



Creating low energy paint surface using hollow sub-micron-latex particles



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ABSTRACT

In this study, core-shell hollow nano-particles in latex form (nano-HLPs) were successfully prepared by using a hydrophobic styrene/methyl methacrylate mixture as shell materials and methacrylic acid/methyl methacrylate/butyl acrylate as core material. Scanning electron microscopy (SEM) images and dynamic light scattering measurements showed that the HLPs had average size of 600 nm. The nano-HLPs were used to obtain more hydrophobic paint surfaces. They were mixed with water based acrylic outdoor paint in different proportions and applied to metal surfaces. The coated surfaces were kept at 60 °C and 80 °C for 1 h to allow the nano-HLPs to move to the surface, which resulted in their surface enrichment. Thus, more hydrophobic paint surfaces were obtained. The changes in surface energy values of the coated surfaces with temperature and composition were followed by contact angle measurements using Young-Dupre equation. The surface energy was observed to decrease with increasing temperature and nano-HLPs portion of the outdoor paint.

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1. Introduction

In the coating process, the surface energy of substrate and coating material are of great importance. Polyethylene and polypropylene are examples of low energy surfaces as they consist of non-polar hydrocarbon bonds so that polar liquids tend to form droplets on the surface rather than spread out Lee, [1]. Although, due to the dissimilarity, it is difficult to coat low energy surfaces with polar materials, and vice versa, there are numerous ways for converting the surfaces to be compatible with each other by modifications. All the methods aim to create compatibility at the interface, which can be achieved by coating the substrate surfaces with amphiphilic molecules or moving the hydrophobic species to the surface.

Over the last decade, there have been growing interests in the use of nano-hollow latex particles (nano-HLPs) in controlled drug delivery as drug carriers, in the paint industry as opacifying agents and controlling the vibrational resistance as shock absorbers in a polymeric matrix etc., [2–4]. Due to the low cost and increasing environmental sensitivity, in paint formulations, the use of nano-HLPs as opacifying agents would allow replacement of a portion

of the more expensive TiO₂. Nano-HLPs consist of water soluble core surrounded by hydrophobic and low surface energy shell [5]. Generally, the core is prepared from hydrophilic monomers and the shell is made from hydrophobic monomers, which have low surface energy and relatively high T_g [6]. When the nano-HLPs are mixed with paint in basic pH, the cores become more soluble and then absorb water. After nano-HLPs and paint mixture are applied to substrate surfaces, the absorbed water leaves and air voids are formed at the center of the nano-HLPs. Since the refractive index values of air in the core and the polymer matrix are considerably different, the nano-HLPs create opacity in dried film of the paint emulsion which is useful property in paint applications and gives more whiteness and therefore improves painting performance such as gloss and brightness. Furthermore, due to lower density and surface energy compared to the paint matrix, during application, nano-HLPs have a tendency to move to the surface. Incorporating of such a core-shell hollow polymers in water based paint emulsions together with well dispersed titanium dioxide will enhance the opacity. Migration of hollow particles to surface also enhances the hydrophobicity of surface due to the hydrophobic nature of the shell side of the hollow particles. In this study, the effect of surface enhancement of nano-HLPs on the surface hydrophobicity of painted surface was investigated as a function of temperature and composition.

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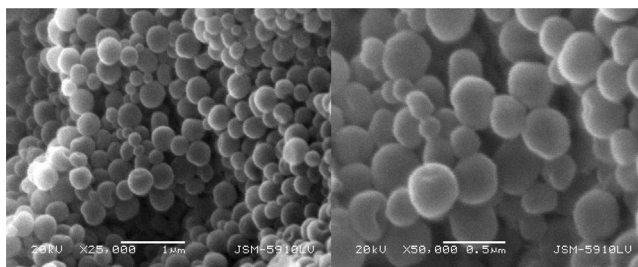


Fig. 1. SEM images of the HLPs at 25000 (left) 50000 (right) magnifications.

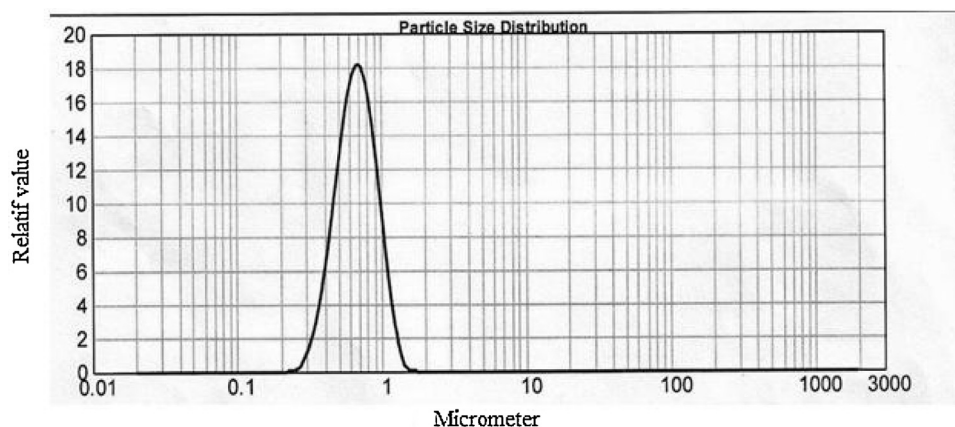


Fig. 2. Particle size distribution of the nano-HLPs.

2. Experimental procedure

2.1. Materials

The following monomers for the HLPs; methyl methacrylate (MMA), *n*-butyl acrylate (BA), styrene(S), and methacrylic acid (MAA) were supplied by Sigma-Aldrich. All the monomers were purified by washing with 5% sodium hydroxide solution for two times followed by vacuum distillation. The initiators, sodium persulfate (SPS), ammonium persulfate (APS), sodium metabisulfite (SMBS), and surfactants were used without purification. De-ionized water was used in the synthesis of the nano-HLPs. The liquid probes used in contact angle measurements, formamide, glycerol, diiodomethane and paraffine (>99% purity) were purchased from Sigma-Aldrich and used without further purification.

2.2. Synthesis of HLPs

The mixture of monomers MMA, MAA and BA were used as core part of the nano-HLPs (step 1) in emulsion polymerization. In the Shell formation step, the core particle synthesized in step 1 was covered with a mixture of shell monomers (styrene, BA, MMA) and they were polymerized on the surface. All the syntheses studies were carried out at Mavi Kimya A.Ş. Turkey.

2.3. Characterization of the nano-HLPs

Solid content: (33%); this was determined by heating as 2 g of residual sample at 120 °C. Viscosity:

(20 cPs); the emulsion viscosity was measured using a Brookfield™ viscometer at 25 °C; pH: 9.0 at 25 °C; density: 1.035 g/cm³, at 25 °C

2.4. SEM

For the determination of size and shape of the nano-HLPs, scanning electron microscopy (SEM) images were taken. For sample preparation, the nano-HLP emulsion were applied to a SEM sample holder and allowed to dry in vacuum at room temperature to form a thin solid polymer film. The SEM images of dried samples were taken after sputter coating in vacuum with a thin layer of gold. Surface morphology was examined using SEM (Jeol JSM-5910 LV, Tokyo, Japan). The SEM images of the nano-HLPs are shown in Fig. 1.

2.5. Particle size distribution

A dynamic light scattering instrument (Malvern Mastersizer 2000) was used to determine the particle size and particle size distribution of nano-HPLs as shown in Fig. 2.

2.6. Preparation of paint formulation

Paints were dispersed by the following formulation using a lab type dissolver at room temperature. The formulation is given in Table 1.

2.7. Contact angle (CA) measurements

Static CA measurements were recorded using a Nikon microscope and digital camera model D90. The CAs of the Liquid probes (deionized water, formamide, glycerol, diiodomethane and paraffine) were evaluated by using Open Source Image software. Drops of each probe (20 μL) were deposited on a dry and clean film surface at room temperature and CAs were measured. Total surface energy of the films and its dispersion and acid-base components were calculated from CAs using van Oss-Good contact-angle evaluation methodology [7].

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