, c) 50 °C, and d) 30 °C.](image-url)
solution was applied onto the silicon wafers. Then the samples were put in a vacuum oven to eliminate the solvents at different evaporation temperatures of the solvents, which are, 90, 70, 50, and 30 °C, respectively. The resulting films show an increasing of water contact angles when the evaporation temperature of solvents was decreased, for example, at 90 °C the contact angle of about 117.8° ± 2.4° as shown in Figure 3(a) when reduce the temperature to 30 °C the value increase to 151.1° ± 2.0° (Figure 3(d)). Decreasing the evaporation temperature of solvent leading to the change of microstructures on the surface (Figure 3(a–d)), resulting in the increase of contact angle. When solvent evaporation temperatures are low, the rate of solvent evaporation will be more slowly. Therefore, the crystallization time of the polymer is increased, which is beneficial for a higher overall crystallinity. Moreover, the lower evaporation temperatures of solvent also increase the rate of nucleation and formation of pore. Consequently, the non-homogeneous and size distribution of the pores increase when decrease the solvent evaporation temperature. As a result, the contact angle value increased to 151.1° ± 2.0° at an evaporation temperature of 30 °C. However, the water droplet behavior on these LDPE film with porous and flat surfaces cannot slide off although the surface is inclined until vertical, this is because the water droplet is “pinned” to the surfaces, indicating the sliding angle is high.

2.5 Spin Coating technique

Spin coating is one of the most common techniques for applying thin films onto substrates. It is used in a wide variety of industries and technology sectors. The advantages of spin coating are the simplicity and relative ease with which a process can be set up, coupled with the thin and uniform coating that can be achieved. Due to the ability to have high spin speeds the high airflow leads to fast drying times, which in turn results in high consistency at both macroscopic and nano length scales.

The use of spin coating in organic electronics and nanotechnology is widespread and has built upon many of the techniques used in other semiconductor industries. It also has some difference due to the relatively thin films and high uniformity required for effective device preparation, as well as the need for self-assembly and organization to occur during the casting process.
Incomplete coating will affect the wetting of an ink onto a substrate is generally characterized by the contact angle of the liquid onto the surface. A low contact angle means good wettability (the ink likes to spread across the substrate) while a high contact angle means poor wettability (the ink likes to ball up).

**2.6 Solvent effect**

The casting technique by solvent is being widely used in the preparation of biopolymer film, such as Poly(lactic acid) (PLA). This technique relates to dissolution, casting, and drying. PLA is known that it is easily dissolve in solvents such as methylene chloride, chloroform, benzene, and dioxane. Each solvent affects properties of film differently. For example, chloroform induces more chain movement of the polymer and dioxane causes a surface roughness of the film due to its evaporate slower than chloroform. PLA has a poor solubility in some solvents for example acetone, toluene, methanol, acetonitrile, and ethyl acetate. Casted PLA films with acetone, toluene, and ethyl acetate presented an increase of hydrophobic property and a surface separation.

The conformational changes of crystallinity of the PLA film is affected by solvent. There are many studies stated that dissolved PLA in chloroform and methylene chloride leads to a random conformation of the molecules (Youngjae Byun et al., 2012). From the study of Byun Y., the crystallization of the PLA depends on the interaction within the molecules rather than intermolecular interactions. Homo-crystallization occurred when PLA was dissolved in solvent (chloroform) due to the strong interaction between PLA and the solvent. Nevertheless, crystallization of stereo complex occurred when PLA was dissolved in another solvent (methanol) because of the strong interactive bonding between PLA chains. Moreover, they found that there was swelling and changes of conformation on the surface of the PLA when its dissolved in a poor solvent. Treatment PLA with a solvent mixture of chloroform and methanol increased film crystallinity and makes film hazy and milky white.

Referred to previous study, there is an evident presenting that the solvent can change some properties of PLA film by changing the crystallinity. Some studies have been operated about the effect of solvent on the PLA’s crystallinity and ductility. Moreover, there is no research has been reported about the effect of solvent on thermal
expansion stability of PLA related with the crystallinity. The production of PLA films with various solvents and mixed solvent system and the investigation of solvents effect on the properties of film such as film crystallinity, thermal expansion stability, and mechanical, barrier, optical and thermal properties was the main objective of this research.

2.7 Solvent/Nonsolvent technique

Solvent mixtures or solvent/nonsolvent, which can be created for preferential solubility to specific components in a multicomponent polymer system. The mixed solvent can affect to segregate and composite on surface in several ways. Study of the surface composition of diblock copolymers of poly(dimethylsiloxane)-nylon 6 (PDMS-co-PA6) using solvent mixtures exhibit the complication effects of mixed solvent on surface segregation (Thomas et al., 1979). Meaning of solvent is that, the solvent which is good dissolve for substrate. While nonsolvent here refers to the solvent which is poor dissolve for the substrate. Gardella et al., 1995 studied the effect of preferential solvents in a mixed solvent on polyurethane surface composition. He used tetrahydrofuran (THF) as a solvent and mineral spirits (MS) as nonsolvent in a solvent mixture shows that the volatility of solvent plays an important role on correlation with the extent of surface segregation leading to surface pattern creation. A boiling point of tetrahydrofuran is 66 °C whereas MS boils at 179 - 210 °C. Therefore, rates of evaporation of THF is faster, leading to an increasing on concentration of MS in the mixed solvent encourages early precipitation of the hard fragment, whereas the soft fragment remains highly mobile because the polymer is poor dissolve in MS.

2.8 Solubility parameter and dissolution behavior of PMMA

2.8.1 Solubility parameter of PMMA

Industry often use solubility parameters to predict polymers compatible, swelling of crosslinked elastomers using of solvent, chemical resistance, rate of permeation of solvents, and characterization of the surfaces of other materials such as pigments, fibers, and fillers. Moreover, the benefit of polymers in many technological applications is mainly depended on the solubility parameter, δ, as noted by Bicerano.
In theory of solution, the solubility parameter is important it links to other physical properties includes surface tension, wettability, boiling points liquids, the ratio of the coefficient of thermal expansion to compressibility, the ultimate strength of materials, and glass transition temperature ($T_g$) of polymers. Leading to, the ability to prediction of solubility parameters, which is advantage to predict the physical performance and properties of systems.

**2.8.2 Dissolution behavior of PMMA**

Ueberreiter is known as one of the participators who first study dissolution of polymer. He summarized the formation process of surface layer as below:

- first, the solvent starts to aggres by forcing the swollen polymer substance into the solvent.
- then, an upper layer which is more dilute will be pushed in the direction of the solvent stream. The subsequent absorption of the solvent in the solid polymer improves the swelling layer until, finish the swelling time, a quasi-stationary state is reached where the transporting of the macromolecules from the surface into the solution prevents a further increase of the layer.

Ueberreiter summarized the structure of the surface layer of glassy polymers during dissolution from the virgin polymer to the pure solvent as follows: the infiltration layer, the solid swollen layer, the gel layer, and the liquid layer. The steps occur as below;

1. the infiltration layer is the first layer connected to the virgin polymer. A polymer in the glassy state contains free volume in the form of a number of channels and holes of molecular dimensions, and the first penetrating solvent molecules fill these paces and start the process of diffusion without any need for creating new holes, and
2. the solid swollen layer where the polymer–solvent system building up in this layer is still in the glassy state, and
3. the gel layer which contains swollen polymer in a rubber-like state, and
4. a liquid layer which surrounds whole solid in a streaming liquid, respectively.
Dissolution can be divided into two types. The first one is ‘normal dissolution’, all the layers that already described above are formed. The second type of dissolution occurs when gel layer is absented. Asmussen and Raptis found that

1. poly(methyl methacrylate) (PMMA) can be dissolved in various solvents and showed the normal process of dissolution beginning at the glass transition temperature.

2. in order to decrease the temperature of an experiment, a stable decrease in the thickness of gel layer could be seen until a final temperature was reached, where this part of the total surface layer was so thin that it was no longer visible. Below this temperature, it is observed that cracks run into the polymer matrix, and these cracks coalesced and caused small blocks of the polymer to leave the surface in a kind of eruption process. It is understood that the reason for the cracking mechanism was the freezing-in of large amounts of stress energy in the polymer in the glass transition interval. The gel temperature (where the transition from normal dissolution to cracking) was formally defined as the temperature at which the gel layer disappeared.

However, Ueberreiter and Asmussen had the converse result with the other polystyrene (PS), experiments. They found that PS underwent normal dissolution in most solvents due to its low gel temperature.

During the dissolution process, Krasicky et al. found that the transition layer increases with the molecular weight of the polymer. Also, when PMMA dissolved in methyl ethyl ketone (MEK), the transition layer was not detectable below a polymer number average molecular weight, MN; of about 30 000. It is concluded that the rate of the dissolution process is mainly governed by what is occurring near the interface with the solid polymer, rather than by what is occurring elsewhere in the transition layer.

Pekcan et al. monitored the dissolution of annealed high-Tg latex films in real time, and defined this into 3 stages of dissolution.

1. In the first stage, swelling dominates and the gel layer thickness increases with time. This stage occurs within the first 60–100 s, depending on the annealing time of the film.

2. In the second stage, there is a time period where the gel layer thickness remains constant due to swelling and dissolution.
3. In the final (third) stage, the gel layer thickness is less and less due to desorption of polymer chains.

2.9 Wettability

Wetting force is surrounding us and can be applied in our day-to-day lives. For example, it makes the rain beading up from the newly waxed car and protect car from rust, or when wetting force bind the sand which holds the child’s sand castle. It affects the hydrocarbon reservoir behavior, in variety ways, including saturation, and multiphase flowing. However, it is best to verify the meaning of wettability before getting into the details. Wettability expresses the preference of solid’s surfaces that contact with one fluid instead of other. The word “preference” suitable describes the balance of surface and force of interface. A drop of an especially wetting fluid will eliminate another fluid, it can be spread over the whole surface in some extreme case. On the other hand, if the non-wetting fluid is dropped onto a solid’s surface that is covered by the wetting fluid already, it will bead up, and minimize its contact with its surface. If the condition is neither strongly water-wetting nor strongly oil-wetting, the balance of force in the system contains oil/water/solid will result in a contact angle, θ, between the fluid on the surface of solid.

Another important is that a surface that prefer water-wetting can contact with oil or gas. Wettability does not describe the state of saturation but it describes the preference of the solid for wetting by an exact fluid, lead to the presence of the preferred wetting fluid. Therefore, a water-wet solid can be washed, cleaned, and dried. The method to measure the wettability are next described. There are several methods to measure a wetting preference are obtained.

2.10 Water Contact Angle

Contact angle measurement is one of the common ways to identify the wettability of a surface or material. Wetting means the study of a liquid’s behavior on a solid substrate’s surface or the ability of liquids to form boundary surfaces with solid states. In order to measure the wetting of solids surface, the contact angle is easy method, which the liquid stands in contact with the surface of solids substrate. If the contact angle is larger, the wetting trend to small. A wetting liquid means a liquid that
forms a contact angle smaller than 90° on the solid surface. While non-wetting liquid creates a contact angle value between 90 and 180° on the surface of solid.

The contact angle is an angle that a liquid occurs between a solid surface and liquid when they are contact together. The angle is defined by both properties of the liquid and the solid and the interaction and repulsion forces between them and by the property of 3 phase interfaces (gas, liquid, and solid). The interactions are explained by intermolecular forces which are adhesion and cohesion forces. The balance between the cohesive forces of similar molecules and the adhesive forces between different molecules will determine the contact angle created in the interface of liquid and solid. Similar molecules such as between the liquid molecules (i.e. hydrogen bonds and Van der Waals forces). Different molecules such as between the liquid and solid molecules (i.e. mechanical and electrostatic forces).

![Figure 4. Water contact angle of solid surface.](image-url)
Chapter 3
Experimental

3.1 Materials and Chemicals

Chemicals and other materials used in this study are shown in Table 1, which displays the structure of each and name of suppliers.

Table 1. List of Chemical names, structures, and suppliers, which were used in the experiments.

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Chemical Structure</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Methacrylate (MMA)</td>
<td>![Methyl Methacrylate Structure]</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ethylene Glycol Dimethacrylate (EGDMA)</td>
<td>![Ethylene Glycol Dimethacrylate Structure]</td>
<td></td>
</tr>
<tr>
<td>Benzoyl Peroxide (BPO)</td>
<td>![Benzoyl Peroxide Structure]</td>
<td></td>
</tr>
<tr>
<td>Poly(vinyl alcohol) (PVA)</td>
<td>![Poly(vinyl alcohol Structure)]</td>
<td></td>
</tr>
<tr>
<td>Chloroform (CHCl₃), analytical grade</td>
<td>![Chloroform Structure]</td>
<td>VRW Chemicals</td>
</tr>
<tr>
<td>Cyclohexane (C₆H₁₂), analytical grade</td>
<td>![Cyclohexane Structure]</td>
<td>CARLO ERBA</td>
</tr>
<tr>
<td>Chemical Name</td>
<td>Chemical Structure</td>
<td>Supplier</td>
</tr>
<tr>
<td>---------------------------------------</td>
<td>--------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF), analytical grade</td>
<td><img src="image1.png" alt="Chemical Structure" /></td>
<td>Merck KGaA</td>
</tr>
<tr>
<td>Poly(methyl methacrylate) (PMMA), Acrypet VH001</td>
<td><img src="image2.png" alt="Chemical Structure" /></td>
<td>Mitsubishi Chemical Corp.</td>
</tr>
<tr>
<td>Alkyl Ketene Dimer (AKD), Fennosize KD 364 MP</td>
<td><img src="image3.png" alt="Chemical Structure" /></td>
<td>Kemira</td>
</tr>
</tbody>
</table>

### 3.2 Equipment and Instrumental
- Homogenizer (IKA T25)
- Round bottom flask
- Hot plate stirrer (IKA C-MAG HS7)
- Compression machine (Chareontut, PR2D-W300L300 HD-WCL)
- Electrospinning machine (kd Scientific)
- Spin coating machine
- ATR-FTIR (Thermo Scientific, iD5) spectrometer
- FE-SEM (JEOL JSM-7800F)
- Dino-Lite (Dino-Lite Edge Digital Microscope, AM4815 Series)

### 3.3 Synthesis of Micro- and Nanobeads
MMA and EGDMA monomers from Sigma-Aldrich were employed in the preparation of P(MMA-co-EGDMA) spheres, using benzoyl peroxide (BPO) and poly(vinyl alcohol) (PVA) from Sigma-Aldrich as initiator and surfactant, respectively. Chloroform from VRW Chemicals and cyclohexane from CARLO ERBA were utilized to create patterned structures on the surface of PMMA product in the solvent/nonsolvent technique.
P(MMA-co-EGDMA) nano-/microspheres were prepared by micro-suspension polymerization. Essentially, a mixture of 9.01 g of MMA and 1.13 g of EGDMA monomers, and 0.80 g of BPO initiator was prepared, and then transferred to 90 ml of 1% PVA aqueous solution. The mixture was homogenized at 5,000 rpm for 5 min, in which droplets of monomers were formed. The polymerization reaction, as summarized in Figure 5, was subsequently conducted under nitrogen atmosphere at 80 °C for 8 h, with continuing stirring at 500 rpm. Nano-/micro-sized particles of cured P(MMA-co-EGDMA) copolymers were formed. Finally, the mixture was centrifuged at 3,000 rpm for 20 min.

Figure 5. Synthesis route of cured P(MMA-co-EGDMA) copolymers.
Before P(MMA-co-EGDMA) particles of copolymers are used for creation of nano-structures on the polymer’s surfaces, their stability in various conditions were tested. The introduction of a hydrophobic agent containing reactive functional groups was then applied on the surface of the bead products.

3.4 Stability test of P(MMA-co-EGDMA) beads

As the cured P(MMA-co-EGDMA) particles will be further chemically treated, their stability in various solvent systems and high temperature were examined. Solubility of the particles in chloroform solvent was first investigated by placing a specific amount (1 wt%) of the particles in the solvent. After sonication for 30 min, chloroform was removed and the weight of the remaining particles was recorded. Thermal stability of the particles was tested by placing a specific amount of the particles (1 wt%) into an inert soybean oil at 200°C for 30 min. Finally, the final weight of the particles was recorded. An optical microscope was used to examine size and shape of the remaining particles (Figure 6). Moreover, some of P(MMA-co-EGDMA) nanobeads were took to calculate degree of crosslinking and %swelling by Soxhlet extraction using THF as a solvent (Figure 7).

![Figure 6. Optical microscope (OM) pictures of tested beads in a) chloroform and b) 200 °C of soybean oil at a magnification of 40X.](image-url)
Figure 7. Soxhlet extraction of nanobeads in THF at 100 °C for 24 h.

Soxhlet extraction is used by many manufacturers in order to control the quality for the production of goods. After the treatment, non-crosslinked fraction was supposed to be completely dissolved in THF and could be separated from the remaining and crosslinked and hence insoluble elastomer matrix (called “gel”). This insoluble residue was dried at 60 °C for 24 - 48 h, followed by the determination of its net weight (W_2). The ratio of the mass of the insoluble residue divided by the initial weight (W_1) of the test sample yields the “gel content”.


gel content = \frac{W_2}{W_1} \times 100 \tag{1}

where; \quad W_1 = \text{Weight of dried beads before extraction} \\

W_2 = \text{Weight of remaining dried beads after Soxhlet extraction}

Another alternative method that could provide data which is the solvent swelling properties of the polymer. The basis of this analysis in this experiment is to determine the solvent uptake into the polymer matrix, which is expected to decrease with increased crosslinking.
After treatment by THF for 24 h the solvent was then decanted, the liquid solvent adheres to the sample's surface removed by short contact with filter paper, and the weight of the swollen polymer \( W_s \) was determined immediately. The analyst is thus the relative weight gain due to incorporation of solvent molecules into the polymer matrix.

Degree of swelling was calculated by

\[
\text{degree of swelling} = \left( \frac{W_s - W_d}{W_d} \right) \times 100
\]

(2)

where;

\( W_d \) = Weight of dried beads after extraction

\( W_s \) = Weight of swollen beads immediately measured after swelling test

3.5 Preparation of PMMA/nanobeads films

To prepare PMMA/nanobeads films, 1.25 g of PMMA resins were dissolved in 10 ml of chloroform solvent and then 0.025 g of beads (2% wt) were added. The mixture was stirred for 24 h at room temperature. Then, gently pour the mixture into the Petri dish and let the solvent slowly evaporate. After that, the film was taken from the Petri dish. ATR-FTIR spectroscopy and water contact angle measurements were studied in order to compared the composition and wettability between the modified film and the original film without beads.

3.6 Preparation of PMMA sheet by compression technique

PMMA Acrypet VH001 is a standard grade PMMA resins from Mitsubishi Chemical Corp., which has a density of 1.19 g/cm\(^3\) (ISO 1183) and melting temperature of 160 °C. Table 2 shows suitable conditions for preparation of PMMA sheets. After using PMMA resins of 6 g, controlling steps of pressure and time can give the suitable thickness and good appearance of PMMA sheet; completely melt, no air bubble, no weld line etc.
Table 2. Suitable conditions for preparation of PMMA by compression molding.

<table>
<thead>
<tr>
<th>Step</th>
<th>Plate temp. U/L (°C)</th>
<th>Pre-heat time (min)</th>
<th>Compress time (min)</th>
<th>Compression pressure (psi)</th>
<th>Cooling time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>190</td>
<td>20</td>
<td>10</td>
<td>1,000</td>
<td>20 or more</td>
</tr>
<tr>
<td>2</td>
<td>190</td>
<td>-</td>
<td>5</td>
<td>1,500</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>190</td>
<td>-</td>
<td>10</td>
<td>2,000</td>
<td></td>
</tr>
</tbody>
</table>

3.7 Electrospray of nanobeads suspension on the surface of PMMA sheets

Electrospray of nanobeads suspension on the PMMA sheets was conducted using 10 kV with a 2 ml/h flow rate. Time of spraying of 10 min was used with the distance between PMMA sheet and the nozzle of needle from 5, 8, and 10 cm. From the above conditions, PMMA sheets show better dispersion of mixtures that can benefit with the contact angle value.

Table 3. Suitable condition for electrospraying of nanobeads suspension on PMMA surface.

<table>
<thead>
<tr>
<th>Mixture Ratio</th>
<th>Voltage (kV)</th>
<th>Flow rate (ml/h)</th>
<th>Distance (cm)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ml:0.08 g</td>
<td>10</td>
<td>2</td>
<td>5, 8, 10</td>
<td>Each sheet was divided into polishing and non-polishing process</td>
</tr>
<tr>
<td>(Chloroform: Nanobeads)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In order to make sure that the mixture was well spread on the surface of PMMA sheet, second processing was introduced, which was polishing by Lens Cleaning Tissue. The hydrophobicity of each sheets was then measured.

3.8 Preparation of P(MMA-co-EGDMA) treated with Alkyl Ketene Dimer

Surface hydrophobicity of P(MMA-co-EGDMA) nanoparticles was enhanced by treating with an Alkyl Ketene Dimer (AKD) agent by mixing the milky suspension of beads with the AKD agent at a 5:1 ratio (beads: AKD) at 90 °C for 30 min. After the reaction completed, the mixture was dried until powder of nanobead products was obtained.
3.9 Spin coating

As electrospraying is quite complicated and requires several steps, easier and more convenient technique, i.e. spin coating technique and solvent/nonsolvent technique were used to apply simultaneously.

3.9.1 With mixed solvent without nanobeads

PMMA sheets were treated with only solvent mixture at different ratio between chloroform and cyclohexane, which are 1:1, 1:2, and 2:1 were examined.

3.9.2 With treated nanobeads

The coated nanobeads, obtained from 3.8, were added into solvent mixture at the same ratio between chloroform and cyclohexane as previous, which are 1:1, 1:2, and 2:1. Table 4 shows amount of nanobeads, chloroform, and cyclohexane at 3 difference ratios.

Table 4. Composition of nanobeads, chloroform, and cyclohexane at 1:1, 1:2, and 2:1 ratios of mixed solvent.

<table>
<thead>
<tr>
<th>Mixture Ratio (CHCl₃ : C₆H₁₂)</th>
<th>Weight of nanobeads (g)</th>
<th>Volume of chloroform (ml)</th>
<th>Volume of cyclohexane (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>0.08</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>1:2</td>
<td>0.06</td>
<td>0.25</td>
<td>0.50</td>
</tr>
<tr>
<td>2:1</td>
<td>0.06</td>
<td>0.50</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Treated nanobeads were mixed with chloroform then sonication was used to homogenize the mixture for 10 min. After that, cyclohexane was also added into the mixture and sonicate for 10 min. The mixture was prepared for 3 sets at different temperature (RT, 45, and 60 °C). Finally, 15 µl of the mixture at each temperature was dropped onto the surface of PMMA sheet which was rotating on the spin coating machine with the speed of 850 - 950 rpm. The mixture was spread and evaporate immediately, and dried within 15 seconds. After that the white area generated by the etching of solvent mixture present on the surface of PMMA sheet. These areas were further analyzed, in terms of water contact angle, and by ATR-FTIR spectroscopy, and FE-SEM techniques.
Figure 8. Spin coating machine with speed adjustment from 750-1,200 rpm.

3.10 Dip coating

After success in finding suitable condition from spin coating, dip coating that is easier applying technique was examined. The number of beads, solvent mixture ratio, and different in temperatures were prepared similar to spin coating technique. In this technique, PMMA slabs were vertically immersed inside a glass beaker containing the suspended P(MMA-co-EGDMA) beads in mixed solvents at 2 ratios (1:1 and 1:2) of chloroform and cyclohexane. The samples were left immersed inside the solvent mixture with beads for 10 seconds at different temperatures (RT, 45, and 60 °C). The samples were then immediately kept in a fume hood by placing horizontally for 10 min until white matted surfaces appeared on the immersed area of samples. The slabs were then further analyzed by water contact angle measurements and FE-SEM.
Chapter 4
Results and Discussion

4.1 PMMA sheet and P(MMA-co-EGDMA) beads

4.1.1 Characteristic of P(MMA-co-EGDMA) beads

After the synthesis of beads by micro-suspension from 3.3. The bead products in micron-sized was obtained as solid sediment with size about 10 – 20 µm, while the nano-sized counterparts present as milky suspension with size distribution of 139.9 ± 38.7 nm which were treated with hydrophobic agent for next studies. The chemical structure of these particles as shown in Figure 9. It is believed that the presence of covalent bonds between MMA and EGDMA monomer leads to a formation of network structure, which enhance resistance to solvent and heat. This can be applied for further use in the next steps.

Moreover, size and shape of these micro- and nanosphere could create nano-structure patterns when impregnated on the surface of PMMA sheet and also other products. Therefore, these particles were modified with hydrophobic agent in order to improve their hydrophobicity.

![Chemical structure of P(MMA-co-EGDMA) particle shows chemical bond between MMA and EGDMA monomer.](image)

Figure 9. Chemical structure of P(MMA-co-EGDMA) particle shows chemical bond between MMA and EGDMA monomer.
4.1.2 Stability test of P(MMA-co-EGDMA) beads

The morphology of beads after treatment in various conditions show that the shape of the particles both before and after Soxhlet treatments in solvent systems including chloroform at room temperature, in THF at 100 °C, and in oils at 200 °C remain unchanged, as shown in Figure 10. This strongly reflects that the cured P(MMA-co-EGDMA) particles have high resistant to high temperatures and strong solvents system. These are because of the strong chemical bond from the crosslinking of P(MMA-co-EGDMA) particles between MMA and EGDMA monomer, as shown in Figure 9. The results from Soxhlet experiment show the gel content of about 100% and degree of swelling of about 89%. It can be said that all of the nanobeads are completely crosslinked and the degree of swelling shows some spaces in the particles that hold the solvent inside. This reason can support the stability of the beads. Hence, the P(MMA-co-EGDMA) particles can be used and applied in many applications. Moreover, they are suitable for further chemical treatment at both normal and high temperature processes.

![Figure 10. FE-SEM images of the P(MMA-co-EGDMA) beads a) before treatment and b) after treatment in THF at 100 °C.](image-url)
4.1.3 Wettability of PMMA sheet

In order to investigate the hydrophobic property, PMMA sheet was measured the water contact angle for five regions. The original PMMA sheet shows water contact angle value about $76.4^\circ \pm 0.8^\circ$. While PMMA sheet after mixing with P(MMA-co-EGMA) beads by dispersing PMMA in chloroform (from 3.5) gives the value about $83.3^\circ \pm 3.4^\circ$ as shown in Table 5. The small increase of contact angle of treated PMMA sheet resulted from micro-/nanostructures created by the P(MMA-co-EGDMA) particles which coated on the surface of the sheet.

Table 5. Results of water contact angle of original PMMA sheet compared to PMMA/nanobeads films.

<table>
<thead>
<tr>
<th>Water contact angle</th>
<th>Original PMMA sheet</th>
<th>PMMA/nanobeads films</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$76.4^\circ \pm 0.8^\circ$</td>
<td>$83.3^\circ \pm 3.4^\circ$</td>
</tr>
</tbody>
</table>

4.1.4 FTIR spectroscopy

P(MMA-co-EGDMA) nanobeads, prepared by micro-suspension polymerization were characterized by ATR-FTIR spectroscopy. From Figure 11, neat PMMA sheet shows characteristic bands at 1720 (C=O stretching) and 1145 cm$^{-1}$ (O–C and C–O stretching), while the P(MMA-co-EGDMA) beads exhibit an additional unique band at 1766 cm$^{-1}$ (C=O stretching). From the ATR-FTIR’s result, the beads’ unique band (1766 cm$^{-1}$) disappeared. This can be said that all particles were covered by dissolved PMMA in chloroform, prepared by mix P(MMA-co-EGDMA) particles into dissolved PMMA. When the solvent evaporates slowly, PMMA became very thin film and covered the whole particles. Therefore, FTIR characteristics band of beads on treated PMMA sheet disappeared, but present the identical peaks to original PMMA at 1720 and 1145 cm$^{-1}$. However, the results from several measurements of water contact angle indicate that the surface roughness created by these particles can improve the wettability of PMMA sheet. So, P(MMA-co-EGDMA) particles would be used by other techniques.
**Figure 11.** ATR-FTIR spectra of PMMA film, P(MMA-co-EGDMA) beads, and PMMA embedded with P(MMA-co-EGDMA) beads.

### 4.1.5 FE-SEM Analysis of treated PMMA sheet in mixed solvent

To analyze the effect of solvent/nonsolvent on the surface properties of PMMA sheet, solvent mixture was applied at various ratios and temperature of the solution. Chloroform was used as a good solvent for PMMA. The nonsolvent in this experiment was cyclohexane because it is a poor solvent for PMMA. The mixture of chloroform and cyclohexane (1:1, 1:2, and 2:1 ratios of chloroform: cyclohexane) were applied by spin coating technique on the surface of PMMA sheet at different temperatures. FE-SEM images in **Figure 12** display spherical microstructures and also hole patterns. From pictures a-c, PMMA sheets were coated with a 1:1 ratio of chloroform: cyclohexane at room temperature, 45, and 60 °C, respectively. The spherical microstructures of treated PMMA sheet are resulted from the competition crystallization and small area separation. When chloroform which is a good solvent for PMMA was applied on the surface of PMMA, the microdomains are impregnated in the crystallized phase because of the poor solubility of PMMA in cyclohexane. When the ratio of cyclohexane increased to a 1:2 of chloroform: cyclohexane (in **Figure 12(d-f)**), the formation of microsphere structures decreases (Jiaxing Chen et al., 2001) and absence in **Figure 12(f)**. While the addition of chloroform to a 2:1 ratio (chloroform: cyclohexane) in
Figure 12(g-i), the surface structure of PMMA sheet appear the hole structures instead. This phenomenon can be explained that the vapor of cyclohexane (density = 0.78 g/cm³) condense as small droplets above the PMMA (density = 1.19 g/cm³) dissolved in chloroform (density = 1.48 g/cm³) was evaporated at the same time. This is leading to polymer phase separation results in the present of holes on the phase separated polymer when the cyclohexane has been evaporated completely. When compare the size of hole between Figure 12 (g), (h), and (i). At room temperature (Figure 12 (g)) size of holes is bigger than at 45°C (Figure 12 (h)) and 60 °C (Figure 12 (i)). This is because the effect of the vaporization rate of solvent at room temperature is lower than others. Hence, there is more time for vapor of cyclohexane condensation to become bigger in diameter (Farnaz Farbod et al., 2013).

Furthermore, the inner layers underneath the upper layers are observed in Figure 12(g-i). The size and arrangement of inner cell structures are random, depending on the processing temperature. This is likely because a surface multilayer was formed between pure solvent and the bulk PMMA polymer consisting of liquid layer, gel layer, solid swollen layer, and an infiltration layer, as shown in Figure 13.

Figure 12 shows FE-SEM images, which indicate that when the temperature increased, the ratio of solvent mixture may be changed, leading to changes in the ability of surface etching or solubility of PMMA in mixed solvent. From these rough surfaces creation, the nanoparticle of P(MMA-co-EGDMA) are embedded easily, which will give higher value of water contact angle.
Figure 12. FE-SEM images of PMMA sheets after treatment with chloroform: cyclohexane mixed solvent at room temperature, 45, and 60 °C, respectively. a-c) at 1:1, d-f) 1:2, and g-i) 2:1 ratios, with 3,000X magnification by spin coating technique.

Figure 13. Surface multilayer structure formed between pure solvent and the bulk of the glassy polymer consisting of a liquid layer, a gel layer, solid swollen layer, and an infiltration layer. (Adopted from B. B. Ke et al, 2010.)
4.2 PMMA sheets coated by beads by electrospray technique

4.2.1 Wettability

Water contact angle results of PMMA sheets coated by beads are shown in Table 6. To get the better dispersion of mixture on the PMMA sheet’s surface, polishing process had been applied. The distance between sheet and nozzle in the experiment was conducted at 5, 8, and 10 cm. Moreover, treatment time was varied from 5, 10, and 15 min. The results show that the sheet prepared at 5 cm distance, with polishing, has the highest contact angle of about 81.0° ± 1.8°.

Table 6. Results on water contact angle of PMMA sheets after electrospray with chloroform and nanobeads, with polishing and non-polishing step at various distances and time.

<table>
<thead>
<tr>
<th>Distance 5 cm.</th>
<th>Time (min.)</th>
<th>Polishing</th>
<th>Polished</th>
<th>Non-polish</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>10</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Polishing</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polished</td>
<td>81.0° ± 1.8°</td>
<td>79.9° ± 0.9°</td>
<td>80.8° ± 0.7°</td>
<td></td>
</tr>
<tr>
<td>Non-polish</td>
<td>74.4° ± 0.5°</td>
<td>71.2° ± 0.3°</td>
<td>70.6° ± 0.1°</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Distance 8 cm.</th>
<th>Time (min.)</th>
<th>Polishing</th>
<th>Polished</th>
<th>Non-polish</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>10</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Polishing</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polished</td>
<td>79.1° ± 0.6°</td>
<td>77.9° ± 0.4°</td>
<td>77.4° ± 4.0°</td>
<td></td>
</tr>
<tr>
<td>Non-polish</td>
<td>71.3° ± 0.1°</td>
<td>68.2° ± 3.8°</td>
<td>70.1° ± 0.1°</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Distance 10 cm.</th>
<th>Time (min.)</th>
<th>Polishing</th>
<th>Polished</th>
<th>Non-polish</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>10</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Polishing</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polished</td>
<td>79.7° ± 0.3°</td>
<td>79.9° ± 0.1°</td>
<td>79.2° ± 1.2°</td>
<td></td>
</tr>
<tr>
<td>Non-polish</td>
<td>75.1° ± 0.2°</td>
<td>79.5° ± 0.3°</td>
<td>73.6° ± 0.6°</td>
<td></td>
</tr>
</tbody>
</table>
4.2.2 FTIR spectroscopy

PMMA sheets after electrospraying with P(MMA-co-EGDMA) nanobeads suspension were characterized by ATR-FTIR spectroscopy. From Figure 14, PMMA sheets after spraying exhibits similar spectra characteristics as untreated PMMA sheet. The characteristic band of P(MMA-co-EGDMA) beads at 1766 cm\(^{-1}\) is not observed. This is likely because the beads were stuck at the nozzle of electrospray’s needle. Therefore, the increase in contact angle value of the treated PMMA sheet is mainly due to the effect of solvent (chloroform), which created roughness on the surface of PMMA sheet. Therefore, this technique was not suitable to use with particle such as nanobeads.

![Figure 14](image)

**Figure 14.** ATR-FTIR spectra of pure chloroform, PMMA sheet, P(MMA-co-EGDMA) beads, and PMMA sheets after electrospraying with nanobeads suspension at 5 and 10 min.
4.3 P(MMA-co-EGDMA) nanobeads treated with Alkyl Ketene Dimer (AKD)

4.3.1 Stability test of treated P(MMA-co-EGDMA) beads

Results on character of modified beads after Soxhlet treatment in THF at 100 °C for 24 h shows that the shape and size of the particles before and after treatment remain unchanged, as shown in Figure 15. This is because P(MMA-co-EGDMA) particles have high resistant to high temperature and solvent, similar to untreated beads in 4.1.1. In terms beads agglomerating dispersion, the treated beads after washing in THF were more dispersed, compared to beads before Soxhlet treatment. This was because the treated beads with AKD agglomerate together by excess AKD wax. But the wax can be dissolved in THF, then the wax was washed during the extraction process, leading to more dispersion of P(MMA-co-EGDMA) nanoparticles.

![Figure 15. FE-SEM images of the coated P(MMA-co-EGDMA) beads a) before treatment in THF and b) after treatment in THF at 100 °C for 24 h.](image)

4.3.2 FTIR spectroscopy

P(MMA-co-EGDMA) nanobeads which were treated by Alkyl Ketene Dimer (AKD) were characterized by ATR-FTIR technique. From Figure 16, the characteristic bands of the treated P(MMA-co-EGDMA) beads with AKD present an additional unique band at 1848 (C=O stretching) and strong bands at 2847 and 2915 cm⁻¹, due to stretching vibration of C-H in methylene and methyl groups in AKD. Another intensive peak, such as 1470 cm⁻¹, is owing to -CH₂- bending, compared to the untreated
P(MMA-co-EGDA) beads at 1720 (C=O stretching) and 1145 cm\(^{-1}\) (O–C and C–O stretching).

![FTIR spectra](image)

**Figure 16.** ATR-FTIR spectra of P(MMA-co-EGDMA) beads before and after treatment with AKD, compared with AKD agent.

4.4 **PMMA sheets embedded with treated nanobeads by spin coating with solvent/nonsolvent mixture**

4.4.1 **Wettability**

As the result from PMMA sheets prepared from electrospray technique shows slight increase of water contact angle on the surface of the samples. Therefore, another technique that should be easier and more convenient than electrospray, which is spin coating is employed. To increase the hydrophobicity of PMMA sheet, treated P(MMA-co-EGDMA) beads with Alkyl Ketene Dimer were applied in this technique.

The contact angle values of water droplet on the surface of PMMA sheets after treatment by treated P(MMA-co-EGDMA) beads at room temperatures, 45, and 60 °C using different ratios of chloroform: cyclohexane (1:1, 1:2, and 2:1) are shown in **Table 7**. The samples were measured for 3 sets. At a 1:1 ratio of mixed solvent, the highest contact angle value of about 153.2° ± 12.3° and 160.2° ± 4.5° are observed at
45 and 60 °C respectively. While the contact angle value at room temperature was about 135.1° ± 5.4°. The result from the next ratio of 1:2 shows high contact angle as 1:1 ratio, which was 160.0° ± 4.3° and 154.4° ± 5.7° at 45 and 60 °C respectively, while at room temperature the contact angle value was 149.9° ± 2.8°. The last ratio of 2:1 exhibits the lowest contact angle values, compared to others ratios at every temperature conditions. But contact angle values of this ratio still shows improvements in hydrophobicity of PMMA sheets, compared with neat PMMA sheet which has the contact angle value about 76.4°. The CA values of this system can be said that they increase in the range of about 41.6° to 83.8° from the original PMMA.

Table 7. Results of water contact angle of PMMA sheets after spin coating with nanobeads treated with AKD in chloroform: cyclohexane mixed solvent at various ratios and temperatures.

<table>
<thead>
<tr>
<th>Water Contact Angle</th>
<th>RT</th>
<th>45 °C</th>
<th>60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1 (CHCl₃: C₆H₁₂)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>with 8% beads</td>
<td>135.1° ± 5.4°</td>
<td>153.2° ± 12.3°</td>
<td>160.2° ± 4.5°</td>
</tr>
<tr>
<td>without beads</td>
<td>86.7° ± 3.7°</td>
<td>116.8° ± 14.2°</td>
<td>106.1° ± 8.9°</td>
</tr>
<tr>
<td>1:2 (CHCl₃: C₆H₁₂)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>with 8% beads</td>
<td>149.9° ± 2.8°</td>
<td>160.0° ± 4.3°</td>
<td>154.4° ± 5.7°</td>
</tr>
<tr>
<td>without beads</td>
<td>89.4° ± 4.2°</td>
<td>82.7° ± 2.7°</td>
<td>90.1° ± 1.7°</td>
</tr>
<tr>
<td>2:1 (CHCl₃: C₆H₁₂)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>with 8% beads</td>
<td>124.8° ± 5.1°</td>
<td>118.0° ± 3.8°</td>
<td>151.6° ± 3.0°</td>
</tr>
<tr>
<td>without beads</td>
<td>101.9° ± 4.5°</td>
<td>92.4° ± 6.2°</td>
<td>98.9° ± 12.6°</td>
</tr>
</tbody>
</table>

Moreover, the results from PMMA sheets treated with mixed solvent (without beads) also shown in Table 7 in order to compared the wettability between 2 systems. At a 1:1 ratio of mixed solvent, the highest contact angle values are observed at 45 and 60 °C respectively of about 116.8° ± 14.2° and 106.1° ± 8.9°. While the contact angle value at room temperature was about 86.7° ± 3.7°. The result from 1:2 ratio shows contact angle value less than 1:1 ratio, which was 82.7° ± 2.7° and 90.1° ± 1.7° at 45
and 60 °C respectively, while at room temperature the contact angle value was 89.4° ± 4.2°. For the final 2:1 ratio, the values were observed at the same range of temperatures. At room temperature was 101.9° ± 4.5°, which is close to 98.9° ± 12.6° observed from 60 °C. While the value from 45 °C was 92.4° ± 6.2°. These enhancement properties were obtained from the surface roughness created by solvent mixture effect.

4.4.2 FTIR spectroscopy

From water contact angle results, the suitable temperatures for the experiment that give high contact angle value are 45 and 60 °C. Samples prepared at these temperatures were characterized by ATR-FTIR spectroscopy. The spectra of PMMA products after treatments at optimum conditions show a characteristic band of P(MMA-co-EGDMA) at 1766 cm⁻¹, indicating the presence of the particles as embedded species on the surface. The relative intensity of the band is significantly similar, however, reflecting comparable contents of the impregnated particles. A major difference in the spectra is observed in the relative intensities of vibrational modes due to Alkyl Ketene Dimer. The different between 2 temperatures is that the higher relative intensities of these modes in the treated products at 45°C (Figure 17), is likely a result from the higher efficiency of the mixed solvent system (chloroform: cyclohexane). When the treatment was conducted at 60°C, an evaporation of the solvent may lead to a change in the mixed solvent ratio, and leads to lower efficiency (Figure 18).
Figure 17. ATR-FTIR spectra of PMMA sheets after spin coating with P(MMA-co-EGDMA) at 45 °C using mixed solvent at various ratios.

Figure 18. ATR-FTIR spectra of PMMA sheets after spin coating with P(MMA-co-EGDMA) at 60 °C using mixed solvent at various ratios.
4.4.3 FE-SEM Analysis

PMMA sheets prepared from spin coating by treated beads suspension in mixed solvent at 1:1 ratio was investigated by FE-SEM analysis, as this ratio show a high contact angle value, as summarized in Table 7. At this mixture ratio, many spherical microstructures were generated on the surface of PMMA sheet which were described in Figure 12(a-c). Figure 19 shows the appearance of coated sheet at various temperatures. Figure 19 (a-b) shows many particles of P(MMA-co-EGDMA) conglomerate because of AKD wax, which was similar to Figure 15(a). While, there are plenty of hole microstructures picture c-d) but these structures are different from Figure 12(g-i), as these holes were created by AKD wax that coated on the surface of PMMA sheet in which the reasons of this generation believed the same. The last two pictures e) and f) which was conducted at temperature 60 °C, the surface of PMMA sheet was less etched by chloroform because the solvent evaporate very fast at this temperature. Therefore, the P(MMA-co-EGDMA) particles were combined together in very short time.
Figure 19. FE-SEM images of PMMA sheets after treatment with treated P(MMA-co-EGDMA) nanobeads in mixed solvent a-b) at room temperature, c-d) at 45 °C, and e-f) at 60 °C by spin coating technique at magnification of 3,000X and 25,000X, respectively.
4.5 PMMA sheets prepared from a dip coating technique by treated nanobeads suspension in solvent/nonsolvent mixture

4.5.1 Wettability

The results of water contact angle of the samples prepared from spin coating technique provides the suitable ratio of solvent mixture and processing temperature. The next step of the experimental was optimization of embedding methods. Dip coating is one of the easy process, in terms of simple process and short time treatment.

Contact angle values of water droplet on the surface of PMMA sheets after treatments at room temperatures, 45, and 60 °C with different ratios of chloroform: cyclohexane (1:1 and 1:2) are summarized in Table 8. The samples were measured for 3 sets. At a 1:2 ratio of mixed solvent, the highest contact angle value of about 139.6° ± 1.0° and 152.2° ± 3.8° are observed at room temperature and 45 °C, respectively, while the contact angle value at 60 °C was about 126.2° ± 2.4°. The result from the next ratio of 1:1 shows smaller contact angle than the 1:2 ratio, which was 133.4° ± 1.2° and 107.0° ± 9.1° at room temperature and 45 °C, respectively, while the contact angle value at 60 °C was about 90.7° ± 1.8°, which was the smallest compared to others. The ratio of 2:1 was not examined due to its lower values obtained from the spin coating technique. Due to contact angle values of this method lower than the spin coating technique. Therefore, dip coating technique was not applied to further study.

Table 8. Results of water contact angle of PMMA sheets after dip coating with nanobeads treated with AKD in chloroform: cyclohexane at different ratios and temperatures.

<table>
<thead>
<tr>
<th>Water Contact Angle</th>
<th>RT</th>
<th>45 °C</th>
<th>60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>8% Beads in 1:1 (CHCl₃:C₆H₁₂)</td>
<td>133.4° ± 1.2°</td>
<td>107.0° ± 9.1°</td>
<td>90.7° ± 1.8°</td>
</tr>
<tr>
<td>8% Beads in 1:2 (CHCl₃:C₆H₁₂)</td>
<td>139.6° ± 1.0°</td>
<td>152.2° ± 3.8°</td>
<td>126.2° ± 2.4°</td>
</tr>
</tbody>
</table>
5.1 Conclusion

P(MMA-co-EGDMA) micro-/nanoparticles were obtained from micro-suspension polymerization. Nanoparticles were treated with AKD agent to enhance hydrophobic property for development of PMMA’s surfaces. The treated particles were applied for surface treatment of polymer product. There are many techniques were examined for this study, such as dissolution in solvent, electrospray, spin coating and solvent/nonsolvent, and dip coating techniques.

For the stability test of nanoparticles, after treatment with high heat and solvent systems. The morphology of particles still unchanged as confirmation by FE-SEM images. Therefore, they are suitable for further chemical treatment at both normal and high temperature processes.

PMMA sheets after treatment with both micro- and nanobeads, the contact angle slightly increases, the result as shown in Table 6 (by electrospray technique). The contact angle value of treated sheets is about 81.0° ± 1.8° which is about 5° increased from original PMMA sheets. After applied spin coating instead the CA is sharp increase to greater than 150° and up to 160° when treated at suitable conditions and mixed solvent ratio.

From the result of ATR-FTIR spectra, its provide confirmation on the presence of treated P(MMA-co-EGDMA) particles on the surface of PMMA’s products, as shown in Figure 14. Original PMMA sheet shows characteristic bands at 1720 (C=O stretching) and 1145 cm⁻¹ (O–C and C–O stretching), while the P(MMA-co-EGDMA) particles exhibit an additional unique band at 1766 cm⁻¹ (C=O stretching). Figure 16 shows other sharp modes at 1848, 1720, 1470, and 1085 cm⁻¹ are associated with the hydrophobic agent.

ATR-FTIR spectra of the PMMA products after the treatments at optimum conditions at 45 and 60°C show a characteristic band of P(MMA-co-EGDMA) at 1145 cm⁻¹, indicating the presence of the particles as embedded species on the surface. The relative intensity of the band is significantly similar, however, reflecting comparable
Contents of the impregnated particles. A major difference in the spectra is observed in the relative intensities of the 1848 and 1470 cm\(^{-1}\) modes, which are due to the hydrophobic agent (AKD). The higher relative intensities of these modes in the products treated at 45 °C, is likely a result from the higher efficiency of the mixed solvent system. When the treatment was conducted 60 °C, which is close to the boiling point of chloroform, an evaporation of the solvent may lead to a change in the mixed ratio and hence lowers the efficiency of the solvent/nonsolvent system. However, all functional groups present in spectra between Figure. 17 & 18 are similar.

5.2 Recommendations

The solvents used in the experiment can evaporate quickly and can cause skin and respiratory system irritation. The experiment should be conducted with care by wearing protective costume, equipment such as glasses, gloves, and fume hood in order to reduce the risk of vapor diffusion. Moreover, as the solvents evaporates fast the experiment must be conducted and completed within short time, otherwise the ratio of solvent mixture will be changed leading to some inaccurate results.
References


Y. S. Song, et al. (2003). Effectiveness of polypropylene film as a barrier to migration from recycled paperboard packaging to fatty and high-moisture food, Food Additives & Contaminants, 20:9, 875-883.
Appendices
Appendix A

Figure A.1 PMMA sheets before and after treatment by solvent mixtures with treated nanobeads by spin coating technique at different temperature (RT, 45, and 60 °C) and various ratios (1:1, 1:2, and 2:1) of chloroform: cyclohexane.

Figure A.2 PMMA slabs after immersion in solvent mixtures with treated nanobeads at different temperature (RT and 45 °C) and various ratios (1:1 and 1:2) of chloroform: cyclohexane.