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UV-curable nanostructural composites: preparation and properties

Saeed Bastani^{1,2*}, Mohsen Mohammad Raei Nayini¹, Majid Mohseni¹

¹ Surface Coatings and Corrosion Department, Institute for Color Science and Technology, Tehran, Iran

² Center of Excellence for Color Science and Technology, Tehran, Iran

*Corresponding author

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UV-curable systems, Significance and use

Radiation curable coatings and materials solidify by reactions initiated by radiation rather than heat initiated polymerization, solvent evaporation or oxidation. These systems can be stored indefinitely stable and safe in the absence of radiation, and curing reactions occurs on exposure to radiation at ambient temperature [1, 2].

Photopolymerization reactions are commonly characterized by low electrical power input and energy requirements, low temperature operation and no volatile organic compounds release (solvent-free systems) and so the photopolymerization reaction is presented as belonging to a green technology [3]. Radiation cure technology is used in an increasing number of industrial applications because of the remarkable advantages of the process such as ultrafast curing of system and variety of ingredient in their formulations result in wide range of applications. This technology has found its main markets in the graphic arts, microlithography [4-6] and surface treatment of materials with protective coatings [7].

Radiation curable coatings and materials can be classified into two main categories base on the type of radiation: (1) UV-curable materials and (2) EB (Electron beam) curable materials. In UV-curable systems the photon absorption of UV-visible electromagnetic radiation initiates the curing reactions where in EB cure systems the high energy electrons play the role of excitation [3].

"UV-Curing" is based on the principle of photoamorcured polymerizations, the conversion of a liquid resin into an insoluble polymer material under the irradiation of a light source (in this case, the ultra-violet radiation).

UV-curing is consisting of two classes of reactions: free radical polymerization and cationic-initiated chain-growth polymerization.

Acrylate monomers are highly reactive and so are the most widely used in UV curing formulations as well as acrylated oligomers.

Chain growth polymerization

Chain growth and step growth polymerization are proceeds by a distinctly different mechanism. In chain growth polymerization, a reactive center produced, such as a radical, an anion or cation, adds many monomer units in a chain reaction and grows rapidly to immediate formation of a high-molecular weight polymer [8].

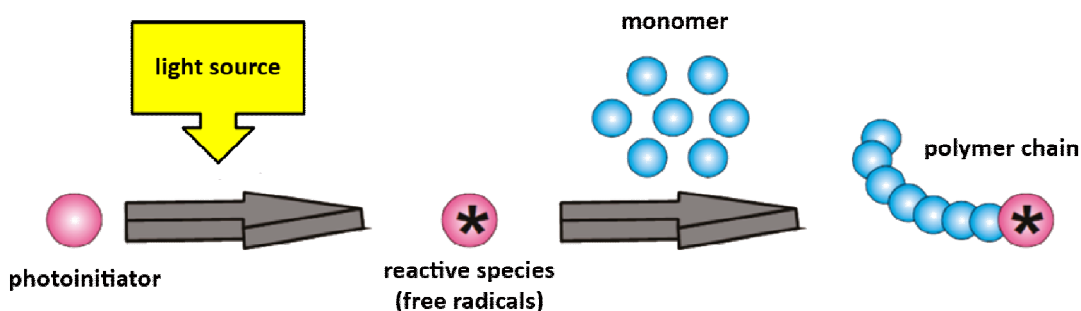
The monomer concentration decreases as the reaction proceeds and the overall percent conversion of monomer to polymer increases with time. At any time the reaction mixture contains monomer, polymer and growing chains. During the polymerization the molecular weight of the polymer remains relatively unchanged.

For a step growth polymerization the situation is different and any two molecular species present can react, whereas only monomer and propagating chains can react with each other in chain polymerization [8].

Kinetics and chemistry of photopolymerization

Initiation reactions

Radically photoinitiated polymerization is usually applied to a chain process that is initiated by light and both the initiating species and the growing chain ends are radicals (Scheme 1) [9].



SCHEME 1

Radically photoinitiated polymerization

Although it gives the name to the whole process, the role that light plays in photopolymerization is restricted to the very first step, namely the absorption and generation of initiating species. A photoinitiator or photoinitiator system is defined as a molecule or combinations of molecules that, upon absorption of light, initiate the polymerization. Photoinitiators for radical polymerization are classified as α -cleavage initiator (via photofragmentation process, type I) and H-abstraction type (type II) initiators [2, 9].

From the point of view of elementary reaction steps, free radical cross-linking polymerization does not differ from the linear polymerization of monovinyl compounds and involves initiation, propagation, chain transfer and termination. The rate of photochemical initiation is given by [2, 8]

$$R_i = 2\phi I_{\text{abs}} \quad 1-1$$

Where I_{abs} is the intensity of absorbed light in moles (called Einsteins in photochemistry) of light quanta per liter-second and ϕ is the number of propagating chains initiated per light photon absorbed. ϕ is referred to as the quantum yield for initiation. The factor of 2 in Eq. 1-1 is used to indicate that two radicals are produced per molecule undergoing photolysis. The factor of 2 is not used for those initiating systems that yield only one radical instead of two. Thus the maximum value of ϕ is 1 for all photoinitiating systems. ϕ is synonymous with f in that both describe the efficiency of radicals in initiating polymerization. The classical equation for the polymerization rate is [2, 8]

$$R_p = k_p[M]\left(\frac{R_i}{2k_t}\right)^{1/2} \quad 1-2$$

Where $[M]$ is the concentration of functional groups, R_i initiation rate and k_p and k_t are the propagation and termination rate coefficients, respectively. An expression for the polymerization rate is obtained by substitution of Eq 1-1 into Eq 1-2 [2, 8]

$$R_p = k_p[M]\left(\frac{\phi I_{abs}}{k_t}\right)^{1/2} \quad 1-3$$

The absorbed light intensity I_{abs} is obtained from a consideration of the Beer–Lambert law in the form [8]

$$I_a = I_0 - I_0 e^{-\alpha[PI]D} \quad 1-4$$

Where I_0 is the incident light intensity at the outer surface of the reaction system and I_a is the intensity of absorbed light on a layer at a distance D (cm) into the reaction system. $[PI]$ is the molar concentration of light-absorbing photoinitiator and α is the absorption coefficient of PI and varies with wavelength and temperature [8].

Photocuring process is characterized by autoacceleration-autodeceleration behavior and the determination of actual rate coefficients is very difficult due to the very early onset of autoacceleration. Although a number of researches estimated the polymerization rate coefficients, the calculated values were not the actual rate coefficients and may be considered as composite values for several processes contributing to propagation and termination. However these measurements reflect the overall suppression of all rate processes during cross-linking of matrix. The determination of rate coefficients for photo-crosslinking systems is depends mainly of the kinetic model describing the polymerization behavior [2].

The main models describing the photopolymerization are partly integrated model, fully integrated model and auto-catalytic model [2, 10].

The partly integrated model was first introduced by Tryson and Schultz [11] in 1979. This model assumes that the only termination mechanism is the reaction between two macroradical, namely bimolecular termination. The experimental procedure is based on dark polymerization so that the polymerization initiates by irradiation following by cutting off the light at a known degree of conversion, and monitoring the reaction in dark (post-effect) [2, 11]. Another model of dark polymerization assumes that the only means of termination is radical trappings. This type of dark polymerization model was introduced by Batch and Macosko [12] for describing the polymerization of vinyl ester resin [2].

In the photopolymerization of acrylates, the usual interaction of polymer radicals (bimolecular termination) and radical trapping (monomolecular termination) occur in parallel. Fully integrated models provide three termination model describing polymerization in the dark. These models are more accurate and require the knowledge of the degree of conversion in the dark as a function of time. Fully integrated models were first introduced by Timpe and Strehmel in 1991 [2].

Photopolymerization reactions kinetically resemble an autocatalytic reaction. During cross-linking, restricted diffusion of reactive species cause the increase in the polymerization rate. As a result, the shape of reaction rate vs. conversion rate for photopolymerization process is the same as that for autocatalytic reactions. Usually an autocatalytic effect is due to some intermediate species that can accelerate the reaction. Reactions of these types are often described by the Kamal model. When the initial rate of reaction is considerable, the expression becomes: [2, 13]

$$\frac{dp}{dt} = (k_1 + k_2 p^m)(1 - p)^n \quad 1-5$$

UV-curable composites

Composite materials are emerged in the middle of the 20th century as a promising class of engineering materials providing new prospects for modern technology. Generally speaking any material consisting of two or more components with different properties and distinct boundaries between the components can be referred to as a composite material. Moreover, the idea of combining several components to produce a material with properties that are not attainable with the individual components has been used by man for thousands of years. Such materials offer advantages over conventional isotropic structural materials such as steel, aluminum or unfilled polymers. These advantages include high strength, low weight, good fatigue, corrosion resistance and also desirable optical properties and appearance. As it may obvious, composites are composed of two phases: one phase is somewhat continues which is called matrix and fillers and fibers that are dispersed through the matrix known as dispersed phase. The excellent properties of composites are achieved by the favourable characteristics of the two major constituents namely matrix and filler/fiber. [14]

We can classify existing composite materials (composites) into two main groups. The first group of composite materials are called “reinforced materials”. The basic components of these materials (sometimes referred to as “advanced composites”) are long and thin fibers possessing high strength and stiffness. The fibers are bound with a matrix material whose volume fraction in a composite is usually less than 50%. The main properties of advanced composites due to which these materials find a wide application in engineering are governed by fibers. This group of composites is not touched on in the book.

The second group comprises composites that are known as “filled materials”. The main feature of these materials is the existence of some basic or matrix material whose properties are improved by filling it with some particles. Usually the matrix volume fraction is more than 50% in such materials, and material properties, being naturally modified by the fillers, are governed mainly by the matrix. As a rule, filled materials can be treated as homogeneous and isotropic, i.e., traditional models of Mechanics of Materials developed for metals and other conventional materials can be used to describe their behavior. [15]

UV-Curable composites have the advantages of both UV-curable systems and composite materials [16]. As a result, they have been considered extensively in industries of coatings, inks, adhesives and printing. Most of the works done on radiation curing nanocomposites have been based on nanosilica [17, 18] and nanoclay. Preparing coatings with high scratch and mar resistance are examples of these materials [19]. Filled composites themselves can also be classified as nanocomposites and microcomposites regarding the size of the fillers that are incorporated into them. If the moieties blended on molecular extent –which is probable in nanocomposites- the nanocomposite can be counted as hybrid material [20].

Assuming the preparation methods, filled composites can be divided into two categories: 1- composites that the particles are directly incorporated into them. 2- Composites that instead of incorporating particles directly into them, a precursor is incorporated and the particles are produced in-situ. Assuming the preparation methods, filled composites can be divided into two categories: 1-composites that the particles are directly incorporated into them. 2- Composites that

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Preparation of UV-curable composites

Composites can be prepared by various methods including blending or in-situ polymerization. The blending method can be done either by melting if the ingredients bear the blending temperature that is above the melting temperature of the polymer or by solution, if an appropriate solvent is available. Irrespective of preparation method, the good compatibility between ingredients is necessary to make a homogenous polymer composite. In order to enhance the compatibility of the system, appropriate blending condition can be used. Many researches have accomplished preparation of composites by adjusting the temperature profile and mixing speed or by treatment of disperse or continuous phase.

In-situ method

In this method, particles are introduced into the organic matrix or liquid monomer solution and the formation of composite occur by polymerization of continuous phase which can be initiated by UV irradiation. The in-situ formation of inorganic phase through the sol-gel process can also occur simultaneously in the system. In this way, an inorganic constituent or precursor, along with solvent and a calculated amount of water, are mixed into the organic phase. In the sol-gel process, silanol groups are condensed to form a network, and ultimately an inorganic amorphous network is created from the solution phase. During these reactions, a transition state from colloidal (liquid) to an irreversible gel (solid) is expected. The in-situ polymerization is shown in Figure 6.1.

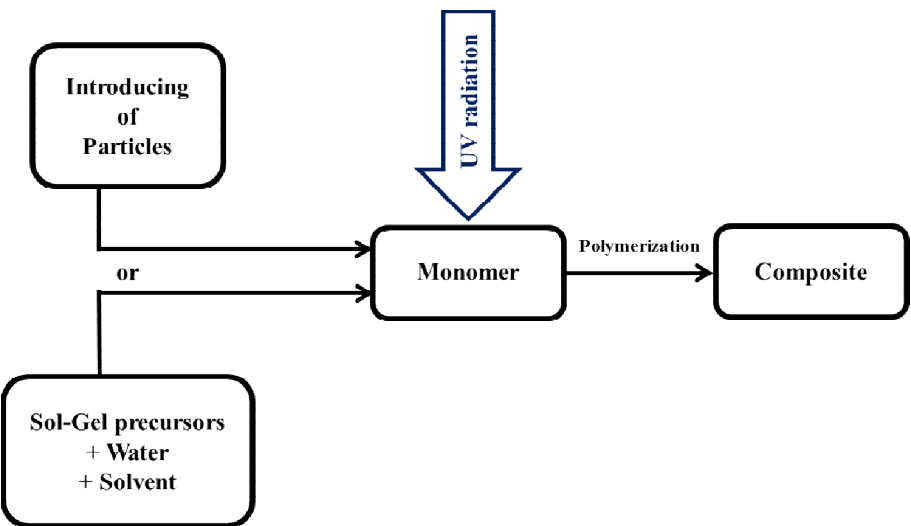


FIGURE 6.1
Block diagram of UV-curable composite preparation via in-situ method

Solution blending method

Solution blending method is a suitable method for the polymer and monomers that are soluble. First the inorganic phase is dispersed in a suitable solvent and when the solutions of organic and inorganic phases are mixed, particles are well-dispersed in the system. Composite is prepared after solvent evaporation and upon irradiation of UV. Typical UV-curable systems are normally low viscosity and solvent free. In addition, the residual solvent in the system causes the final conversion to decrease. Thus, using of solvent in the organic phase for the preparation of UV-curable composites is not usual. Figure 6.2 shows the block diagram for the solvent blending method for the preparation of UV-curable composites.

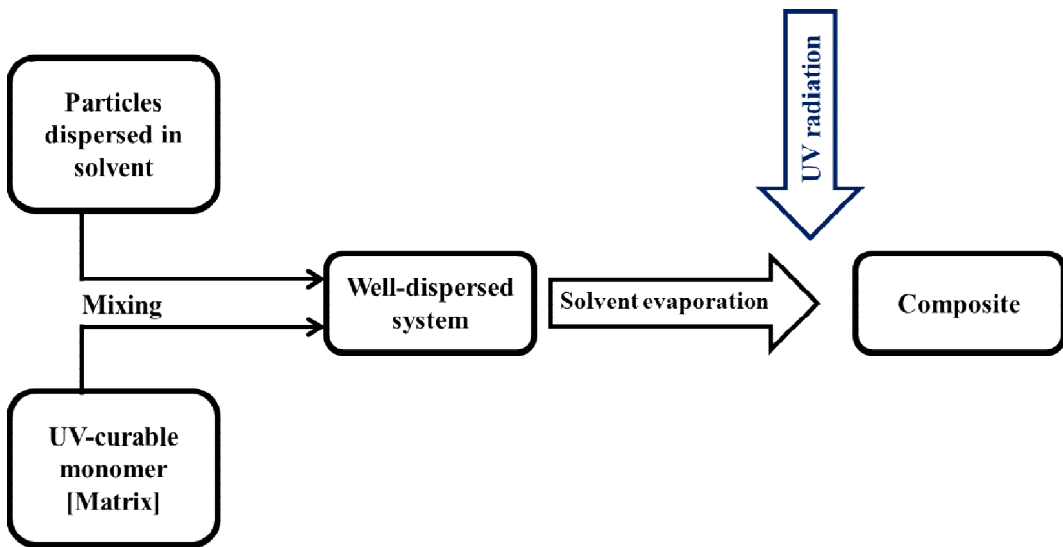


FIGURE 6.2

Block diagram of UV-curable composite preparation via solution blending method

Melt intercalation method

The melt intercalation technique is the most efficient method for some nanocomposites and is quite compatible with the industrial instruments. In this method, polymer and modified filler mixture are blended in the molten state under shear using extruders. UV-curable materials are chemically reactive and should be protected from radiation, thermal shocks and mechanical tension. In addition, this technique can be used only for thermoplastic polymer matrices and thus could not be used for preparation of UV-curable composites.

Difficulties in composite preparation

Many researchers have focused on composites preparation of various types for several applications and faced mainly lack of good dispersion and low mechanical properties in their works. The physical dispersion methods generally included ultrasonication, ball milling grinding and high speed

shearing. One of the primary reasons for adding inorganic fillers to polymers is to improve mechanical performance. The main requirements for effective reinforcement are large aspect ratio for maximum load transfer and uniform dispersion. The mechanical properties of composites can also be affected by interface behavior. In other words, the major requirement for polymers composites is to optimize the balance between the strength and the toughness as much as possible. So, the interaction of fillers is crucial in optimizing the properties of the polymer composite.

Weak interfacial bonding, bad dispersion and degradation of fillers may also cause low mechanical properties of composites. To overcome the problem of insufficient dispersion, surface modification of the filler can be used. Inorganic fillers are typically hydrophilic and do not disperse easily within hydrophobic polymeric materials.

Surfactants are materials that when added to a liquid at low concentration change the surface or interface properties. By using surfactants, the nature of the fillers can be changed and improved dispersion can be achieved.

A variety of coupling agents including silanes, titanates and zirconates have been used to enhance the bonding between fillers and polymer matrices. Precursors that are often used in radiation curing systems are selected based on the type of oligomers used in formulation and typically include Vinyltrimethoxysilane (VTMS) and 3-methacryloxypropyl trimethoxy silane (MPS) [21]. In order to increase functionality of the sol-gel process and the fractalinity of the inorganic phase, these inorganic precursors are usually mixed with tetraethoxysilane (TEOS) [17, 22]. In such cases, TEOS is referred to as a network forming agent and MPS or VTMS is referred to as the network-modifying agent.

Such modification, either physical or chemical, also prevents sedimentation and agglomeration as well as impacting rheological properties.

Properties of UV-cured composites

There are many reasons for using composite materials rather than the simpler homogenous polymers. Some of these reasons are:

- ✓ Increased stiffness, strength and dimensional stability
- ✓ Increased toughness and impact strength
- ✓ Increased heat distortion temperature
- ✓ Increased mechanical damping
- ✓ Increased permeability to gasses and liquids
- ✓ Enhanced electrical properties
- ✓ Reduced cost

Not all of these desirable features are found in any single composite. The advantages that composite materials have to offer must be balanced against their undesirable properties, which include difficult fabrication techniques as well as a reduction in some physical and mechanical properties. It must be noted that one of the undesirable effects which especially related to UV curable composites is that the particles that refract, reflect or absorb UV radiation, highly affect the curing. The particles and moieties that have high refraction index or absorption coefficient at the curing wavelength of UV curable matrix prevent large part of the UV radiations to reach the photo-

initiator. In this case, raising the curing time, reducing the load of dispersed phase, reducing thickness of coating film and also using dual curing process (combining radiation curing and another curing process such as redox) can be helpful. Generally, Properties of composite materials are determined by the:

- ✓ Properties of components
- ✓ Shape and size of the dispersed phase
- ✓ Morphology of the system
- ✓ Nature of the interface between the phases [23]

The effect of component properties on the composite properties

As it was mentioned before, composite materials consist of two or more components with different properties and distinct boundaries. The final properties of the composite is not obtainable with any of the distinct components but is highly influenced by their components properties.

Mechanical properties. Generally, incorporating hard particles into a soft matrix, improves its stiffness and strength. Usually in inorganic-organic composite materials, the organic component accounts for flexibility of the composites whereas the inorganic component is responsible for hardness and mechanical impact resistance. In an investigation it was shown that introducing hard inorganic oxides such as Al_2O_3 , SiO_2 , zirconia ZrO_2 and even TiO_2 with Mohs's hardness parameters of 9, 7, 7 and 6 respectively into an acrylate UV curable system, can significantly improves Hardness and abrasion resistance of the coating [24]. Now a days, alumina and silica are the main candidates to be used to enhance the hardness and abrasion resistance of UV-curable coating systems on an industrial scale. This way hard nature of inorganic oxide particles improves the hardness of composite. It can be done by in-situ formation of nano particles instead of incorporating them directly into the coating. In an investigation, the hardness of acrylate UV curable coating system was improved governing in-situ formed nanosilica particles [25]. In another work, mechanical, rheological and tribological properties of UV curable urethane/acrylate systems were improved using nano silica emulsion that was synthesised from tetraethylortosilicate (TEOS) via sol-gel process. Three different UV curable resin systems have developed this way. In all of them, tensile strength was improved by increasing the amount of silica emulsion in formulation, until a certain amount at which, macrophase separation was occurred. It means that by increasing the amount of nano silica particles in the composite systems, mechanical properties are improved but it will be happened if the particle distribution in the matrix remains uniform. [26, 27]

Physical properties. Same approach can be made to enhance electrical properties of UV curable composites. Conductive transparent UV curable coatings that can be used in wide range of applications such as touch screens are produced by incorporating conductive particles into a UV curable coating formulation [28]. One of the best candidates for this purpose is graphite and other conductive allotropes of carbon. These particles are widely used to introduce conductivity to the polymer matrix. However this must be taking into account that these particles have negative effect on curing of UV curable matrix because these particles have significant screen effect. It means that these particles highly absorb UV spectrum, especially in the frequency range that is absorbed by photo-initiators [29].

Structures with special optical properties can be obtained by composites. For example, optical

transparent materials with high refractive index attract great interest among researchers because of their wide range of applications such as optical wave guides, lenses and antireflection films. To obtain such an optically transparent material with high refractive index, it has been shown that the introduction of colloidal particles (with particle size well below 100nm) with high refractive index into a polymer matrix is so effective. While the density of these high refractive index nano particles is much higher than the organic matrices, they tend to sediment; so rapid curing photopolymerizable polymer matrices can be utilized to overcome this problem [30]. In an study, thiophenol (PhSH)–4-thiomethyl styrene (TMSt)-capped ZnS nanoparticles have been synthesized and introduced into UV-curable urethane-methacrylate macromers (UMM). It was found that increasing the amount of ZnS nanoparticles in the nanocomposite systems, significantly raising the refractive index from 1.645 for pristine polymer matrix up to 1.796 for ZnS containing samples [31]. In another investigation, surface modified nano ZrO/TiO₂ have been incorporated into a PU/methacrylate UV curable system to increase its refractive index [32].

The effect of shape and size of the dispersed phase on composite properties

The shape and size of particles and phases that are present in composites have a great effect on their properties. This factor is so important that composites are divided into two categories according to the size of dispersed phase, namely micro composites and nano composites. In nanocomposites, the scale of dispersion of one phase into another is in general below 100 nm. Nanostructured composites very often exhibit unique properties that are directly attributed to the presence of structural entities having dimensions in the nanometer range. It is due to size reduction to the point where critical length scales of physical phenomena become comparable to or larger than the size of the structure. Applications of such particles take advantage of high surface area and confinement effects, leading to interesting nano-structures with different properties that cannot be produced using conventional methods. Clearly, such changes offer an extraordinary potential for developing new materials in the form of bulk, composites, and blends that can be used for coatings, opto-electronic components, magnetic media, ceramics and special metals, micro- or nano-manufacturing, and bioengineering. The idealized morphology of these systems is characterized by the molecular level dispersion of the phases that leads to a considerable enhancement in the mechanical properties, especially the modulus [33, 34]. Let's give an example to clarify this issue. In a research project, UV-curable acrylate coatings have been developed using micro and organoclay. Mechanical properties of the composites can be evaluated by determining their tensile strength and elongation at break. It was found that increasing the amount of micro particles and nanoclay in the composite formulation, changes the mechanical properties in opposite ways (Figure 6.3). While incorporation of micro particles reduces tensile strength and elongation at break, nanoparticles improve it. [35]

Also in another job, montmorillonite (MMT) with different modifications and in various loading percentages was incorporated into a UV-curable urethane acrylate resin. Evaluation of the modified and un-modified particles with XRD and TEM revealed that the organically modified MMTs, in contrary to the un-modified samples are effectively exfoliated in the UV curable matrix. So nanocomposites were generated using the organically modified MMTs. DMA analysis of the composites showed that mechanical properties of composites contained exfoliated nano particles was much greater than the neat resin. On the other hand, composites contained un-modified

MMTs had lower glass transition temperature (T_g) and elastic modulus in comparison to un-loaded matrix. The results are shown in TA [36].

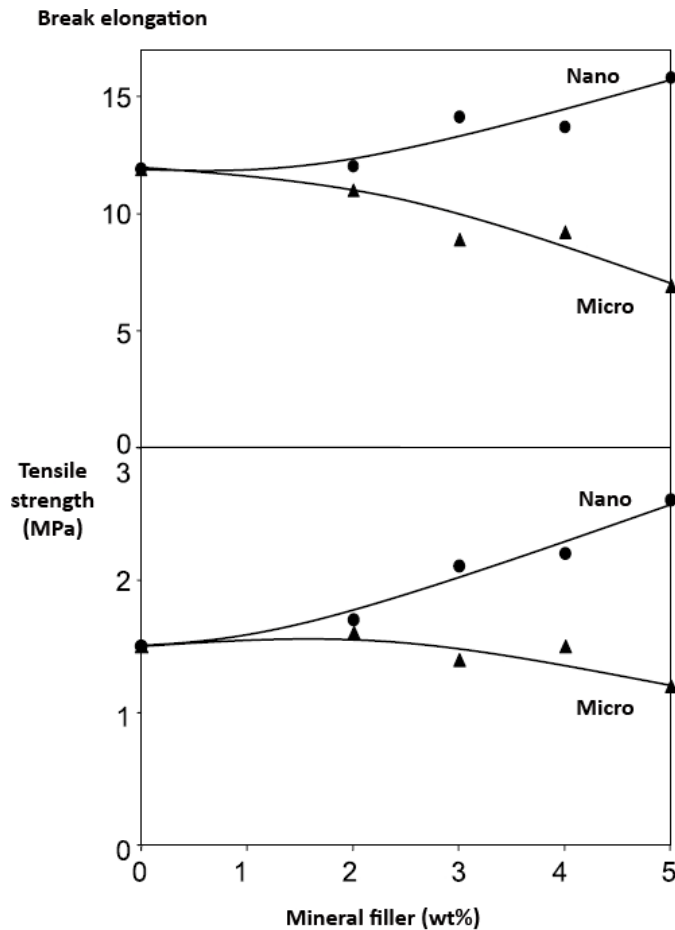


FIGURE 6.3
Influence of the mineral filler content on the tensile properties of a soft UV-cured polyurethane-acrylate composite [35]

TABLE 6.1
Mechanical properties of polyurethane acrylate/MMT composites [36]

	MMT loading percentage (%)	T_g ($^{\circ}\text{C}$)	Elastic modulus @ 25°C (GPa)
Neat resin	0	74.5	1.32
Composites contained organically modified MMTs	1	74.8	1.62
	3	78.8	1.77
	5	78.8	1.56
	1	73.6	1.09
Composites contained un-modified MMTs	3	78.7	1.45
	5	78.7	1.54

The particle size of the dispersed phase in composites can also affect the thermal stability of composites. It can be attributed to the higher interface between the phases that can catalysis the thermal degradation of organic phase which decline thermal stability of composite. On the other hand, reducing the particle size of dispersed phase can improves thermal stability according to labyrinth effect [37].

In addition to size, shape of dispersed phase has great effect on properties of UV curable composites. Shape of dispersed phase is so important that the filled composites can be classified considering this factor. In UV curable composites, the shape of dispersed phase is usually one of the followings: sphere like, fiber shape and layered. In general, UV curable nanocomposites can be distinguished as three types, accounting the shape of their particles [38]. If the three dimensions of the dispersed phase are in the nanoscale range, the particle is isodimensional such as spherical silica nanoparticles, produced by in situ sol-gel process [17, 19, 39, 40]. When two dimensions are in nanoscale, the particle is an elongated structure such as carbon nanotubes and whiskers [41]. This kind of particles is widely studied as reinforcing fillers and successfully improved mechanical properties of composites. The third type of the nanocomposites, contains dispersed particles that only one dimension of them is in the nanometer range. Such particles are nanometer thick sheets such as nano clay or graphene.

Mechanical properties.

Particulate: Silica nano particles can significantly improve mechanical properties of UV-curable surface coatings. In a study the silica nano particles were surface functionalized by mercaptopropyl trimethoxysilane via sol-gel method. The mechanical properties of composites were investigated by DMTA and it was shown that, Tg and storage modulus of nanocomposites are increased –specially at elevated temperatures – by incorporating higher amount of nanoparticles into them. In addition to that, these particles increase the curing rate of composites because of their thiol end groups [42].

Elongated particles: in general, these elongated particles can greatly reinforce matrix and affect the mechanical properties of composites because of their high aspect ratio. As an instance, in a research project, surface modified tetrapod zinc oxide whiskers (STZnO-W) were synthesized and introduced into a UV curable Polyurethane acrylate resin [41]. It was found that both, elongation at break and also tensile strength of composites are improved by incorporating the surface modified whiskers. By incorporating whiskers into polymer matrix, the stress which is applied to the composite will easily transfer to the elongated whiskers. This way, mechanical properties of the composite is improved. However when the whiskers content in the composite exceeds a certain value –in this case it was 1%– they can no longer disperse in the matrix uniformly, so the mechanical properties will be reduced [41].

Sheet: a group of researchers produced UV curable nanocomposites using graphene oxide. It was shown that the presence of graphene oxide nanosheets in the nanocomposite systems can significantly enhance the mechanical properties of UV curable composites. The glass transition temperature (Tg) of pristine cured coating was increased from 155°C to 167°C by incorporating only 0.5% of graphene oxide into the system. The Tg can raise up to 195°C by increasing the graphene oxide content to 1.5%. Although the storage modulus of the coating at ambient temperature is not enhanced by introducing graphene oxide sheets into it, but at elevated temperatures the effect of graphene oxide is obvious. The storage modulus at high temperatures can be enhanced more than 33% by incorporating 1.5% graphene oxide into the polymer matrix. Graphene oxide was also improved the surface hardness and surface modulus of the UV curable nanocomposite [43].

Physical properties.

Particulate: Researchers have developed hydrophobic UV curable coating, utilizing surface

functionalized nanosilica particles. They have functionalized nanosilica particles using hydrophobic perfluoroalkylsilane and incorporated the surface treated particles into an acrylate coating. According to the low surface tension of the treated particles, they were migrated to the composite-air interface. This way, the surface energy of the composite film was reduced and on the other hand the surface roughness was increased. So the water contact angle of nanocomposite surface which was 54° for the pristine cured resin was raised up to 90° for the samples contained 15% surface treated nanosilica. Therefore the surface of the coating which had been hydrophilic was changed in a way that it was not hydrophilic anymore [40].

Elongated particles: It was found that incorporating surface modified tetrapod zinc oxide whiskers into a UV curable Polyurethane acrylate resin not only enhance its mechanical properties, but also improves the thermal stability of composite. In addition to that, by improving the barrier effect of composite, it also reduces water uptake and oxygen permeability that are so important for packaging applications [41].

Morphology of UV-Curable composites and its effect on composite properties

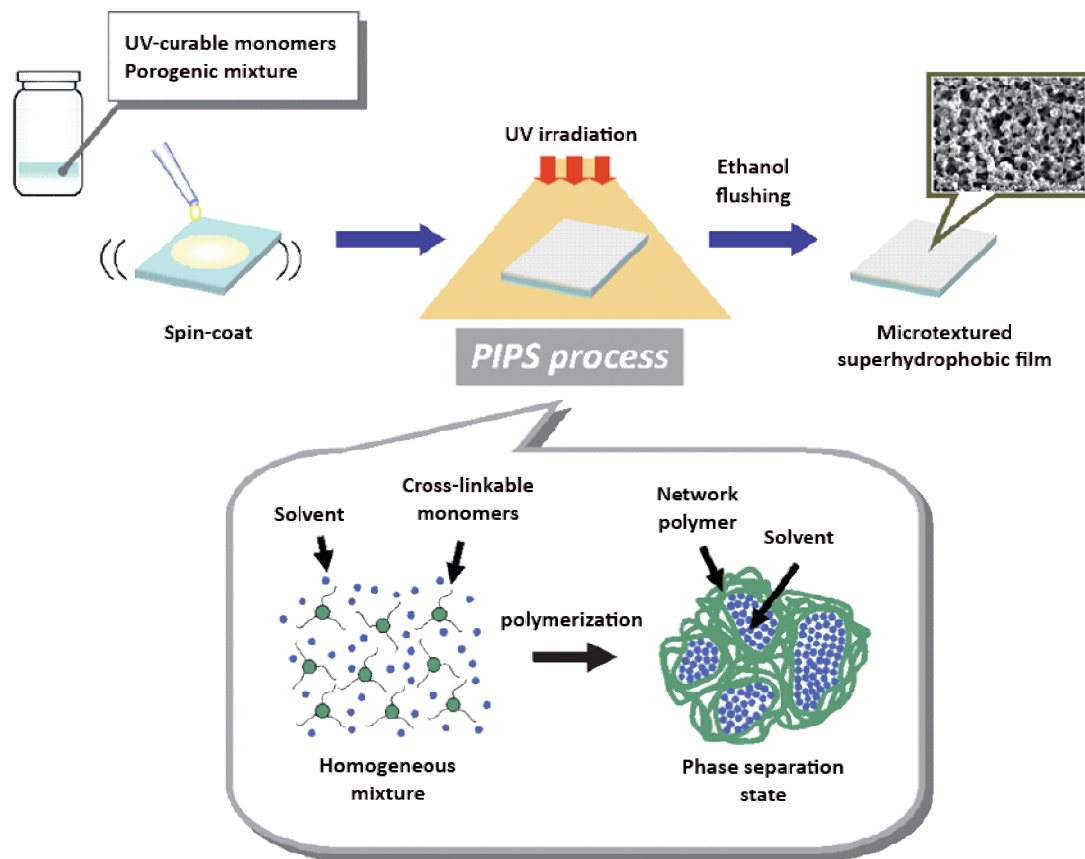
In general, the term morphology refers to the shape and organization on a scale above the atomic level (e.g., the arrangement of polymer molecules into amorphous or crystalline regions) and the manner in which they are organized into more complex units. On the other hand, morphology of a polymer composite indicates the size, shape, and spatial distribution of the component phases with respect to each other. Since It is well established that most of the properties — mechanical [44, 45], optical [46, 47], dielectric [48], and barrier [49, 50] properties — of polymer blends are strongly influenced by the type and fineness of the phase structure, the study of the control of the morphology of polymer composites is of great importance [34].

In general, the scale of dispersion of one moiety is of great importance. In nanocomposites, the size of the dispersed phase is in general below 100 nm. Nanocomposites very often exhibit unique properties that are directly attributed to the presence of structural entities having dimensions in the nanometer scale. The idealized morphology of these systems is characterized by the molecular level dispersion of the phases that leads to a considerable enhancement in the mechanical properties, especially the modulus [34].

Polyurethane acrylates are UV curable resin systems that attract lots of interest according to their special properties such as high tensile strength, abrasion resistance and toughness and also excellent chemical and solvent resistance. Polyurethane acrylates are generally consist PU oligomer tipped with acrylate or methacrylate functionality. These polymeric systems contain soft and hard segments; the hard segments are formed by isocyanate and acrylate or methacrylate functionalities, while the soft segments are usually consist of polyester polyol or polyethers. The soft segments and hard segments are immiscible, so these systems are prone to phase separation. The final morphology of the phase separated films is significantly affecting the properties of these systems such as flexibility, hardness, toughness and abrasability. In general the higher the hydrogen bonds form between soft and hard segments, the higher the uniformity of the final product. Also increasing the molecular weight of soft segment causes microphase separation [51].

Morphological aspects of UV curable composites have great effect on their properties. So, many researchers around the world have been focusing on controlling the morphology of the UV curable composites to fabricate nanostructured materials with special properties. As an instance,

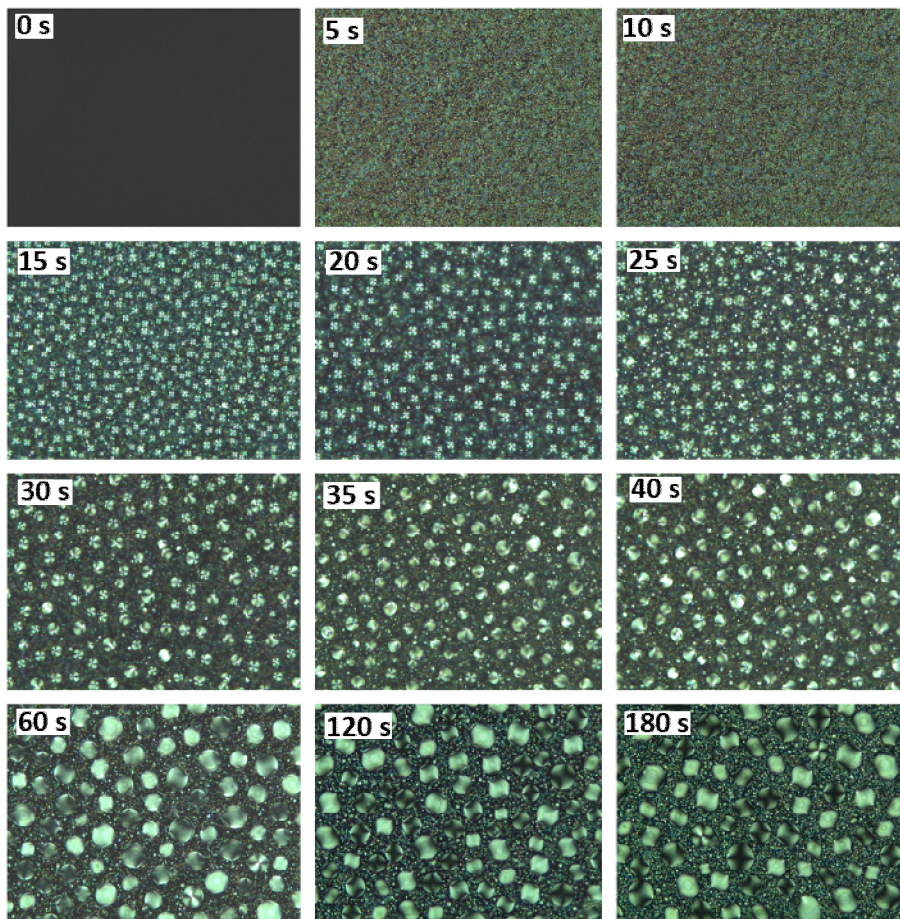
superhydrophobic surfaces produced by governing photopolymerization induced phase separation. A facile approach have been used to produce specific surfaces having both micro and nano surfaces. The underlying phenomenon, this strategy is based upon, is controlling the surface morphology of a UV curing system by manipulating the photopolymerization induced phase separation (PIPS). The process consisted of three steps: 1- coating the precursor mixture (consisted of methacrylate monomer mixture and a solvent that dissolves monomer but phase separates during photopolymerization) on a pretreated glass slide -2- UV curing the applied film -3- flushing out the solvent. The process is represented in Scheme 2 [52].



Scheme 2

Schematic description of the process of fabricating superhydrophobic UV-curable coating governing PIPS. First the solution mixture spins coats on a pretreated glass substrate. Then it undergoes PIPS during photopolymerization. By flushing the ethanol out of the coating, a superhydrophobic, micro and nano textured coating will be remained [52]

Controlling the morphology of the UV curable coatings can also be used for producing thin film membranes. Manipulating the photopolymerization induced phase separation in these systems and hence the morphology of the final products. So, it makes the possibility to produce membrane with structures from very open structures (for microfiltration) to very dense (for gas separation or etc.) ones [53].

**FIGURE 6.4**

Morphological evolution of LC-polymer mixture during polymerization with respect to curing time [54]

Polymer dispersed liquid crystals (PDLCs) are composed of liquid crystal (LC) droplets, dispersed in an isotropic polymer matrix. PDLCs are produced via phase separation of initially miscible LC and polymer mixture which undergoes phase separation during photopolymerization. In PDLCs, desirable mechanical properties of polymer matrix combines with unique electro-optical properties of LCs. PDLCs have great advantages over other LC technologies such as low cost and facile production process, quick electro-optical response and no leakage of material. In PDLCs, the initial mixture is composed of UV curable monomers, photoinitiator and LCs. At first they are miscible and form a uniform mixture. During photopolymerization and by increasing the molecular weight of polymer they start to phase separation. As the curing reaction proceeds, the microphases start to appear and the final morphology forms. An example of the morphology evolution of PDLC during photopolymerization can be seen in Figure 6.4

F [54]. The phase separation and formation of micro and nano phases continue until the solidification of the composite happens. So, the final morphology is determined by two competitive processes, PIPS and polymer curing. Hence, any factor that affects the phase separation kinetics and curing rate of the polymer matrix any, can change the final morphology of the composite.

Factors such as curing reaction temperature [55], UV light intensity [56], photo initiator concentration and performance [57], the interaction between the LC domains and polymer matrix [58] and structure of UV curable polymer [59].

Nature of the interface between the phases and its effect on composite properties

Matrix-dispersed phase interface is a major determinant of the final properties of any composites, including UV-curable. The degree of compatibility between the matrix and the dispersed phase can also affect other key factors such as morphology of the composite and also the particle size of the dispersed phase. The more the phases compatible, the stronger the interconnection between them.

Mechanical properties. UV curable polymeric systems are good options to be governed in furniture coating systems. UV curable wood coatings should have high rub and abrasion resistance so the surface hardness of these systems is of great importance. These coatings are widely being reinforced by Silica and Alumina nanoparticles in order to improve their hardness and scratch resistance. In an attempt, nano Alumina and nano silica were added to a waterborne UV curable wood coating. In contrary to what was expected, the hardness of coating was decreased by incorporating nano particles into the system. It was attributed to the aggregation of nanoparticles in the system which was stemmed from the fact that the interaction between organic matrix and inorganic particle was not sufficiently high. However, when the nanoparticles were surface treated by Methacryloxypropyltrimethoxysilane, not only the particles dispersed in the matrix uniformly, but also the scratch resistance and adhesion of coating systems were markedly improved even for the coatings contained only 1% surface treated nano particles [60]. Also it was found that although incorporating untreated nanosilica particles into acrylate UV-curable nanocomposites significantly improve surface hardness, but surface treatment of the nanoparticles by mercaptopropyl trimethoxysilane (MPTMS) as coupling agent improves surface properties of the final coating even more. It was attributed to the better interaction between polymer matrix and the particle surface and according to that improved dispersion of particles in the matrix [61].

Physical properties. The nature of the interface can also influence the physical properties such as thermal stability. In an investigation, UV curable polyurethane acrylate matrix was reinforced using graphene oxide nanosheets. The nano graphene oxide was introduced either with surface functionalization or without further functionalization. The surface functionalization was performed in a way that active acrylate functionality was formed on it. So they were capable to covalently bond to the poly urethane/acrylate matrix during the curing process [62].

While the surface functionalized graphene oxide nanosheets connected to the polymer matrix with strong covalent bonds instead of weak van der Waals linkage, the stronger dispersed phase/matrix interface was formed. Hence, the surface functionalized nanosheets dispersed better and more uniformly in the matrix in comparison with nonfunctionalized graphene oxide nanosheets which lead to improved mechanical properties (storage modulus and tensile strength) and higher thermal resistance. While the initial thermal decomposition temperature of pristine poly urethane acrylate coating was 299°C, it was raised up to 316°C for the sample contained 1%wt functionalized graphene oxide. However the initial thermal decomposition temperature of the sample contained non-functionalized graphene oxide was less than 299°C. [62]

As it was mentioned before, one of the best strategies to produce materials with high refractive index, is to introducing nanoparticles with high refractive index into the polymer matrix and it is so important to disperse the particles in the matrix so well to ensure that the particle size remain below one tenth of wave length of optical light to prevent Rayleigh scattering. So the surface functionalization of particles and the surface interaction of polymer-particle are so important [31].

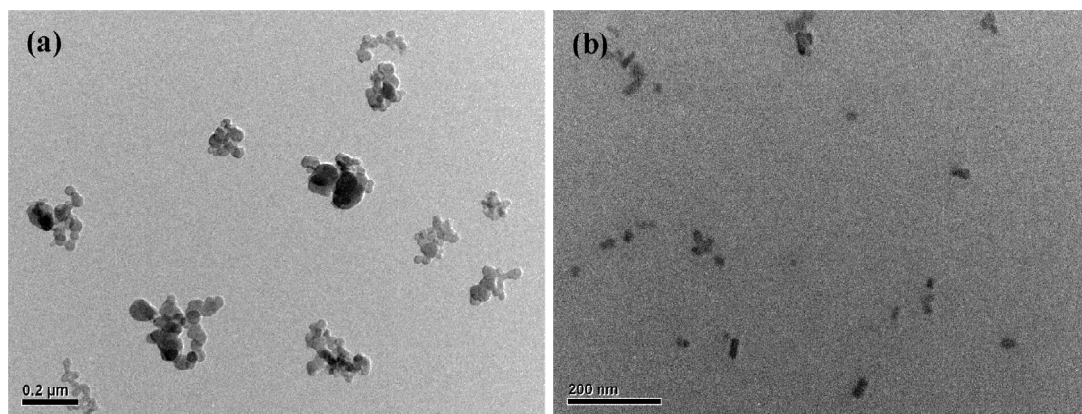


FIGURE 6.5

TEM micrographs of (a) nonfunctionalized graphene oxide/poly urethane acrylate 1%wt and (b) nonfunctionalized graphene oxide/poly urethane acrylate 1%wt. The effect of surface functionalization on the dispersion quality of nanosheets is obvious [62]

Conclusion

UV curable systems are greatly attract researcher's interest in recent decades because of their brilliant properties including low or no VOC, low energy consumption, fast and low temperature curing process. UV curable nanocomposites combine the advantages of fast and low temperature processing condition of UV curable systems with the outstanding properties of nanocomposites. Therefore, they must be prepared in such a way that neither UV curing process nor the uniform dispersion of the dispersed phase in nanometer scale are interrupted. One of the most challenging issues in this field is preparation method of the nanocomposite that can be classified into two main categories: 1- introduction of nanoparticles into the polymer matrix and 2- in-situ formation of nano meter scale dispersed phase. Nanocomposites can be used in a wide variety of applications such as wood coating, automotive coating, printing inks, dental materials, PDLCs and optical devices because their final properties can flexibly be controlled by various factors. These factors include polymer matrix and dispersed phase intrinsic properties, shape and particle size of dispersed phase, system morphology as well as nature of particle/matrix interface. The effects of these factors on final physical and mechanical properties of UV curable nanocomposites were briefly discussed herein.

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