



## Multi-functional urethane epoxy acrylates (UEAs) and their visible-light cured UEA/MSMA-colloid silica nanocomposite films as reinforcement on polycarbonate matrix



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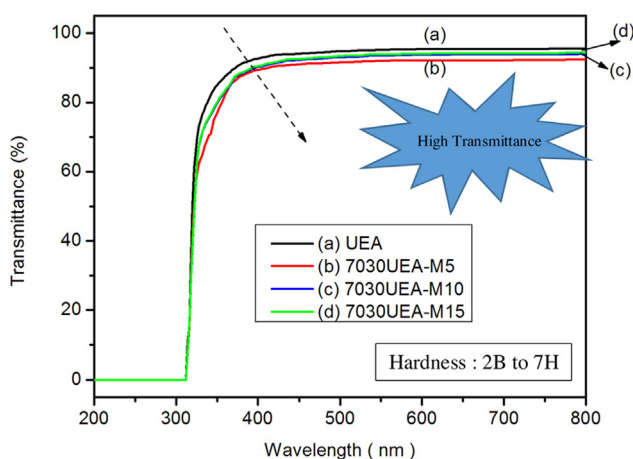
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### HIGHLIGHTS

- The **urethane epoxy acrylate (UEA)** and **MSMA-colloidal silica** nano-hybrids materials showed the homogeneously films.
- The nano-hybrids films showed the highly transmittance (91.2%).
- The hardness and adhesion tests of nano-hybrids films cured on polycarbonate (PC) reached 7H and 5B.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The multi-functional methacrylates are prepared through polycondensation by isophorone diisocyanate (IPDI), pentaerythritol triacrylate (PETA) reacting with epoxy acrylate, 2,2-bis[4-(20-hydroxy-30-methacryloyloxypropoxy)phenyl]propane (Bis-GMA), the series of urethane epoxy acrylate resins are successfully synthesized. The urethane epoxy acrylate oligomer's structure is characterized by Fourier transform infrared spectroscopy (FT-IR). In order to enhance the hardness of the resins, the colloidal silica is successfully reacted with 3-(trimethoxy silyl)propyl methacrylate (MSMA). The characteristics of the colloidal silica/MSMA are measured by means of dynamic light scattering (DLS). The acrylate functional groups are chemically bonded to the surface of the silica spheres, enhancing the compatibility of the organic/inorganic interface; the highest hardness can reach 7H, and the adhesion of the PC reaches 5B.

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The thermal properties of the cured coating are investigated by means of thermal gravimetric analysis (TGA), with the decomposition temperature ( $T_d$ ) reaching up to 440 °C.

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## 1. Introduction

In the past few years, polycarbonate (PC) is one of the most important thermoplastics for a wide variety of applications [21], especially in cases where optical clarity is important and conspicuous mechanical properties are required. PC is easily worked, molded, and thermoformed [19,20]. The global polycarbonate market forecast to 2020 is projected to grow from more than \$12.0 Billion. It is expected for the near future that rigid plastic optical components will replace parts made from glass whenever improved properties or lower costs can be achieved. Polycarbonate has higher impact strength and considerable thermal stability, attended to bisphenol A. However, the disadvantages of this material are related to its low mechanical hardness and its sensitivity to UV light [22]. In order to enhance the PC mechanical hardness for applications, coatings exhibiting a high resistance to protect are required. These poor physical properties pose a barrier for the adoption of PC in a wide range of industrial applications. Several approaches have been presented for the modification of PC, aimed at extending and widening its application within the engineering field without affecting its transparency. The vast majority of the scientific efforts have been dedicated to the preparation and characterization of the relative nanocomposites obtained by inclusion of nano-objects of different nature, due to the fact that the addition of well-dispersed nanofillers to transparent polymer matrices or improve the properties of the surface of these polymers without altering their bulk properties to transparent polymer matrices could preserve their optical clarity with the additional improvement of stiffness, impact resistance and scratch resistance.

Acrylic resin is a thermoplastic polymer which can be heated and manipulated repeatedly [1]. The prepolymers or oligomers are often complex structures based on, for example, epoxy acrylates [2,3], urethane acrylates [1,4–7], polyether urethane acrylates [8,9], polyester acrylates [9–11], polyether acrylates [12,13] and acrylated oils [14]. The structures and formulations of the diluent monomers and prepolymers can be varied to suit particular applications and property requirements. From previous studies [7], the urethane-modified epoxy acrylates exhibited low degrees of polymerization shrinkage because of their relatively high molecular weight and cohesive energy density resulting from the presence of the urethane group. In this study, we used isophorone diisocyanate (IPDI), pentaerythritol triacrylate (PETA) reacting with 2,2-bis[4-(20-hydroxy-30-methacryloyloxypropoxy) phenyl]propane (Bis-GMA), which is the base monomer most commonly used in restorative materials to synthesize urethane epoxy acrylates (UEA) as reinforcement. As for enforcing the hardness of the **urethane epoxy acrylates (UEAs)**, the colloidal silica played an important role in this study. Colloidal silica has a relatively high hardness and a good compatibility of the organic/inorganic interface after being modified with 3-(trimethoxy silyl) propyl methacrylate (MSMA) [7,15–18]. From a previous study [16], the highest hardness of the waterborne polyurethane hybrid with 30% MSMA-colloidal silica reached 4H. Therefore, the use of colloidal silica as filler was an indispensable component.

In this study, we focused our attention on synthesizing **urethane epoxy acrylates (UEAs)** and having them react with functionalized colloidal silica to form hardness composites, cured by visible light curing on polycarbonate (PC) optical film. A hybrid

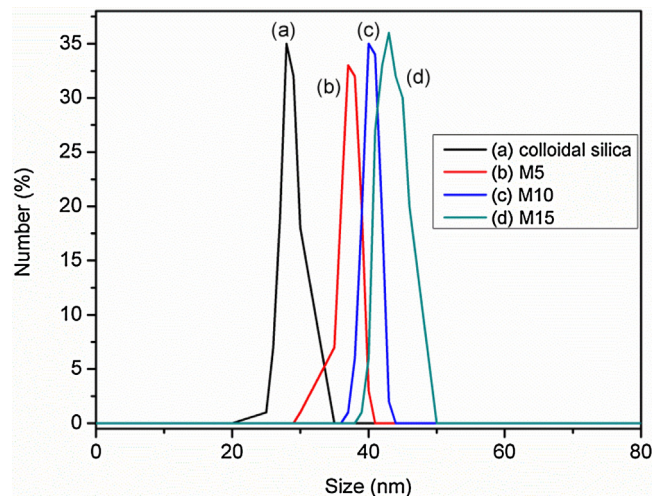


Fig. 1. Particle size of MSMA-colloidal silica (a) colloidal silica, (b) M5, (c) M10, and (d) M15.

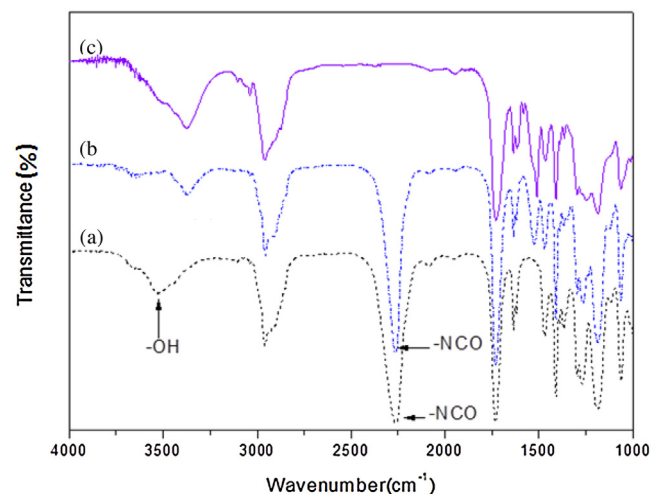


Fig. 2. FT-IR spectra of **urethane epoxy acrylates (UEAs)** (a) initial reaction of IPDI and PETA, (b) 2 h of IPDI and PETA reaction, (c) the end of synthesis.

organic/inorganic urethane acrylate oligomer was synthesized and characterized by FT-IR with the characteristics of the **colloidal silica/MSMA** measured by dynamic light scattering (DLS) and scanning electron microscope (SEM). The thermal properties of the cured coating were investigated using thermal gravimetric analysis (TGA).

## 2. Experiment

### 2.1. Materials

Isophorone diisocyanate (IPDI, 98%) was purchased from Acros. Pentaerythritol triacrylate (PETA, 99%), 2-bis[4-(20-hydroxy-30-methacryloyloxypropoxy) phenyl]propane (Bis-GMA, 98%) and Irgacure 184 (I184, 99%) as a photoinitiator were purchased

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