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Morphology and microstructure of core-shell hybrid latexes containing fluoropolymer and acrylic copolymer

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Abstract Novel core-shell hybrid latex composed by two immiscible polymers has been prepared. For the first time, we utilized fluoropolymer (FKM-40) as the core while polyacrylates as the shell in this latex, leading two immiscible components mixable under micro-molecular scale. To determine the chemical structure, in particular the miscibility between the core and the shell in this hybrid, transmission electron microscopy (TEM), attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and FTIR imaging have been performed. All experiments indicate that FKM-40 mixed well with polyacrylates, particularly FTIR image demonstrated unambiguously that FKM-40 dispersed, under micro-molecular scale, in continuous polyacrylates at a concentration of 20%. Further morphology (X-ray diffraction) investigations suggest that the hybrid latex had a less crystalline domain for samples with a lower concentration of FKM-40. Interestingly, we found that the water contact angle and the water absorption of the core-shell hybrid can be readily adjustable by varying the proportion of each species during copolymerization. Finally it is worth mentioning that the core-shell methodology as demonstrated herein is superior to physical blending with regard to its capability of achieving copolymer system under micro-molecular miscibility.

Keyword Micro-molecular mixing · Core-shell microstructure · FKM-40 fluoropolymer · Acrylic copolymer · FTIR image

Introduction

Fluoropolymers have become one of the intensive research area due to their high thermal, chemical and weather resistance, unique surface and optical properties that allow them to be used in numerous applications. Much effort has been made to develop various fluorinated copolymers, which are applied to reduce surface tension and to decrease wetting on many types of surfaces [1–11]. Among the fluoropolymers, fluorinated acrylic copolymers are finding increasing popularity even as components for high performance paint and varnish formulation in the textile, paper, leather and construction industry [12]. For practical reasons, fluorinated copolymers and the blends containing fluoropolymers and acrylic copolymers can be well designed to overcome the drawback of incompatibility and some poor mechanical properties of fluoropolymers. Also making a fluorinated dispersion by classic emulsion polymerization is not trivial [13, 14]. On account of the extremely low solubility of fluorinated monomer in water, this technique relies on the monomer transporting from the monomer droplets to the growing particles [15]. Many hybrid latexes containing fluoropolymers have been achieved by physical and chemical mixing of fluorinated and fluorine-free acrylates. For the physical mixing, latex blending is a good choice. The development of latex blends is attracting attention in aiming at reducing the content of volatile organic compounds (VOC) and promoting film formation [16]. In addition, latex blends of highly immiscible polymers offer attractive opportunities of controlling morphology development during film formation. The effects on this issue are studied and well documented [17, 18]. Linemann et al. [19] reported using atomic force microscopy (AFM) to study the film formation of latex blends of fluorinated and fluorine-free acrylates. The asymmetric (different particle size) mixture of fluorinated acrylic copolymer and hydrocarbon acrylic copolymer latexes was also investigated in the percolation and excluded volume, which could obtain a substantial excess of fluorinated, low free energy material [20].

The physical blending, however, is only a mixture in macro-molecular scale, which may result in serious surface segregation and phase separation. In the matter of this point, chemical mixing may make it possible to solve the separation by blending in micro-molecular scale during polymerization. On the molecular level mixing, the methods include graft copolymerization of fluoropolymer chain [21], fluorinated polyurethane [22–24] and core-shell methodology [15, 25, 26]. For all the core-shell fluorinated acrylate latexes reported, the hydrocarbon acrylate was usually used as the core, while the fluorinated acrylate was used as the shell [20, 25, 26]. Moreover, the conversion of fluorinated monomer during polymerization was very low. Experimentally determined fluorine values were found to be much low for the copolymers incorporating the fluorinated monomer compared to the polymerization recipe [19, 20].

In the present work, we report on a novel approach to the molecular level mixing of fluoro-monomer and hydrocarbon acrylate for the core-shell methodology by using fluoro-monomer as core and hydrocarbon acrylate as shell. This new approach is based on incorporating the acrylic monomer into the fluoropolymer in the polymerization stage. The result is an intimate mixing of the acrylic copolymer and fluoropolymer phases on a micro-molecular level. The composition and chemical structure of the core-shell latex obtained in the present work are investigated by transmission electron microscopy (TEM), attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and FTIR image. The core-shell latex is also characterized by water contact angle as well as X-ray diffraction (XRD) analysis. The core-shell latex obtained in the present work has the combined properties of fluoropolymer and acrylic copolymer.

Experimental

Materials

Methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA), *N*-hydroxylmethyl acrylamide (NMA) were all analytical grade and were obtained from Aldrich. OP-10 and MS-1 surfactants were purchased from Rays Co. and the emulsifier of FSO was from Dupont. The fluoropolymer emulsion FKM-40 (particle size 110 nm), copolymer of vinylidene fluoride and perfluoropropylene, was from Meilan Inc. and had a solid content of 20 wt%. All the chemicals were used as received. Water used was freshly distilled.

Latex synthesis

For the core-shell latex synthesis, the commercial emulsion FKM-40 was usually used as seed and core. The following FKM-40 seeded emulsion polymerization was done by semi-continuous free radical polymerization using ammonium persulfate as an initiator. The detailed procedure was described by Zhao et al. [27].

In a four-neck round flask, a recipe was added with 3 g MS-1, 3 g OP-10, 0.3 g FSO, 1.5 g protection colloid and 92 g distilled water. After stirring for half an hour, the flask was charged with 20 g monomer mixture, containing 53 wt% BA, 40 wt% MMA, 3 wt% AA and 4 wt% NMA. The above mixture was kept stirring for 1 h and, consequently, a pre-emulsion was obtained for the following emulsion polymerization. To carry out the core-shell latex synthesis, the pre-emulsion was mixed with rationed FKM-40 seed and stirred at 70 °C for 1 h to allow 20 g monomer mixture swell and diffuse into FKM-40 seed particles. Then, the reaction was initiated when 4 g ammonium persulfate solution (4 wt%) was introduced and the reaction temperature was raised to 75 °C. The reaction was continued for 3 h until another 68 g monomer mixture containing same ratio as above and 6 g ammonium persulfate solution (4 wt%) were added within 1.5 h. Finally, the reaction temperature was increased to 85 °C and was kept at this temperature for 1 h. The weight ratio of FKM-40 fluoropolymer to the total weight of acrylic monomer in the recipe was expressed as the core/shell ratio. The controlled weight ratio for the core-shell latex in the present study is from core/shell (0.04:0.96) to core/shell (0.5:0.5).

Characterization of latex

The synthesized core-shell latex was characterized by TEM, ATR-FTIR spectroscopy and IR imaging and water contact angle as well as XRD. The morphology of the latex was observed by using HITACHI H-600 with a magnification of $3–10\times10^4$. The diluted latex was applied to a 400 mesh carbon-coated copper grid and left to dry. The morphology was observed after the dried and ultramicrotomed thin film was stained by exposing the sample to osmium tetraoxide vapor for 48 h. The crystalline structure was analyzed by XRD on a D/Max-C.

The observation angle is between 5° and 45° and the step is 0.05° per second. The particle size of the core-shell latex was measured on an IETASIZER 3000HSA from Malvern Instrument. The ATR-FTIR spectra and FTIR imaging were measured on a Bio-Rad (Cambridge, MA) FT-60A step-scanning Stringray 6000 FTIR spectrometer with a UMA 300A FTIR microscope and 64×64 MCT focal plane array (FPA) detectors.

For water contact angle, it was measured using a contact angle meter type CA-A from Kyowa Interface Science Co. The shape of the droplet on the film was picked up on a photographic film, and then the contact angle was obtained. For the water adsorption, the film was first sliced into rectangular strips of about 10×10 mm^2 in size. The water adsorption was calculated as follows:

$$\%\text{Water Adsorption} = (W_2 - W_1)/W_1 \times 100\% \qquad (1)$$

where W_1 is the initial weight of the dried latex film and W_2 is the latex film weight after immersion in distilled water for 24 h. Each water adsorption reported was the average of at least three sample measurements.

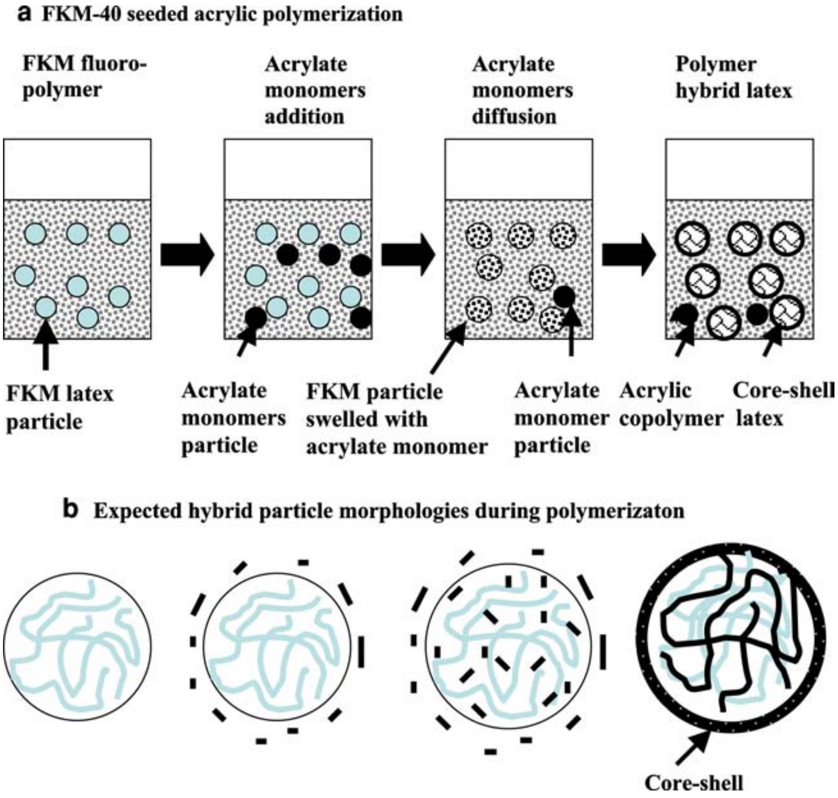
Results and discussion

One of the most prominent advantages of core-shell latex is that it allows micro-molecular level mixing of very different polarities in hetero-phase situation, including fluoropolymer and acrylic copolymer [19, 20]. The FKM-40 seeded acrylic polymerization process, characterization and structure, and some physical properties are described in detail below.

Core-shell latex synthesis

The core-shell latex containing FKM-40 fluoropolymer latex and acrylic copolymer was obtained by FKM-40 seeded acrylic emulsion polymerization as shown schematically in Fig. 1a. The commercial fluoropolymer latex FKM-40 with the particle size of 110 nm was used as the seed. After FKM-40 was mixed with acrylic monomers and initiator, they were immersed and dispersed in acrylic monomer solution. Because of the acrylic monomers' concentration difference inside and outside FKM-40 seed, monomers were driven to diffuse into FKM-40 particles. After that, the acrylic monomers and the initiator swell the inside and surface of FKM-40 seeds as shown in Fig. 1a. Under the temperature ranging from 75 to 85 °C, acrylic monomers had in-situ polymerization inside FKM-40 seed and on the surface of FKM-40 surface as well as in the bulk reaction solution. The desired morphology and structure of latex particles after polymerization are seen in Fig. 1b. In the FKM-40 seed core, the entanglement network of acrylic

Fig. 1 Schematic latex particle formation and microstructure of the hybrid latex containing FKM-40 fluoropolymer and acrylic copolymer



polymer and fluoropolymer is formed, which results in micro-molecular level mixing fluoropolymer and acrylic copolymer. On the other hand, acrylic copolymer shell is developed surrounding the surface of FKM-40 seed core, which is generated by the polymerization of acrylic monomers entangled on the fluoropolymer seed surface. The final result of acrylic polymerization inside and on the surface of FKM-40 seed leads to the core-shell hybrid latex with micro-molecular level mixing two immiscible polymers due to forming interpenetrating polymer network of acrylic copolymers through FKM-40 core structure and the latex shell structure. The part of acrylic monomers, however, could also polymerize in the bulk reaction solution, which generates the acrylic homopolymer latex particle in the solution. This is another factor that allows obtaining core-shell hybrid latex with micro-molecular level mixing. The detailed structure of the core-shell hybrid latex is illustrated in the following TEM morphology and FTIR image analysis.

Core-shell latex morphology

It is noted that RuO_4 is an effective staining agent to discriminate the fluorinated phase from the hydrogenated one of such polymers [28]. Actually, RuO_4 is a strong oxidizing agent of many chemical groups present in polymers [29, 30], such as aromatic rings and ethers. Perfluorinated chains do not react with it, even after several hours of exposure to its vapor. Therefore, the dark area in the following TEM micrographs refers to acrylic copolymer while the light or white area refers to fluoropolymer FMK-40.

Figure 2 is TEM micrographs of latex particles of acrylic copolymer with a magnification of 10^4 (a), core/shell (0.08:0.92) hybrid latex with magnification 3×10^4 (b), the corresponding higher magnification of 10^5 for the core/shell (0.08:0.92) hybrid latex (c), core/shell (0.08/0.92) hybrid latex containing FKM-40 fluoropolymer and acrylic copolymer with the magnification 6×10^4 stained with phosphotungstic acid (d). The dark spherical-shaped particles in Fig. 2a show the latex particle of acrylic copolymer with the size of about 166 nm. After FKM-40 seeded acrylic emulsion polymerization, FKM-40 fluoropolymer and acrylic polymer were mixed in micro-molecular level as shown in Fig. 2b. As shown in Fig. 2b, the dark domain is the acrylic copolymer particle, which is from acrylic homopolymerization reaction in the bulk reaction solution. The gray spherical-shaped domain in Fig. 2b is FKM-40 particle. The gray color means that there is some acrylic copolymer in FKM-40 particles. It is due to some acrylic monomer polymerization in FKM-40 particle during seeded polymerization.

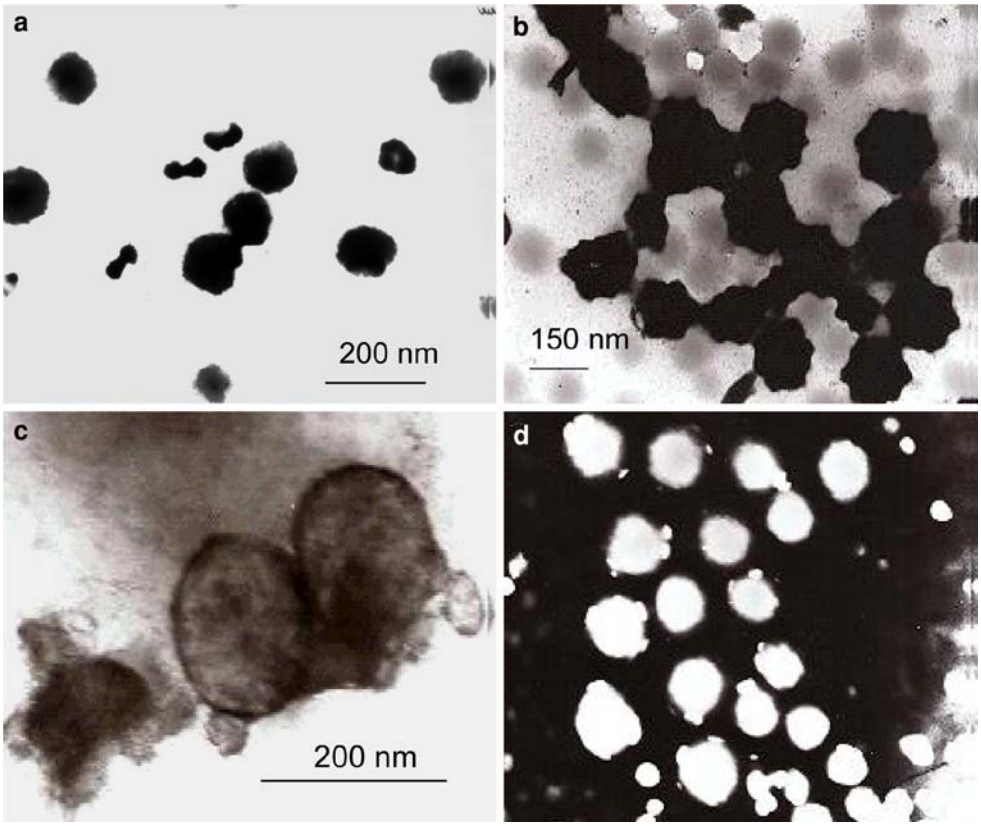


Fig. 2 TEM micrographs of latex particles of acrylic copolymer with the magnification of 10^4 (**a**), core/shell (0.08/0.92) hybrid latex containing FKM-40 fluoropolymer and acrylic copolymer with the magnification of 3×10^4 (**b**), the corresponding higher magnification of 10^5 for the core/shell (0.08/0.92) hybrid latex (**c**), core/shell (0.08/0.92) hybrid latex containing FKM-40 fluoropolymer and acrylic copolymer with the magnification of 6×10^4 stained with phosphotungstic acid (**d**)

To study the core-shell structure in detail, higher magnification was used for the FKM-40/acrylic copolymer latex particles as shown in Fig. 2c. The core-shell (0.08:0.92) latex particle size of FKM-40/acrylic copolymer, as measured by an IETASIZER 3000HSA, is about 130 nm. Figure 2c shows many dark sub-domains in the particles, which suggest the presence of acrylic copolymer chains in the particles. These chains are the results of in-situ polymerization of acrylic monomers swelled in the FKM-40 particles before polymerization. Consequently, the mixing mode of FKM-40 and acrylic polymer is a little like interpenetration network (IPN) in the FKM-40 particles. The micro-molecule level mixing of fluoropolymer and acrylic copolymer was obtained ultimately. In addition, the black contour around the particle is the entanglement of acrylic copolymer and FKM-40 fluoropolymer on seed surface, which forms the shell of the latex. During the FKM-40 seeded polymerization, acrylic polymerization could occur in FKM-40 particles and on the surface of FKM-40 particles and in the bulk reaction solution. However, the monomer concentrations for these three polymerization sites were different with the highest concentration in bulk reaction solution and lowest concentration in the FKM-40 seed particle. This monomer concentration gradient determined the amount of acrylic copolymer content in these three sites after polymerization. As this gradient was reflected in the TEM micrographs, the darkest area are free acrylic copolymer in the bulk reaction solution, and the dark area are the FKM-40 seed surface with acrylic copolymer entanglement as well as the gray area inside the FKM-40 seed particle. The darkness in the above three polymerization sites is further confirmed by TEM micrographs of FKM-40/acrylic copolymer particle stained by phosphotungstic acid (shown in Fig. 2d).

To investigate the thickness of the shell of the latex, the core shell latex particle size was measured by using an IETASIZER 3000HSA. The thickness of the shell should be around 20 nm since the size of the FKM-40 seed used for seeded emulsion polymerization is 110 nm. The detailed structure of the core shell latex in the present study is described in Fig. 1b.

X-ray diffraction (XRD)

The FKM-40 fluoropolymer used in the present work is the copolymer of vinylidene fluoride and perfluoropropylene, which has crystalline structure [32]. On the contrary, acrylic copolymer used here does not have crystalline structure. Figure 3 is XRD of the different weight ratios of FKM-40/acrylic copolymer of core/shell (1.0:0) (a), core/shell (0.5:0.5) (b), core/shell (0.2:0.8) (c), core/shell (0.04:0.96) (d), and core/shell (0:1) (e). The high diffraction peak of the curve in Fig. 4a is consistent with the high crystallization of FKM-40 [32]. With the

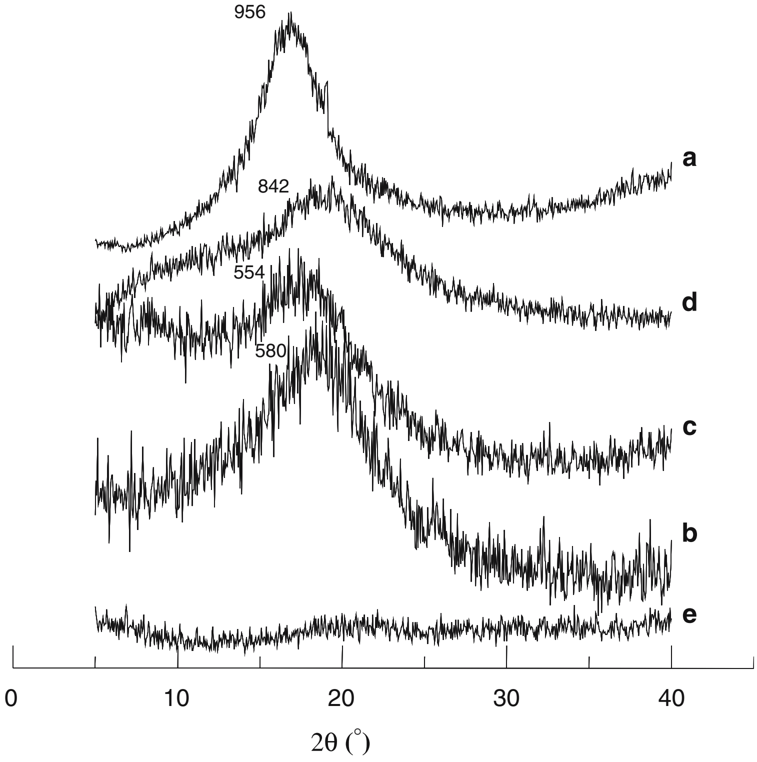


Fig. 3 X-ray diffraction (XRD) picture of the latexes with the different core/shell weight ratios of FKM-40 to acrylic copolymer, core/shell (1:0) (**a**), core/shell (0.5:0.5) (**b**), core/shell (0.2:0.8) (**c**), core/shell (0.04:0.96) (**d**), core/shell (0:1) (**e**)

decreasing concentration of FKM, the diffraction peak becomes shorter and wider, and finally there is no diffraction peak for the single acrylic copolymer—the noncrystalline structure.

ATR-FTIR spectroscopy and FTIR imaging

As mentioned above, the core-shell latex was synthesized herein with FKM-40 fluoropolymer as a core and acrylic copolymer as a shell. In other word, the particles of FKM-40 fluoropolymer were covered with a layer of acrylic copolymer and the entanglement of FKM-40 fluoropolymer and acrylic copolymer was achieved in the latex particles. To study the micromolecular level mixing of these two polymers, FTIR and FTIR imaging (3D) were done. Figure 4 shows the respective ATR-FTIR spectroscopy and FTIR imaging (3D) of C–F bond for the core/shell (0.04:0.96) [(a) FTIR spectroscopy at wave number of 1,156 cm^{-1} and (b) FTIR 3D imaging at wave number of 1,156 cm^{-1}], and the core/shell (0.08:0.92) [(c) FTIR spectroscopy at wave number of 1,156 cm^{-1} and (d) FTIR 3D imaging at wave number of 1,156 cm^{-1}]. The absorption modes at about 1,156 and 1,233 cm^{-1} for the core shell latex film in Fig. 4a and c are associated with the characteristic peak of C–F bond respectively [33]. The presence of C–F bond is consistent with the FKM-40

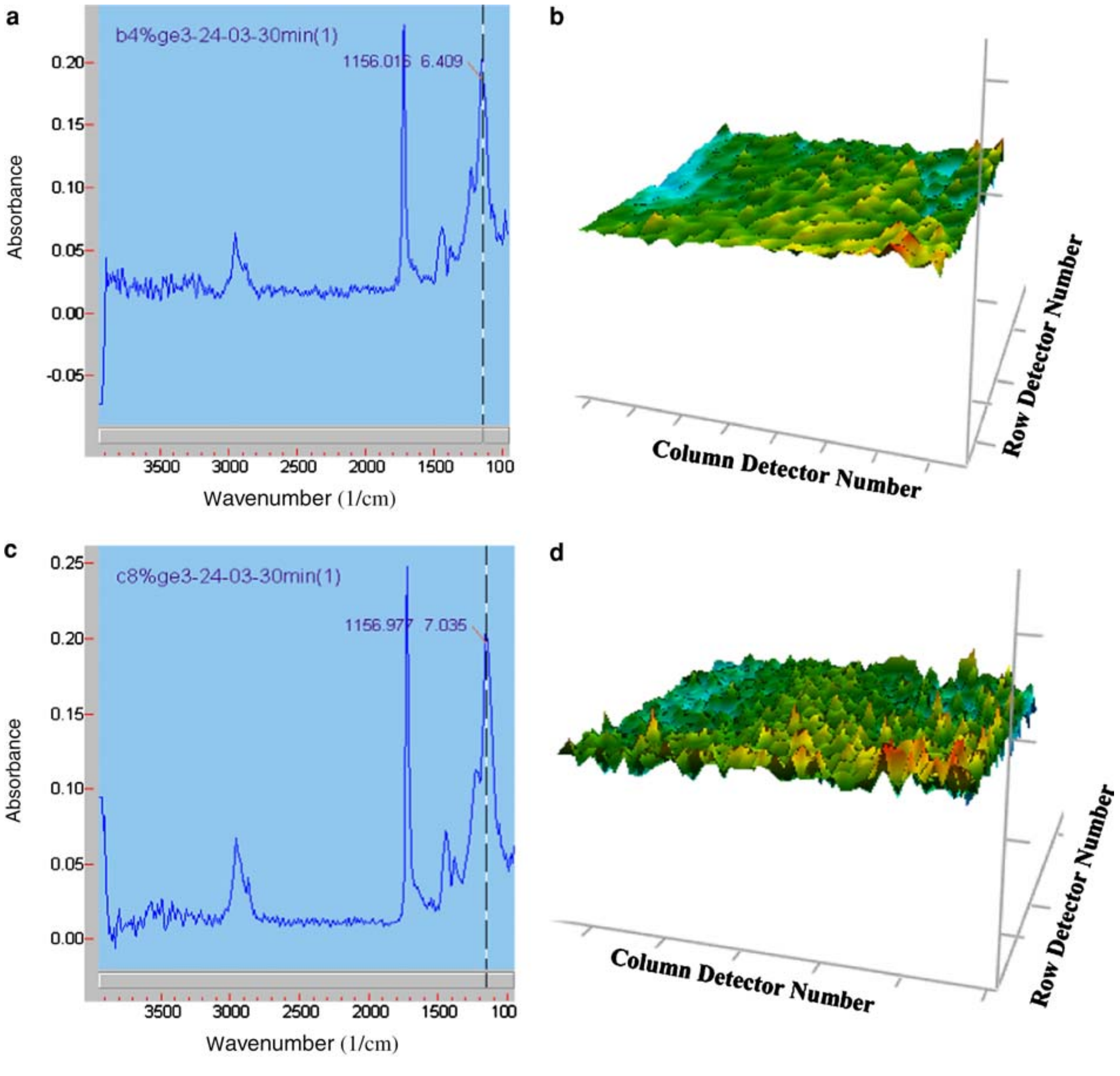


Fig. 4 ATR-FTIR spectra and FTIR imaging (3D) for FKM-40/acrylic copolymer core-shell hybrid latex with different ratios of 0.04:0.96 (wt:wt) (**a**, **b**) and 0.08:0.92 (wt:wt) (**c**, **d**). FTIR imaging (3D) (**b**, **d**) is C–F bond at the wave number 1,156 cm^{-1} imaging

fluoropolymer in the core-shell latex film and suggests that FKM-40 fluoropolymer is within the probing depth of the ATR-FTIR technique on the film surface (1–2 μm in latex matrix) [17]. Furthermore, comparison of Fig. 4c to a for the C–F bond absorption suggests that the higher the FKM-40 percentage in the core-shell latex, the stronger the absorption of C–F bond. In order to study the chemical component distribution and possible phase separation of the film surface, FTIR imaging at wave number of 1,156 cm^{-1} for C–F bond was done. Images based on mid-infrared spectral differences and changes generated using FTIR microscopy instrumentation fitted with FPA detectors have increasingly become useful to highlight chemical structure variations and/or morphology gradients in many materials [34, 35]. Pictures in Fig. 4b and d (3D imaging) show that the distribution of C–F bond is homogeneous. It presents that there is no obvious phase separation, that is to say that FKM-40 fluoropolymer and acrylic copolymer are well mixed to a micro-molecular level. Early study reported that physical blending or macro-molecular level mixing of two immiscible polymers easily resulted in phase separation [19, 20].

Figure 5a shows a strong absorption band at 1,728 cm^{-1}, which can be attributed to the stretching vibration of the carbonyl groups [36]. The high adsorption of the carbonyl group suggests high percentage of acrylic polymer in the core-shell latex. The presence of acrylic copolymer is also confirmed by the absorption band at 1,448 cm^{-1}, which is characteristic of the gauche conformation of the alkyl chains [36] and must have resulted from the acrylic copolymer in the core-shell latex. To probe the acrylic copolymer component distribution and the possible phase separation, FTIR imaging (3D) at 1,728 cm^{-1} for the carbonyl group was also done. Figure 5b shows the FTIR imaging of carbonyl group at 1,728 cm^{-1} for the vision of 3D. It can be seen from Fig. 5b that the surface appears to be generally homogeneous in terms of carbonyl group. Figure 5b further confirms the well mixing of FKM-40 fluoropolymer and acrylic copolymer. It is consistent with the result in Fig. 4b and d and the core-shell latex morphology discussed earlier.

Water contact angle and water adsorption

Fluoropolymer has very low surface energy and, thus, high water contact angle [37–39]. Mixing it with acrylic copolymer can offer optimum property combinations, including high water contact angle, excellent chemical resistance and good weatherability. Figure 6 shows the effect of FKM-40 concentration on water contact angle and water absorption. The water contact angle increases with increasing FKM-40 concentration. It is due to good hydrophobicity of FKM-40 fluoropolymer in films. The water contact angle levels off when FKM-40 concentration is higher than 20 wt%. Thus, the optimum concentration of FKM-40 is 20 wt% in the formulation for the high performance of water contact angle. The water contact angle is only about 55° for the control

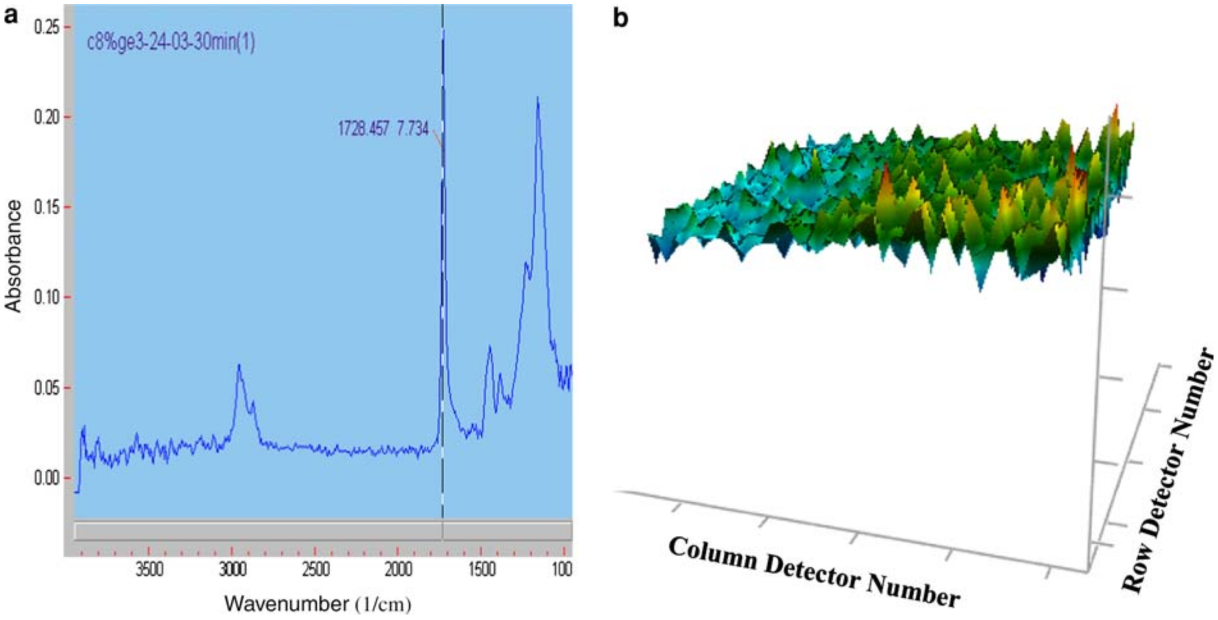


Fig. 5 ATR-FTIR spectroscopy (**a**) and FTIR 3D imaging (**b**) of the carbonyl group at 1,728 cm^{-1} for the FKM-40/acrylic copolymer hybrid latex with core/shell weight ratio (wt:wt) 0.04:0.96

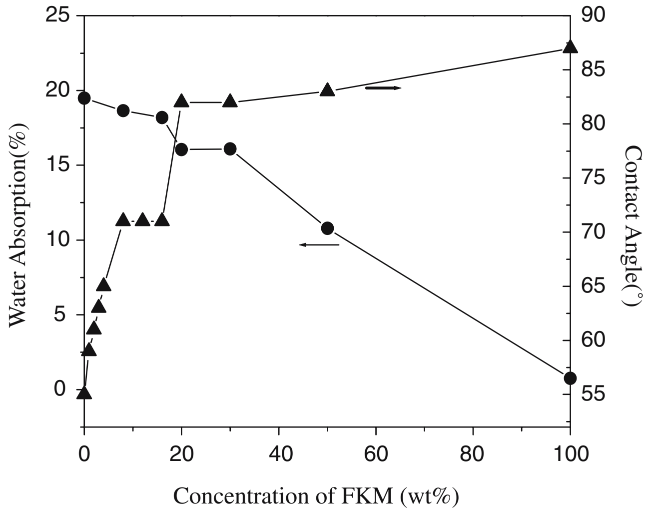


Fig. 6 The effect of FKM-40 fluoropolymer concentration on water contact angle and water absorption of the core-shell latex film

acrylic copolymer in the present study while it can be up to 86° for FKM-40 used here. Thus, the FKM-40 fluoropolymer component contributes to the improved water contact angle and the final contact angle depends on the core/shell ratio.

The above water contact angle is based on mixing FKM-40 fluoropolymer and acrylic copolymer in micro-molecular level by using core-shell methodology in the present study. The water contact angle is higher than that of physical blending—the macro-molecular level mixing. Table 1 shows the water contact angle for mixing in micro-molecular level (named chemical mixing herein) and physical blending. It indicates that higher performance was obtained for the chemical mixing. For physical blending, phase separation occurs and exists since these two kinds of polymer are incompatible, which results in the heterogeneous surface. However, the difference on water absorption becomes smaller for the high concentration of FKM-40 as shown in Table 1. Thus, chemical mixing is a more effective method to obtain high water contact angle at low concentration level of FKM-40.

The results of higher contact angle for the chemical mixing FKM-40 fluoropolymer and acrylic copolymer can also be confirmed from the corresponding result of water adsorption. Figure 6 shows that the water adsorption decreases with increasing FKM-40 concentration. The water adsorption is associated with the hydrophobicity and permeability of the materials. With more hydrophobic material FKM-40 in the film, the hybrid film gets better water resistance and low water adsorption, assuming the water permeability to be the same. For low concentration of FKM-40, the main component in the film is still acrylic copolymer. So the value of corresponding water resistance is close to that of acrylic copolymer.

Similarly, different mixing levels also affect the water adsorption. Table 2 shows the effect of different mixing methods on water adsorption of hybrid latex. Water adsorption of hybrid latexes for chemical mixing was lower than that of physical blending. It also confirms with the above results of water contact angle.

Finally, it is appropriate to emphasize that the micro-molecular level mixing FKM-40 fluoropolymer and acrylic copolymer was achieved by using FKM-40 fluoropolymer as the core and acrylic copolymer as the shell for the latex. The present mixing approach differs from those in the earlier works which involve using acrylic copolymer as the core and fluoropolymer as the shell [15, 25, 26]. In addition, the thickness of the shell—acrylic copolymer—can be changed and it depends on the final desired properties. The tunable film properties as a result of the core-shell structure latex make the present method a viable and promising approach to the preparation of polymeric composites of two immiscible materials.

Conclusion

Core-shell hybrid latexes containing FKM-40 fluoropolymer and acrylic copolymer were obtained for the micro-molecular level mixing two immiscible materials. The latex had the FKM-40 fluoropolymer as the core and acrylic copolymer as the shell for the micro-

Table 1 Effects of different mixing methods on water contact angle of FKM-40/acrylic copolymer hybrid latex

FKM-40 concentration (wt%)	Mixing method	Water contact angle (°)
4	Core-shell	65
4	Physical blending	52
8	Core-shell	71
8	Physical blending	60
12	Core-shell	71
12	Physical blending	67

Table 2 Effects of different mixing methods on water absorption of FKM/acrylic copolymer hybrid latex

FKM-40 concentration (wt%)	Mixing method	Water absorption (%)
4	Core-shell	23
4	Physical blending	25.3
8	Core-shell	18.7
8	Physical blending	23.1
12	Core-shell	17.5
12	Physical blending	22.1

molecular level mixing, as suggested by TEM and FTIR imaging results. TEM pictures illustrated that the core-shell morphology and the microstructures of the core-shell latexes are dominant in the hybrid latex, which conform to our desirable designing structure for the hybrid latex. FTIR imaging pictures presented that FKM-40 fluoropolymer with the 20% maximum concentration could be dispersed well in the acrylic copolymer continuous phase by aid of micro-molecular level mixing. Further morphology (XRD) investigations suggest that the hybrid latex had less crystalline domain for samples with a lower concentration of FKM-40. The water contact angle and water adsorption of the core-shell latex were a function of the FKM-40 fluoropolymer concentration used. Finally it is worth mentioning that core-shell methodology mixing at micro-molecular level as demonstrated herein is superior to physical blending with regard to its capability of achieving copolymer system under micromolecular miscibility. This kind of core-shell methodology gives rise to a micro-molecular level mixing two immiscible materials. Efforts can be under way to extend the utility of this methodology to other hybrid latexes.

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