

Iso-propanol assisted preparation of individualized functional palygorskite fibers and its impact on improving dispersion abilities in polymer nanocomposites

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Abstract—Palygorskite (PAL) as a natural one-dimensional nanomaterial has attracted tremendous attention as reinforcement agent in polymer nanocomposites. But its intrinsic existing form of aggregates or bundles and hydrophilic properties, highly requires an eco-efficient and environmentally benign approach for both of the disaggregation and organo-modification of PAL. We report a facile and effective process to achieve individualized organo-modified PAL fibers. It was carried out through surface modification reactions in the form of PAL *iso*-propanol gels with various alkyl and functional silanes. In contrast to the modifications in highly toxic solvent of toluene, reactions in *iso*-propanol make it possible to modify the surface of individual PAL fibers to obtain isolated organo-modified PAL fibers. With such a relatively green procedure, even higher amount of organic substituent has been grafted on to the surface of PAL fibers. Consequently, excellent dispersion of modified PAL nanofibers in acrylate polymer coatings was achieved, which exhibits outstanding corrosion protection properties.

Keywords: Palygorskite, Organosilane, *Iso*-propanol Gel, Modification, Nanocomposite

INTRODUCTION

Inorganic nanoparticles as polymer reinforcement agents have been studied extensively [1-3]. With a small addition, the resulting nanocomposites can exhibit enhanced thermal, mechanical and functional properties. However, due to the nanometric dimensions of such nanoparticles, they manifest very different surface properties from their micrometric analogues leading them to very easily to aggregate [4]. To take full advantages of the nanoparticle properties, such aggregates must be dispersed into the smallest possible entities.

PAL is a naturally occurred fibrous phyllosilicate mineral with the diameter of about 20-70 nm and a typical length of 1-2 μm [5,6]. Its natural abundance, nano-dimension crystal structure, large aspect ratios and large surface area render PAL as a very promising candidate for reinforcement materials in polymer-based nanocomposites [7]. Unfortunately, the naturally occurring PAL exists in the form of micrometric aggregates in hundreds of micrometers due to the interplate van der Waals and hydrogen bonding interactions, which greatly hinders its applications [6,8]. Therefore, effective dispersion of the agglomerates and crystal bundles to isolated or individualized PAL fibers is of great importance.

In recent years, various physical methods such as high-shear mixing [9], milling [10,11], extrusion [12], ultrasonification [13] and high-pressure homogenization [14,15] have been developed to separate the crystal bundles of PAL. It is possible to reduce the aggregates from the micrometer scale to single fibers by dispersing in

liquid media. But during the drying process, such single fibers will reaggregate again into bundles with tens of micrometers [16]. Furthermore, the intrinsic hydrophilic properties of PAL fibers will lead to the compatible problems with polymer matrices during application. Thus, attempts to achieve further disaggregation and hydrophobic properties require chemical methods. To date, most of the work has focused on organo-modification by using cationic surfactants [17-19], polymer chains [20,21] or coupling agents [22-24]. However, due to the limited loading and high cost, respectively, for the first two approaches, organosilane coupling agents are a good choice for modifying the surface of PAL. First, the surface of PAL fibers has many accessible silanol groups ($4.5 \text{ Si-OH}/100 \text{ \AA}^2$) [25], which can form very stable Si-O-Si covalent bond with the organosilanes. Second, the variety of organosilane chemistry provides extensive selection with desired functionalities.

In general, the organosilane modification of PAL has been performed essentially in two dispersion mediums, either in water/ethanol mixtures [23,26,27] or pure organic solvents [28-31]. Although water/ethanol as dispersion medium makes the process relatively green and low cost, the condensing of organosilane into nano- or micro-particles and its dispersion on the surface of PAL fibers are nonuniform. Furthermore, in most cases, the Si-O-Si covalent bonds between organosilica particles and PAL fibers are so limited that the silica nanoparticles on PAL surface are not stable and can fall off very easily. Additionally, the intercondensation of silanols causes aggregation of PAL fibers forming agglomerates. In the second case, inert organic solvents avoid the presence of organosilica particles and ensure the organosilane grafted on to the PAL. But the use of organic solvents, very frequently with highly toxic toluene, causes problems of environmental and large-scale production issues. Besides, highly hydrophilic PAL has dispersion issue in these solvents, which

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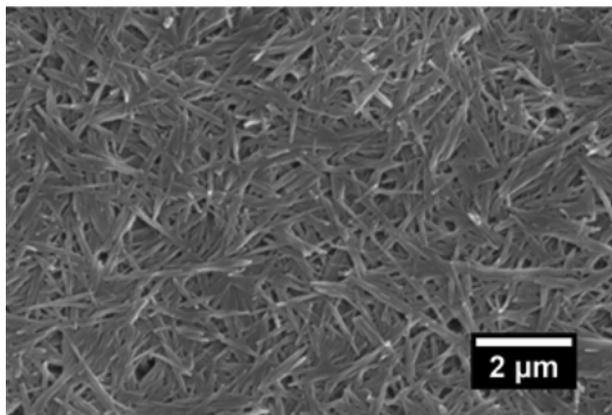


Fig. 1. SEM image of PAL fibers in an *iso*-propanol gel (2 wt% solid content).

makes such surface modification not produced on the surface of individualized PAL fibers, but on the external surface of the PAL aggregates. Therefore, the distribution of the modification functions in these conditions is strongly nonuniform.

Herein, we present a simple and effective modification approach based on the reaction of the PAL in the form of an *iso*-propanol gel, to eliminate limitations of aggregation, instability and even toxic solvents existed in the traditional processes. Very recently, our group found that PAL aggregates can be well dispersed into *iso*-propanol forming stabilized gels via a simple high shear mixing process [32]. As shown in Fig. 1, PAL fibers appeared disaggregated as almost individualized units in the gel. Thus, any chemical modification produced in the gel form occurs on the surface of the individualized fibers, and upon drying, their reaggregation can be avoided. In this study, we show that this chemical modification in *iso*-propanol gel produces a conventional grafting surface modification. Because of the protection of organic groups, the modified PAL fibers remain isolated even after a simple heat drying process. In addition, the effect of the organosilane functionality on their grafting amount has been thoroughly investigated. Excellent dispersions of modified PAL nanofibers in acrylate polymers were observed, as demonstrated by the outstanding optical properties of these composite films showing highly transparent in the visible light region. More interestingly, remarkable corrosion protection properties of such organo-PAL/polyacrylate nanocomposite films were achieved.

EXPERIMENTAL SECTION

1. Materials

Palygorskite (PAL, >90%, wt) were obtained from Jiangsu Zhongyuan Minerals Co. Ltd. (Huai'an, China). Before use, it was treated by hydrochloric acid (HCl) for activation according to the following steps. First, 10 g of received PAL powders were dispersed in 500 ml of 1 M HCl aqueous solution and stirred for 48 h. Then, the suspension was filtered and washed by deionized water until to no Cl⁻ in filtrate detecting by AgNO₃. The filtered PAL was dried with a lyophilizer under -40 °C in vacuum for 48 h. Finally, the white powders were grinded to about 200 meshes.

n-Butyltrimethoxysilane (C₄TMS), *n*-Octyltrimethoxysilane

(C₈TMS), *n*-Dodecyltrimethoxy-silane (C₁₂TMS), *n*-Hexadecyltrimethoxysilane (C₁₆TMS), 3-(Trimethoxysilyl)propylmethacrylate (MAPTMS) and 3-Aminopropyltrimethoxysilane (APTMS) were purchased from Tokyo Chemical Industry (Shanghai, China). Polyethylene glycol 400 dimethacrylate (PEGDMA) was a gift from SARTOMER. The free radical photoinitiator of 2-hydroxy-2-methyl-1-phenyl-propan-1-one (D 1173) was supplied by BASF. *iso*-propanol (≥99.7%, wt) was obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All chemicals were used as received.

2. Palygorskite Surface Modification

Modifications in *iso*-propanol gel were performed by first dispersing 5 g of PAL into 245 g of *iso*-propanol (2 wt% of solids) by means of a lab dissolver (IKA T25) operating at 10,000 rpm for 20 min. Then the mixture was refluxed with an excess amount of desired alkoxy-silane (10 mmol) at 90 °C under magnetic stirring for 8 h. After refluxing, the reaction mixture was cooled and centrifuged (8,000 rpm for 5 min, HITACHI CT15E), washed with *iso*-propanol for four times (100 ml each) and dried in vacuum at 40 °C over night to obtain the final products (denoted as PAL-C_n for alky-silanes, n=carbon number of the alkyl chain; PAL-MAP and PAL-NH₂ for MAPTMS and APTMS, respectively).

For comparison, PAL modifications in toluene followed a previously reported protocol widely used for PAL surface functionalization [28]. The final products have been denoted as PAL-C_n-t or PAL-NH₂-t depending on the kind of organosilanes used. In contrast, PAL aggregates do not disperse in toluene that a non-stable-in-time suspension has been formed.

3. Preparation PAL/PEGDMA Nanocomposite Coatings

PEGDMA resin was mixed with 5 wt% of desired organosilane modified PAL fibers, 4 wt% of radical photoinitiator D1173 and 0.5 wt% surface wetting agent of BYK333 to form a photolabile formulation. Then the resultant formulation was deposited on a silicon wafer or glass substrate by wire wound bar coater. A reproducible liquid film thickness of 10±2 μm was obtained regardless of the formulation composition. The films were irradiated at room temperature through five successive passes under a UV-conveyor (DGXLUV-1009, Xili) with a belt speed of 10 m min⁻¹ to yield cross-linked hybrid films.

4. Characterization Techniques

4-1. Fourier Transform Infrared Spectroscopy (FTIR)

FT-IR spectra of the samples were recorded via a Nicolet 5700 spectrophotometer (Thermo Electron Co., USA) with a resolution of 4 cm⁻¹ from 4,000 to 600 cm⁻¹. For the modified PAL sample powders, they were characterized by using KBr pellet technique.

4-2. X-ray Diffraction

The XRD patterns were recorded on an X-ray power diffractometer (D8Discover, Bruker AXS, Germany) using Cu-Kα radiation (0.15406 nm, 40 kV, 40 mA). Data were collected from 5 to 40° (2θ) with 0.5 s⁻¹ step.

4-3. Element Analysis

The carbon and nitrogen content of the organically modified PAL samples was performed on an Elementar Vario III element analyzer under He atmosphere. Each value was obtained by the means of three replicates with an error of less than 0.1%.

4-4. N₂ Adsorption and Desorption Isotherms

Brunauer-Emmett-Teller (BET) surface area was measured by

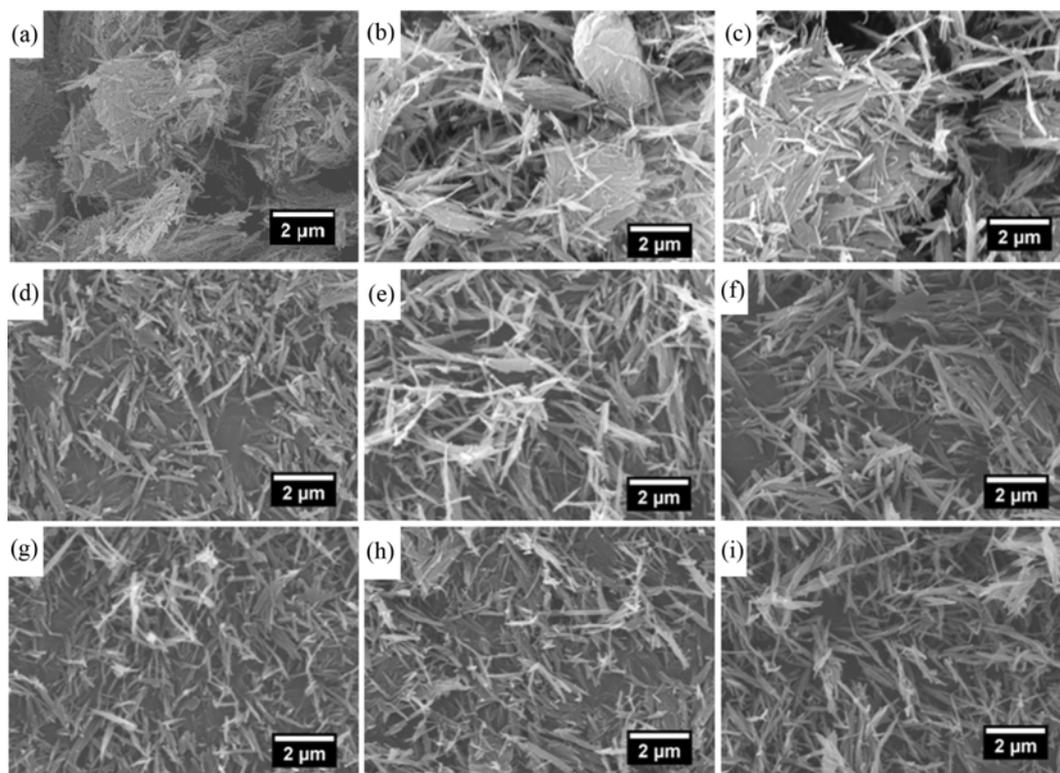


Fig. 2. SEM images of different products obtained after organosilane surface modification of PAL fibers: (a) raw PAL, (b) PAL-C8-t, (c) PAL-NH₂-t, (d) PAL-C4, (e) PAL-C8, (f) PAL-C12, (g) PAL-C16, (h) PAL-MAP, (i) PAL-NH₂.

N₂ adsorption at 77 K in a Micromeritics TriStar II 3020 system (Micromeritics Instrument Co., USA) estimated via the BET method. Before the measurement, the samples were stored at 105 °C for 1.5 h in N₂ atmosphere.

4-5. UV-visible Spectrophotometry

UV-vis spectra of the composite films prepared on borosilicate glass substrate were recorded by a spectrophotometer (UV-2401 PC, Shimadzu, Japan) in 200 to 800 nm range.

4-6. Scanning Electron Microscopy

Morphology of the samples was characterized by SEM (Hitachi S3000N microscope working at 25 kV). Before the analysis, the samples were coated with a 15 nm thick layer of gold to reduce the charging effect on the surface.

4-7. Water Contact Angle

The water contact angle measurement was carried out on Kruss DSA20 equipment. The sample films were prepared via pressing the material powder at a pressure of 30 MPa on tablet press [33].

4-8. Corrosion Protection Performance Test

Corrosion protection performance of the different composite films was measured by immersing the panels in a 0.6 M NaCl aqueous solution at pH 6.5 for various times [34].

RESULTS AND DISCUSSION

1. Surface Modification of PAL Fibers

The modification of PAL fibers in the *iso*-propanol gel was performed with various inert organosilanes based on saturated hydrocarbon chains in different length (C_nTMS, n=4, 8, 12, 16) and with

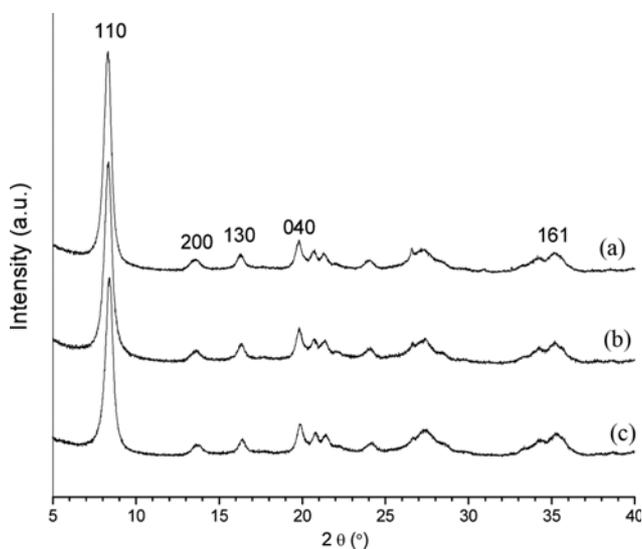
functional silanes of APTMS (3-aminopropyl) or MAPTMS (3-methacrylatepropyl). The dispersion of 2 wt% of PAL in hydrophilic *iso*-propanol with a high shearing force that can efficiently broke down PAL aggregated bundles into single fibers (Fig. 1), forming a time stable *iso*-propanol liquid gel. Such conditions make the possibility of chemical modification on the surface of individualized fibers.

Fig. 2 shows the SEM images of raw PAL (a) and a range of organosilane modified samples from toluene ((b) and (c), following a previous reported protocol) or *iso*-propanol gel ((d) to (i)). Clearly, the modification performed in toluene cannot separate the crystal bundles efficiently. In contrast, no matter what organosilanes used, the modification process performed in *iso*-propanol gel provides better disaggregation as all the micrometer aggregates have disaggregated into single fibers. It demonstrated that chemical modification in *iso*-propanol gel of PAL is an efficient way to obtain the surface functionalization of single fiber.

Further proofs for such effective disaggregation modification procedure have been provided by N₂ adsorption-desorption characterization of raw PAL and various organosilane modified PAL samples. As summarized in Table 1, the specific surface area (S_{BET}) of raw PAL is 161 m²/g. However, S_{BET} for the samples of PAL-NH₂-t and PAL-C8-t, which the modification was performed in toluene, have been diminished sharply to only 57 and 74 m²/g, respectively. Because of organo-functions grafting on the surface of PAL, it is promising for the decrease of S_{BET} as there is no disaggregation of crystal bundles during chemical modification in toluene. In contrast, a slight decrease of S_{BET} was observed for all of the organo-functionalized

Table 1. Specific surface area (S_{BET}) of raw PAL and surface modified PAL samples

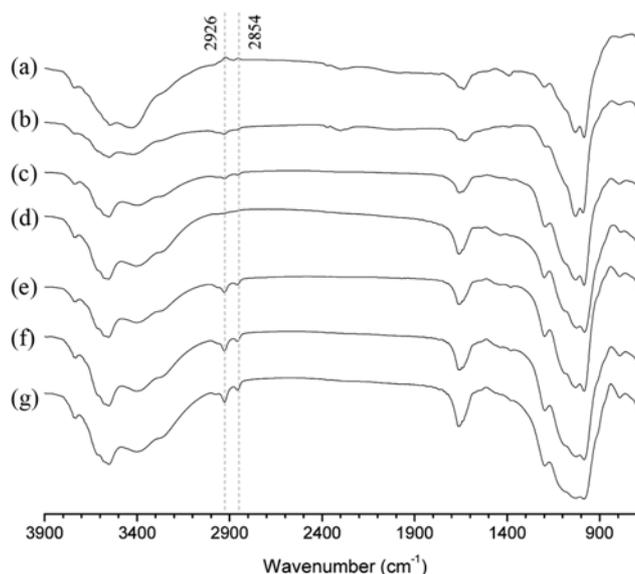
Sample	S_{BET} (m ² /g)
PAL	161
PAL-NH ₂ -t	57
PAL-C8-t	74
PAL-NH ₂	81
PAL-MAP	121
PAL-C4	155
PAL-C8	119
PAL-C12	126
PAL-C16	143

**Fig. 3. XRD patterns of PAL and C8 functionalized samples: (a) PAL, (b) PAL-C8, (c) PAL-C8-t.**

samples modified in *iso*-propanol gels. It suggests that the bundles of PAL have been disaggregated in *iso*-propanol during modification, which prevents the sharp decrease of S_{BET} . These results are quite in accordance to the SEM analysis.

Fig. 3 displays the XRD patterns of raw PAL (a), *n*-octyl (C8) functionalized PAL samples of PAL-C8 (b) and PAL-C8-t (c). In comparison to raw PAL, although the S_{BET} for both PAL-C8 and PAL-C8-t has been varied, their position and intensity of the characteristic diffraction peaks of PAL at 2θ values of 8.34, 13.74, 16.34, 19.83, 27.54 and 34.28° do not change. Apparently, this result suggests that doing organo-modification of PAL in *iso*-propanol gel did not destroy the crystalline structure of PAL. In contrast, the intensity of diffraction peak belongs to quartz impurity at 2θ value of 26.63° has been decreased, suggesting a purification function of our modification procedure.

FTIR spectroscopy is a very powerful tool for examining whether the organosilane functionalities have been successfully grafted onto the surface of particles. Fig. 4 illustrates the IR spectra of raw PAL (a) and its fibers modified with various organosilanes in *iso*-propanol ((b) to (g)). The absorption bands located at 3,800-3,395 cm⁻¹ are belonged to the hydroxyl groups of coordinated water in the

**Fig. 4. FTIR spectra of raw PAL (a) and its fibers modified by a range of organosilanes: (b) PAL-NH₂, (c) PAL-MAP, (d) PAL-C4, (e) PAL-C8, (f) PAL-C12, (g) PAL-C16.****Table 2. The grafted amount of organofunctions on to the surface of palygorskite**

Sample	Grafted amount (mmol/g)
PAL	0
PAL-NH ₂ -t	0.414
PAL-C8-t	0.299
PAL-NH ₂	0.507
PAL-MAP	0.301
PAL-C4	0.099
PAL-C8	0.315
PAL-C12	0.253
PAL-C16	0.14

tunnels of PAL. The peak at 1,657 cm⁻¹ can be assigned to the bending vibration of zeolite water. The two sharp absorptions at 1,030 and 984 cm⁻¹ are ascribed to the asymmetric vibrations of Si-O-Si bonds. In contrast to raw PAL, for all of the organosilane modified PAL samples, two new absorption bands at 2,926 and 2,854 cm⁻¹ attributed to C-H stretching vibrations have appeared, indicating that the 3-aminopropyl (b), 3-methacrylatepropyl (c) and alkyl hydrocarbon chains with different length (d)-(g) have been successfully grafted onto the surface of PAL fibers. The relative weak absorption intensities of samples PAL-NH₂, PAL-MAP and PAL-C4 in comparison to PAL-C16 are due to the less numbers of methylene groups. Unfortunately, the overlapping to the IR absorptions of hydroxyl group existed in the raw PAL lead to the invisibility of the typical IR vibrations of N-H at 3,400 cm⁻¹ and C=C at 1,660 cm⁻¹.

Elemental analysis was further performed to determine the exact grafted amount of organo-functions onto the surface of PAL. The silane molar concentration was determined from the carbon content of modified PAL samples (deducted 0.6 wt% of carbon content in raw PAL), as summarized in Table 2. The total amount of

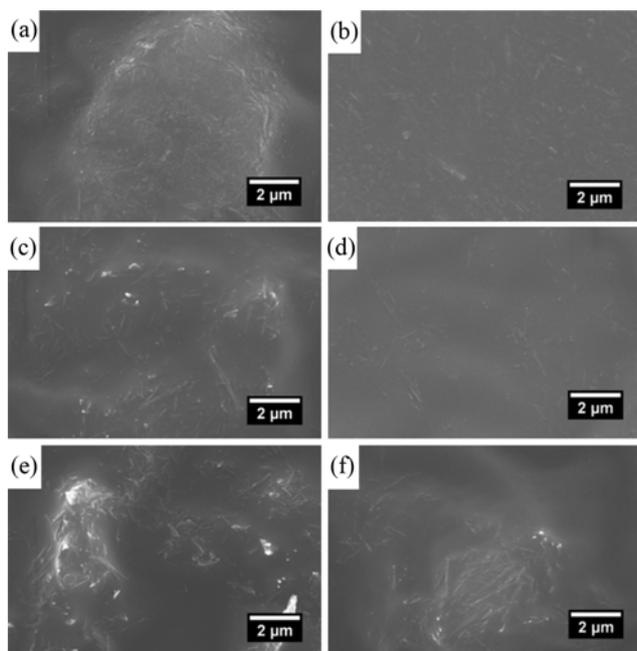


Fig. 5. SEM images of surface of PEGDMA/PAL nanocomposite films prepared with 5 wt% of organo-modified PAL fibers: (a) raw PAL, (b) PAL-MAP, (c) PAL-NH₂, (d) PAL-C8, (e) PAL-NH₂-t, (f) PAL-C8-t.

3-aminopropyl and *n*-octyl functions grafted on to PAL aggregates and fibers that modified in toluene is respectively 0.414 and 0.299 mmol/g. By contrast, the grafted amount for samples of PAL-NH₂ and PAL-C8 that modified in *iso*-propanol gel is, respectively, 0.507 and 0.315 mmol/g, even slightly higher. Obviously, our approach doing organo-modification in PAL *iso*-propanol gel is as efficient as that performed in traditional toxic solvent of toluene. Furthermore, such increasing is probably due to the better disaggregation of PAL in *iso*-propanol gel, which increased the number of reactive silanol groups (Si-OH). Besides, the loading amount decreased from 0.315 to 0.14 mmol per gram along with the increasing of alkyl chain length from C8 to C16. Such reduction can be explained by the hindrance effect of the hydrocarbon chains as the surface of PAL fiber is constant.

2. PAL/PEGDMA Nanocomposites

Fig. 5 illustrates the SEM images of the surface of PAL/PEGDMA composite films which were filled with 5 wt% of raw or various organo-modified PAL. Obviously, the raw PAL fibers have been aggregated into micro-aggregates (~5 μm) in PEGDMA polymer matrices (Fig. 5(a)). In contrast, the aggregation of PAL fibers was decreased, even diminished after organo-modification by organosilanes (Fig. 5(b)-(f)). Quite interestingly, the aggregates disappeared by using organo-PAL modified by methacrylate propyl (b), aminopropyl (c) or *n*-octyl (d) samples in *iso*-propanol gel. All the fibers dispersed well as needle-like entities. In comparison, by using aminopropyl (e) or *n*-octyl (f) modified organo-PAL in toluene, aggregates around 2 μm as a typical feature coexist with some isolated fibers in the composites.

Fig. 6 shows the optical absorption spectra of pure PEGDMA and PAL/PEGDMA nanocomposite films. Accordingly, the optical

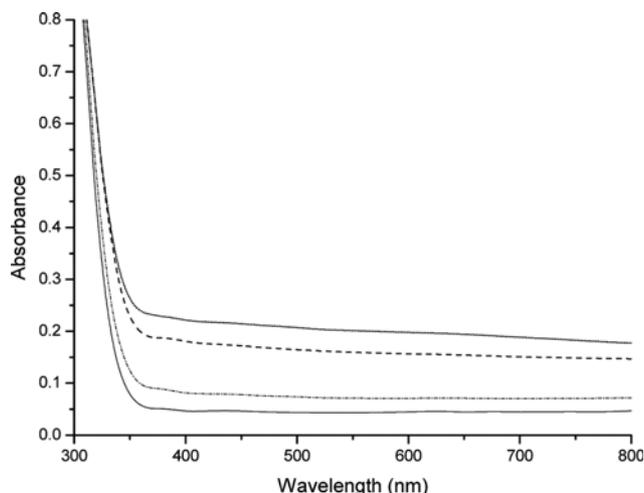


Fig. 6. UV-visible spectra of the PEGDMA/PAL nanocomposite films: (—) PEGDMA, (···) 5 wt% PAL, (---) 5 wt% PAL-C8, (-·-) 5 wt% PAL-C8-t.

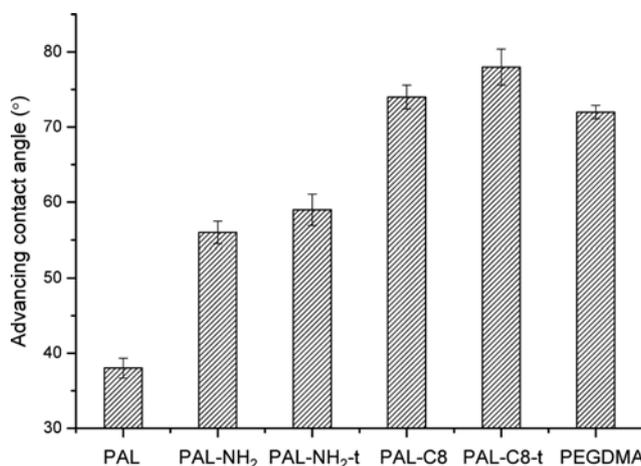


Fig. 7. Surface properties of PAL, organo-PAL and UV-cured PEGDMA coating.

property of the PEGDMA film appears highly transparent in the visible range (<0.05). When doping 5 wt% of raw PAL, the absorbance value of PAL/PEGDMA composite film becomes much higher, up to 0.25, which is already opaque. Adding the same amount of *n*-octyl functionalized PAL, the absorption intensity has been decreased. In particular, for the sample modified in *iso*-propanol gel, the absorbance value is only 0.08, quite close to the pure polymer film.

Fig. 7 provides the water contact angle data of PAL, organo-modified-PAL powders and UV-cured PEGDMA film. Clearly, the hydrophobicity of the PAL has been increased sharply from 37° to more than 56° through 3-aminopropyl modification in *iso*-propanol. By changing the modification function to *n*-octyl, the water contact angle was increased even to 75°. The values of PAL-NH₂-t and PAL-C8-t that modified in toluene are a few degrees higher than those performed in *iso*-propanol gel. It is probably because the residue of toluene molecules is much more hydrophobic than *iso*-propanol, which trapped in the grooves of PAL [35]. It further

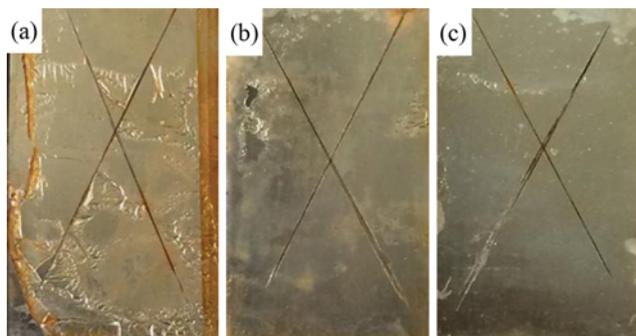


Fig. 8. Photographs of the steel panels after 144 h of 0.6 M NaCl solution immersion. (a) PEGDMA film and PAL/PEGDMA composite films with 5 wt% of PAL; (b) raw PAL, and (c) PAL-C8.

demonstrates the high efficiency of such *iso*-propanol gel modification procedure of PAL. This value is quite close to the PEGDMA film, which may explain why PAL-C8 has a better dispersion and compatibility with the PEGDMA film.

3. Corrosion Protection Properties

Fig. 8 shows the results of the films after 144 hours immersion in a neutral 0.6 M NaCl solution. For organic PEGDMA film (sample a), it has been blistered from the steel panel entirely, which showed an ineffective corrosion protection ability. The blistering phenomenon was drastically reduced by the addition of palygorskite (b) and (c). Although 5 wt% addition of raw pal (b) results in an opaque film, there is only few blistered area around 0.5 cm². Remarkably, a transparent film with good adhesion and corrosion protection properties was obtained by the addition of 5 wt% organo-modified Palygorskite of PAL-C8.

CONCLUSION

We report here a simple, efficient and relatively green process towards individual organo-modified PAL fibers by carrying out the PAL surface modification in the form of *iso*-propanol gels. SEM and N₂ adsorption-desorption characterizations confirmed that the modified PAL fibers from *iso*-propanol gel existed as almost-isolated fibers regardless of the organic functional groups. The results of FTIR and element analysis have demonstrated that organo-functions were grafted onto the surface of individual PAL fibers by chemical bonding successfully. But due to the reactivity of silane precursors and hindrance effect of the organo-functions, the grafted amount is varied depending on the types of functions. Furthermore, this modified PAL fibers have verified to be easily and well dispersed in acrylate polymer coatings, which provides high transparency in the visible light region and excellent corrosion protection abilities for steel panels. Their impacts on other physical and chemical properties of the resulting hybrid films are underway.

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