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Preparation of epoxy-silica-acrylate hybrid coatings

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Abstract

An organic-inorganic epoxy-silica-acrylate hybrid coating had been prepared by radical solution copolymerization and sol-gel process. The room curing reaction of the hybrid coating was discussed, and its structure, optical properties and thermal stability were studied. The hybrid coatings have multiple functional groups, and the inorganic phase and organic phase are linked by the chemical bonding. When tetraethylorthosilicate (TEOS) mass fraction were 10% and 20%, hybrid coatings had inorganic particle mean sizes of 36 nm and 45 nm, respectively, together with their homogeneously distribution within the polymeric matrix. With increasing of TEOS content, the transmittance in the visible region and the yellow index (YI) of the hybrid coatings after UV irradiation decrease, while the absorbency at 300-400nm, the onset decomposition temperature and maximum weight loss temperature increase.

Keywords

hybrid, sol-gel, epoxy, acrylate, silica

1 Introduction

As novel functional materials, hybrid organic–inorganic hybrid materials offer the opportunity to combine the desirable properties of organic polymers (toughness, elasticity) with those of inorganic solids (hardness, chemical resistance) and have been intensively studied in recent years[1-11].

However, one of the major challenges for preparation of homogeneous hybrid materials with high performance is how to control microstructure and phase separation between organic and inorganic components. It is expected that increased interfacial interactions via hydrogen bonds or covalent bonds between the organic and inorganic phases, will result in superior properties compared to classical composites. Recently, a number of researchers utilize polymer functionalized with trialkoxysilane moieties to facilitate crosslinking reactions with inorganic fillers and successfully retard phase separation. Coltrain and co-worker [12] prepared polymer/silica hybrid materials by in situ polymerization of tetraethoxysilane or tetramethoxysilane in the presence of both trialkoxysilane-functionalized and unfunctionalized polyacrylates. The results showed that trialkoxysilane functionalization could retard phase separation and increase the glass transition temperature (*Tg*) with increasing silicate content. Percy[13] prepared a range of new colloidal vinyl polymer-silica nanocomposites by simply homopolymerization of styrene, methyl methacrylate, etc in the presence of the silica sol to produce colloidally stable inorganic/organic hybrid films with reasonably narrow size distributions and exhibited transmittances of more than 93% in the visible spectrum. In the case of the poly (methyl methacrylate)-silica nanocomposites, the carbonyl ester groups in the polymer are hydrogen-bonded to the surface silanol groups. However, the Tg's of several poly (methyl methacrylate) -silica and polystyrene-silica nanocomposites can be either higher or lower than the Tg of the corresponding homopolymer, depending on the nature of the silica sol. Cardiano[14] prepared the epoxy-silica materials by the reaction of the epoxy derivatives (3-glycidyloxypropyl) methyldiethoxysilane (GLYMS) with the primary amine (3-aminopropyl)triethoxysilane (ATS). The results show that the polymeric network develops either on the organic or on the inorganic side with organic polymer chains covalently linked to inorganic domains.

Up to now, most of the organic-inorganic hybrid materials are epoxy-silica, silica-polyacrylates and epoxy- polyacrylates[11-16] and there are only very few literatures reporting the preparation of epoxy-silica-acrylate hybrid materials. Acrylic resins have hydrolytic, light, and oxidative stability. Epoxy resins have functional epoxy groups in them and have subsequent excellent characteristics, such as heat resistance and good adhesion. Silica materials have excellent light, heat and water resistance. We combined epoxy resin and silica with acrylic resins to actualize these advantages to prepare the composites. In this study, a high performance epoxy-silica-acrylate organic–inorganic hybrid coatings based on methacryloxypropyl trimethoxy silane(*KH*570) capped acrylic resin, epoxy resin E-44 and tetraethyl orthosilicate (TEOS) were prepared by mixing *KH*570 capped acrylic copolymers with TEOS sols. Subsequently, the epoxy resin E-44 and aminopropyl triethoxysilane (KH550), as basic catalyst and curing agent were added to form transparent hybrid coatings. The structure, thermal and optical properties of the hybrid coatings were characterized by atomic force microscopy (AFM), thermogravimetric analysis (TGA) and UV-vis spectrum, respectively. These epoxy-silica-acrylate hybrid coatings display the properties associated to epoxy and acrylic polymers and silica-containing compounds.

2 Experimental

2.1 Materials

Butyl acrylate (BA) was purchased from Tianjin Bodi chemical company(China) and washed by 20% sodium hydroxide three times. Maleic anhydride(MA) and tetraethyl orthosilicate(TEOS) were purchased from Chengdu Kelong chemical company(China). Epoxy resin E-44 was purchased from Lanzhou Lanxing company(China); 2-hydroxyethyl methacrylate (HEMA) was purchased from Aldrich company(USA). 3-aminopropyl)triethoxysilane (KH550), 3-methacryloxypropyl) trimethoxy silane(KH570) and ethyl acetate were obtained commercially and used without further treatment. 2,2′- azobisisobutyronitrile (AIBN) was purchased from Shanghai Chemical Reagent Company(China) and recrystallized before use.

2.2 Preparation of KH570-capped acrylic resins

A 250-ml round-bottom flask equipped with mechanical stirrer, thermometer with a temperature controller, and a Graham condenser and a heating mantle was used. Part of solvent ethyl acetate was first charged in the flask. When the flask was heated to 75±2°C, the mixture of, BA and HEMA, MA, KH570 (the weight ratio of BA/HEMA/MA/KH570=6/2.5/1/0.5), 0.5 wt% initiator (AIBN) based on the total monomer weight and residual ethyl acetate were added into the flask using an addition funnel over a period of 1 h. After addition of all ingredients, the reaction was maintained at 70±2°C for additional 4 h to complete the reaction and obtained the KH570-capped acrylic resins.

2.3 Preparation of epoxy-silica-acrylate hybrid coating

To the above formed KH570-capped acrylic resins were added slowly 10% partially hydrolyzed TEOS sol (in weight ratio) and 10% E44(in weight ratio) and 3% KH550(in weight ratio) and the mixtures were evenly stirred at room temperature for a certain time, after which the transparent hybrid organic–inorganic films can be formed after evaporation of the volatile solvent.

2.4 UV light aging test

The epoxy-silica-acrylate hybrid coatings are irradiated by a 1000W high pressure Hg lamp under ambient temperature and humidity. The transmittances of the irradiated hybrid coatings are measured by UV-vis spectrophotometer, and the Yellow Index(YI) can be calculated by the following equation(1):

$$YI = \frac{(T_{420}-T'_{420})-(T_{680}-T'_{680})}{T_{580}} \times 100\% \qquad (1)$$

Where T420 and T′420 are the transmittances at 420nm of the hybrid coatings before and after irradiation; T680 and T′680 are the transmittances at 680nm of the hybrid coatings before and after irradiation; T580 is the transmittances at 580nm of the hybrid coatings before irradiation.

2.5 Characterizations

UV-visible absorption spectra were recorded on a Thermo Spectronic Genesys TM 10 series spectrophotometer with a quarts cuvette possessing an optical path length of 1 cm. Infrared spectra (FTIR) was taken with a 510 Nicolet FTIR spectrometer. Morphologies were examined by AFM measurements using a Digital Instruments NanoScope IIIa scanning probe microscope and a Hitachi S-530 scanning electron microscope(SEM). Thermogravimetric analysis (TGA) was performed on a TGA 2950 (TA Instruments) at a temperature range of 20–800°C with a heating rate of 10°C/min under air atmosphere.

3 Result and discussions

3.1 Curing of the hybrid coatings at room temperature

Fig. 1 shows DSC exotherms of MA- KH550, KH550-EOR, and MA-EOR systems by stoichiometric ratio under nitrogen atmosphere, respectively. MA- KH550 and KH550-EOR systems have low onset temperatures at 20°C and 25°C and peak maximum temperatures at 73°C, 85°C, respectively, indicative of the possible curing of the hybrid coatings at room temperature. However, MA-EOR system exhibit high onset temperature s at 78°C and broad exothermic peaks at 160°C during cure.

From the DSC of MA- KH550, KH550-EOR, MA-EOR systems it can be assumed that silane coupling agent KH550 can both react with EOR and MA at room temperature to covalently link the organic polymer chains with inorganic domains, formed by the co-hydrolyzation and co-polycondensation of partially hydrolyzing TEOS, KH570 and KH550. Therefore it is possible to prepare the room temperature cured epoxy-silica-acrylate hybrid coatings by the above systems.

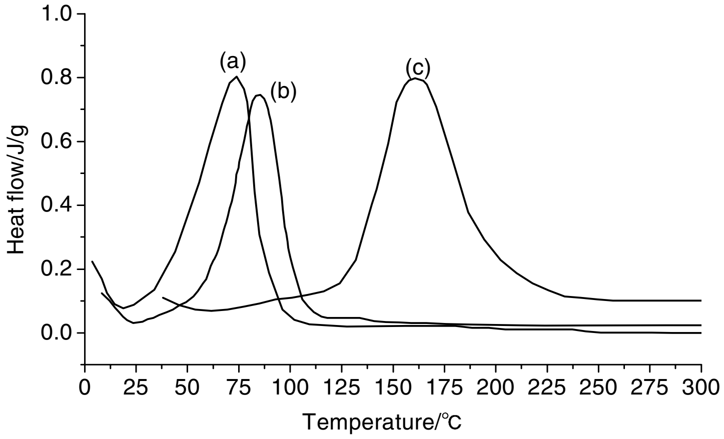


Fig.1 DSC curves of (a) MA- KH550, (b) KH550-EOR and (c) MA-EOR.
MA: maleic anhydride; EOR: epoxy resin.

3.2 Optical properties of the hybrid coatings

Figure 2 illustrates the UV–vis spectra of the hybrid coatings with different TEOS content.

In the range of 400–700 nm wavelengths (visible light), more than 70% transmittance for the hybrid coatings is observed, indicating that silica dispersed within the polymer matrix is in a nanoscale and therefore the hybrid coatings are transparent. However, in the range of 300–400 nm (UV rays), the transmittance of the hybrid coatings decreases dramatically, suggesting nanosilica can shield UV rays.

As TEOS content increased, the absorbance obviously increased and transmittance greatly decreased in the wavelength range of 300-400nm(UV region). This means that nano-silica can clearly increase the UV absorbance of hybrid coatings, and the hybrid coatings containing higher TEOS content seem to have relatively better UV absorbance than that of those with lower ones.

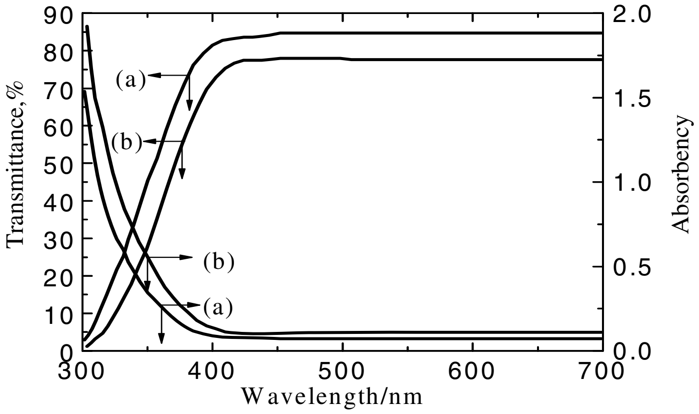


Fig.2 UV-Vis spectra of silicon-acrylic- epoxy resin hybrid coatings with different TEOS content(*w*(EOR)=10%).(a) *w*(TEOS)=10%; (b) *w*(TEOS)=20%.

3.3 FTIR study of the hybrid coatings

The FTIR spectrum in the range 4000–500cm^{-1} of the hybrid coatings was shown in Fig 3. Stretching vibrations of NH and OH were observed at 3477cm^{-1} and the dual peak or multiple peak ascribed to the primary amine does not appear, indicative of complete reaction of the primary amine of KH550 with anhydride and epoxy group at room temperature. It is noteworthy that the characteristic vibrations of amide group at 1650 and 1560cm^{-1}[17] and the characteristic peak of carboxylic acid at 1701cm^{-1} appear as a result of the reaction between the anhydride group of maleic anhydride and amine group of *KH*550 at room temperature. In addition, 1783 and 1858cm^{-1} are assigned to the characteristic peaks of anhydride groups, and 910[19] and 1250cm^{-1}

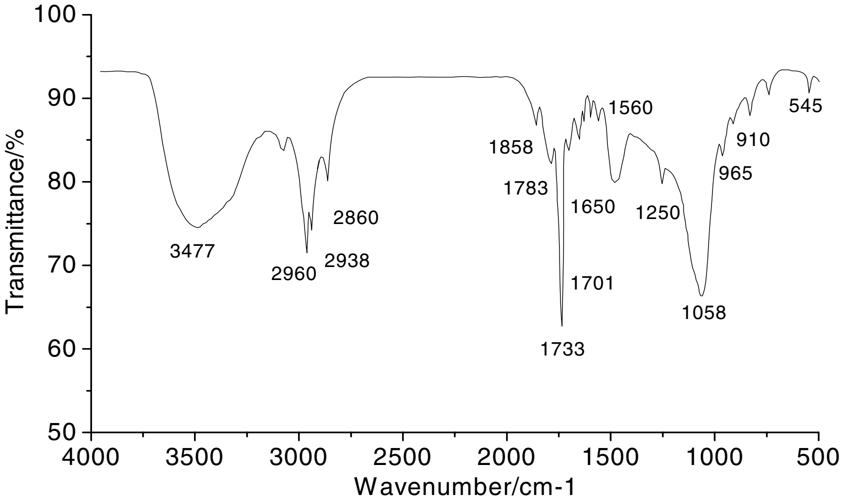
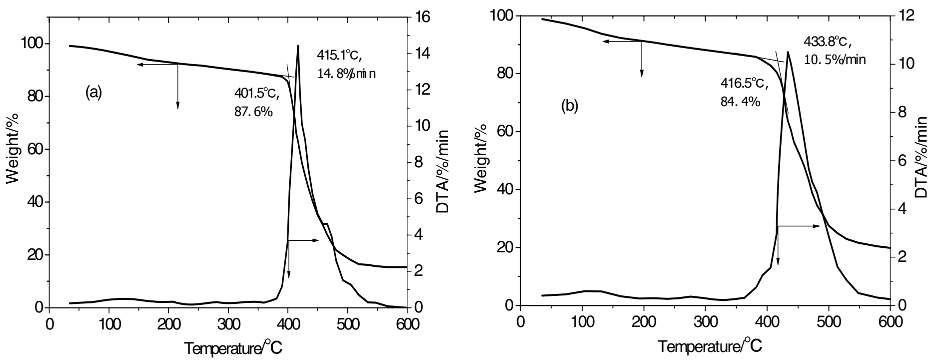


Fig.3 FTIR spectrum of silicon-acrylic- epoxy resin hybrid coatings (*w*(TEOS)=20%, *w*(EOR)=10%).

[18] the characteristic peaks of epoxy groups, respectively, indicating that there still exist some unreacted anhydride and epoxy groups due to the excess amount of anhydride and epoxy groups as compared to that of *KH*550. Besides the characteristic peaks of the organic molecules, the band at 965 cm^{-1} is the bending frequency of Si-O-R group, an indicative of incomplete hydrolysis of TEOS and *KH*550;545cm^{-1}[20] is the vibration peak of Si-O-Si, formed by the condensation between Si-OH. This FTIR analysis indicated a bridging existed between inorganic/organic phases, which could better the compatibility between the inorganic phase and organic phase and retard phase separation.

3.4 Thermal stability of the hybrid coatings

The thermal properties of the hybrid coatings with different TEOS content were evaluated with TGA in a nitrogen environment and are shown in Figure 4. Both the degradation temperature at which drastic weight loss occurs(T_{max}) and the decomposition onset temperature(T_{onset})increases with the increase in the TEOS content. For example, when TEOS content increase from 15% to 25%, T_{onset} and T_{max} increase from 401.5°C to 416.5°C and 415.1°C to 433.8°C, respectively, indicative of an enhanced thermal stability of the hybrid films with TEOS content. The silica particles incorporated in the polymer networks, acts as a network former and therefore the motion of the organic polymer is restricted as a function of the Si–O–Si linkages, and it need much more energy to decompose the organic chains.

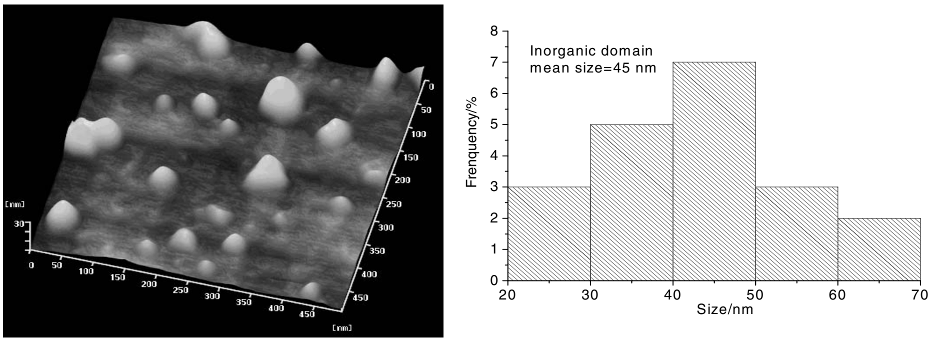


(a) *w*(TEOS)=15% (b) *w*(TEOS)=25%

Fig.4 Effects of TEOS content on thermal stability of the hybrid coatings (w(EOR)=10%).

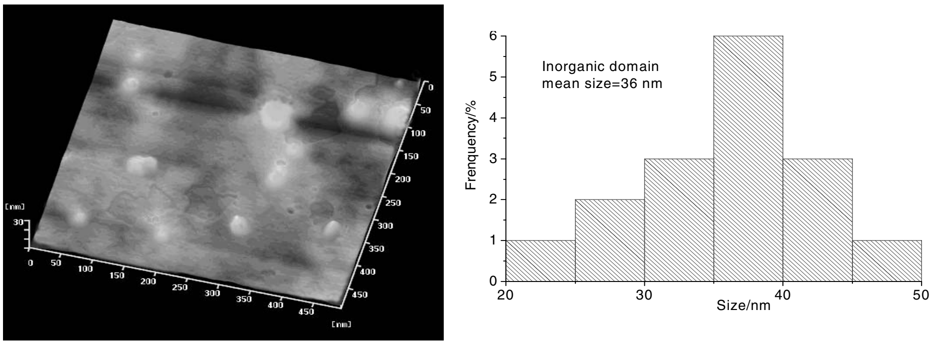
3.5 AFM images of the hybrid coatings

Figure 5 showed the AFM topography images of the epoxy-silica-acrylate hybrid coatings, to investigate the homogeneity of the hybrid coatings. From the AFM micrograph, it can be seen that the silica particles were homogeneously dispersed in the polymer matrix. For 15% TEOS-containing hybrid coatings, the silica particles with the average diameter of 36nm in the range of about 20–50 nm were observed. However, for 25% TEOS- containing hybrid coatings, the higher silica content led to the larger average diameter of 45nm in the range of about 20-70nm, due to the higher degree of hydrolysis and polycondensation.



(a) AFM photo(w(TEOS)=25%)

(b) Histogram of the SiO_2 domain size(w(TEOS)=25%)



(c) AFM photo(w(TEOS)=15%)

(d) Histogram of the SiO_2 domain size(w(TEOS)=15%)

Fig.5 AFM photos of silicon-acrylic- epoxy resin hybrid coatings and histogram of SiO_2 domain size (w(EOR)=10%).

3.6 Photo stability of the hybrid coatings

Fig 6 indicated the effect of TEOS content on the UV-light-resistance of silicon-acrylic- epoxy resin hybrid coatings. The yellow index(YI) increased continuously at the initial irradiation period and then increased rather slowly, especially for higher TEOS content(20%). In addition, *YI* decreased with increase in TEOS content at the same irradiation time. As indicated by UV-vis spectra, the 20% TEOS-containing hybrid coatings has more than 70% transmittance in the visible light region and still keep transparent, and they can absorb more UV light than 10% TEOS-containing ones do.

Fig 7 showed the effect of EOR content on UV-light-resistance of silicon-acrylic-epoxy resin hybrid coatings (w(TEOS)=5%). The yellow index(YI) increased dramatically at the initial irradiation period and then increased slowly, and the *YI* increase more rapidly with the increase in the EOR content. The possible photodegradation of epoxy mechanism is a free radical mechanism involving both photolysis and photodegradation reactions[21-23], and release some oxidation and degradation by-products and therefore increase the yellow index.

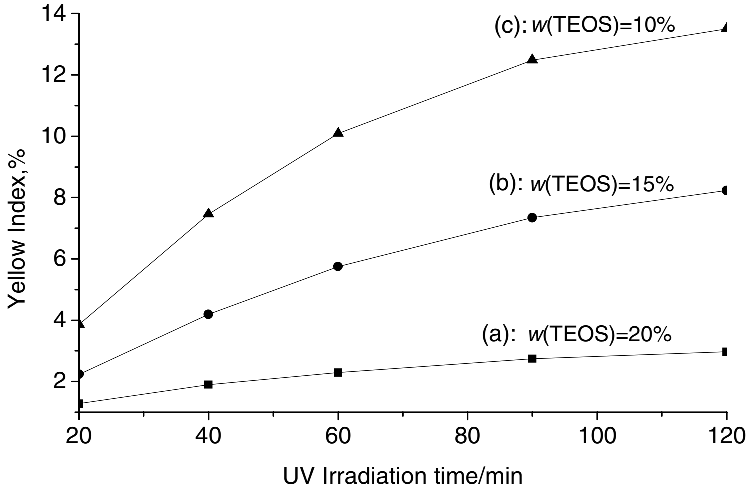


Fig.6 Effect of TEOS content on the UV-light-resistance of silicon-acrylic- epoxy resin hybrid coatings (*w*(EOR)=20%).

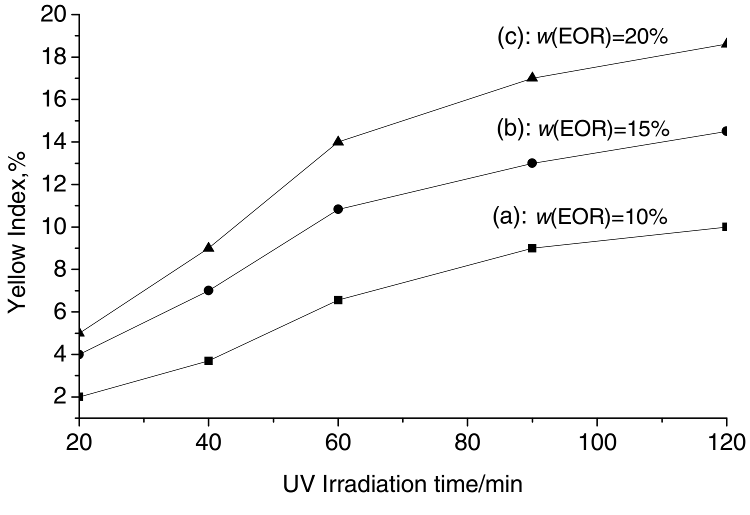


Fig.7 Effects of EOR content on UV-light-resistance of silicon-acrylic- epoxy resin hybrid coatings (*w*(TEOS)=5%).

3.7 Possible formation mechanism of the transparent hybrid coatings

Based on the above data and discussions, a possible formation mechanism of the transparent hybrid films can be given as shown in Fig 8. Firstly MA, BA, KH570 and HEMA can copolymer -ize together to form the KH570 -capped copolymer, and then the partial hydrolysis of TEOS and KH550 and E-44 were added into the above systems. Condensation reactions lead to the formation Si-O-Si bridges and particle growth. These particles are partially hydroxylated, and condensation reactions between them generate a network enclosing the polymeric molecules. From the FTIR spectrum, we can postulate that there exist chemical linkages between the inorganic phase and organic phase. Therefore, the hydrolysis and condensation reactions were controlled by confinement of silica particles inside the polymer matrix, and the phase separation is largely restrained. Finally the transparent hybrid coatings were formed.

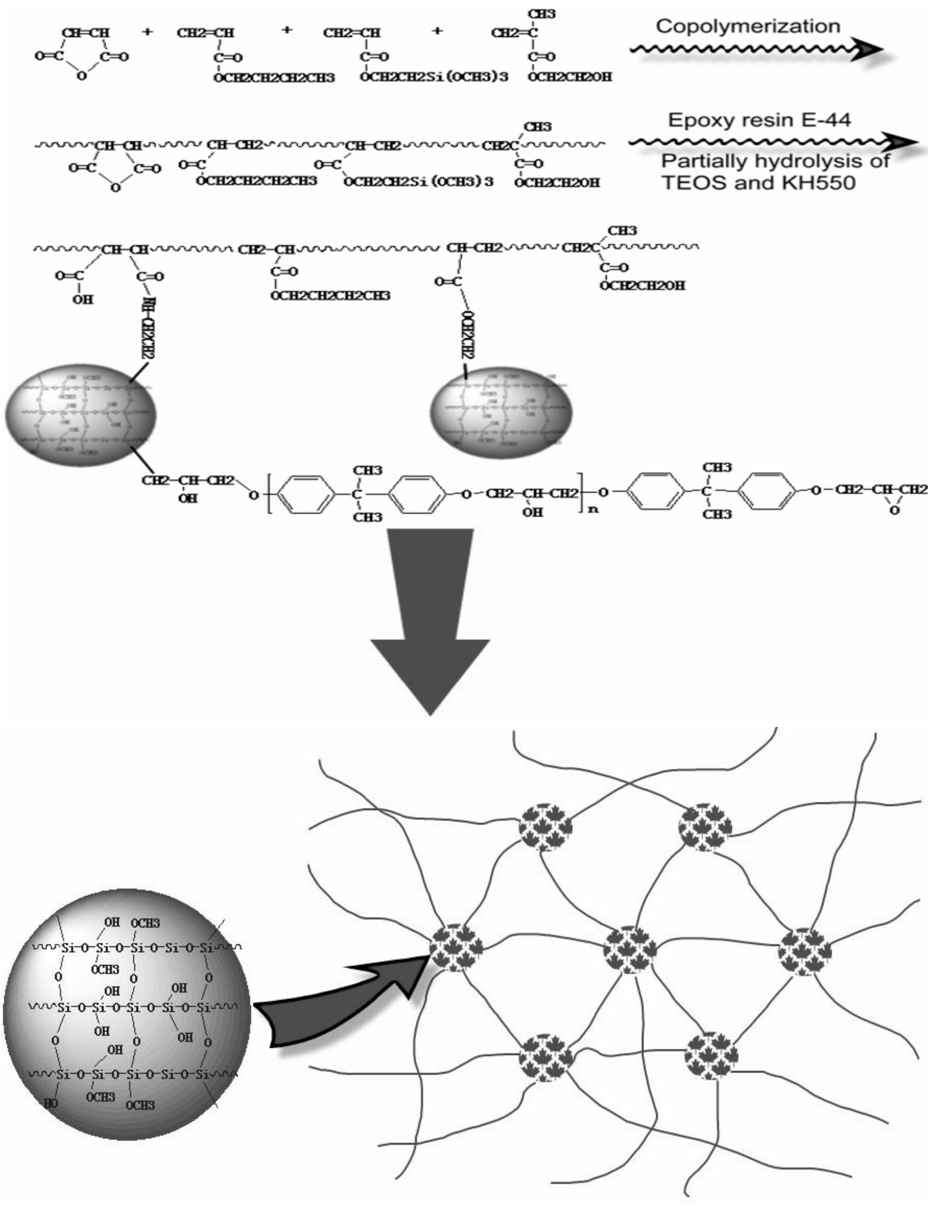


Fig.8 Schematic illustration of the possible formation mechanism of the hybrid coatings.

4 Conclusions

A transparent epoxy-silica-acrylate hybrid material had been prepared by radical solution copolymerization and sol-gel process. FTIR indicate the organic and inorganic phases are linked by chemical bond and the hybrid materials have multiple functional groups, such as anhydride, epoxy, hydroxyl, carboxyl, and alkoxysilane groups which can form networks at room temperature. When tetraethylorthosilicate (TEOS) mass fraction were 10% and 20%, hybrid materials had inorganic particle mean sizes of 36 nm and 45 nm, respectively, together with their homogeneously distribution within the polymeric matrix. With increasing of TEOS content, the transmittance in the visible region of the hybrid materials and the yellow index (YI) decrease, while the absorbency at 300-400nm, the onset decomposition temperature and maximum weight loss temperature increase.

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