

Epoxy Resin/Polyurethane Hybrid Networks Synthesized by Frontal Polymerization

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We report the first synthesis of the epoxy resin/polyurethane (EP/PU) hybrid networks via frontal polymerization (FP). In a typical run, the appropriate amounts of reactants (poly(propylene oxide glycol), epoxy resin diglycidyl ether of bisphenol A, 2,4-toluene diisocyanate, and 1,4-butanediol with stannous caprylate (as the catalyst)) were mixed together at initial temperature in the presence of toluene (as the solvent). FP was thermally ignited at one end of the tubular reactor, and the resultant hot fronts propagated throughout the reaction vessel. Once initiated, no further energy was required for polymerization to occur. The dependence of the front velocity and front temperature on the catalyst concentration was thoroughly investigated. The samples were characterized with a Fourier transform infrared spectrometer, thermogravimetric analysis, and a scanning electron microscope. EP/PU hybrid networks synthesized by FP have the same properties as those synthesized by batch polymerization, but the FP method requires significantly less time and lower energy input.

Introduction

Interest in frontal polymerization (FP) has increased in recent years since FP became a promising new technique for synthesizing uniform polymers and polymeric networks in a rapid fashion. FP is a mode of converting a monomer into a polymer via a localized reaction zone that propagates through a liquid monomer (Figure 1a). First introduced as a way to synthesize poly(methyl methacrylate) at high pressure by Chechilo et al. in 1972,¹ this method was later extended by Pojman and co-workers to perform a large number of experimental and theoretical works.^{2–7}

An overwhelming majority of work has been focused on free-radical polymerization because it is usually highly exothermic, and the heat of the reaction provides autocatalysis for a polymerization front propagating through a liquid monomer. Subsequently, Pojman and co-workers have done a lot of work focusing on the feasibility of traveling fronts in solutions of thermal free-radical initiators in a variety of neat monomers at ambient pressure using liquid monomers^{8,9} or a solid monomer.^{10,11} The availability of their preparation

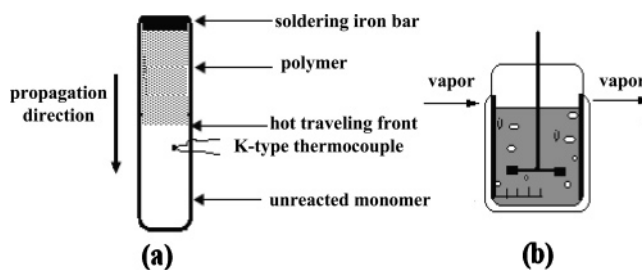


Figure 1. Schematic representation of (a) FP occurring along a tubular reactor and (b) BP occurring in a reaction kettle.

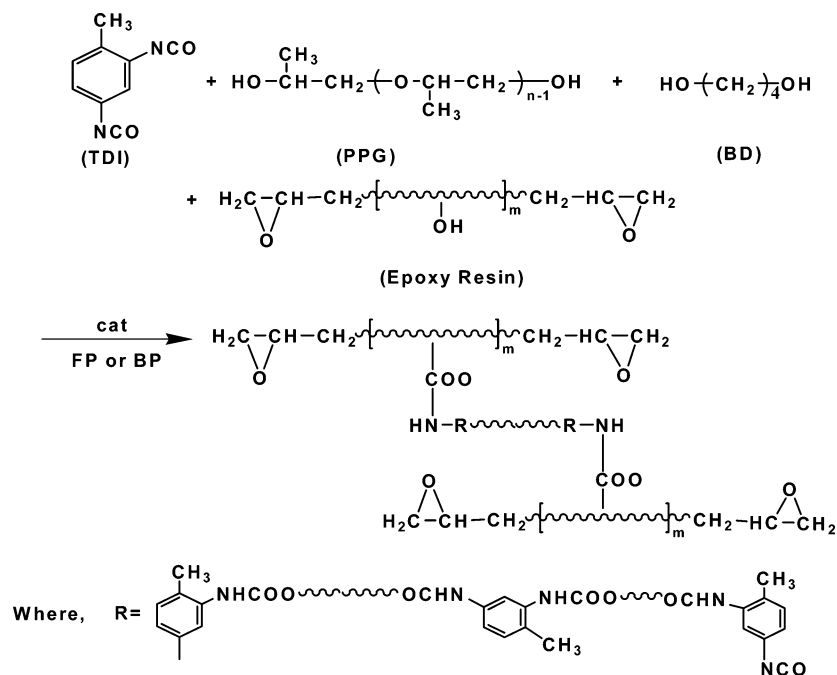
techniques allows traveling fronts in solutions of a thermal free-radical system at ambient pressure without removing initiators from monomers; thus, longer pot lives can be achieved for the latter. Further development of the FP awaited the discovery of other suitable monomers that did not boil at the front temperature for the stable front. Several researchers recently studied frontal copolymerization¹² and UV-induced FP of multifunctional acrylate monomers.¹³ The method was also effectively applied to epoxy resins and their interpenetrating polymer networks (IPNs).^{14,15} Pojman et al.¹⁶ reported on epoxy–acrylate binary systems. Begishev et

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Scheme 1. Formation of EP/PU Hybrid Networks Synthesized by FP or BP



al.^{17,18} studied frontal anionic polymerization of ϵ -caprolactam, and Fiori et al.¹⁹ produced polyacrylate–poly(dicyclopentadiene) networks frontally. FP has been used to prepare a number of polymer materials.^{20–23} Pojman et al.²⁴ prepared thermochromic composites whose color was temperature dependent via FP. Szalay et al.²⁵ reported conductive composites prepared frontally. Vicini et al.²⁶ developed a FP method for the consolidation of stone. Fiori and Mariani²⁷ prepared polyurethanes (PUs) by using 1,6-hexamethylene diisocyanate and ethylene glycol frontally and demonstrated frontal ring-opening metathesis polymerization.²⁸ Recently, Chen et al.^{29–31} reported that segmented PU and PU–nanosilica hybrids were synthesized with FP. It provided a feasible way to use FP to commercially synthesize PUs with less energy and less cost than those of traditional batch polymerization (BP; seen in Figure 1b).

PUs provide a wide range of properties from a variety of starting materials. Tailor-made properties of these materials

can be obtained from well-designed combinations of monomeric materials. On a molecular basis, PU may be described as the linear structure block copolymer of the (AB)_n type. Part A, the hard segment, is composed of oligomers, which are prepared by the reaction of a low molecular weight diol or triol chain extender with diisocyanate. Part B, the soft segment, is normally a polyester and a polyether polyol with a molecular weight of 1000–3000.³² To improve the performance properties of PUs in various applications, hybrid PU nanocomposites^{33–36} and multiphase polymeric systems such as IPNs^{37–39} have been extensively used for more than three decades. In this publication, we describe how we produced epoxy resin/PU hybrid networks using FP. In a typical run, the appropriate amounts of reactants (poly(propylene oxide glycol) (PPG), epoxy resin diglycidyl ether of bisphenol A (E44), 2,4-toluene diisocyanate (TDI), 1,4-butanediol (BD), and stannous caprylate (as the catalyst)) were mixed together at an initial temperature in the presence of toluene (as the solvent). FP was thermally ignited at one end of the tubular reactor, and the resultant hot fronts propagated throughout the reaction vessel. No further energy was required for polymerization to occur. The schematic synthesis of epoxy resin (EP)/PU hybrid networks is presented in Scheme 1.⁴⁰ We determined the effect factors of front velocity, stannous caprylate concentration, and

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temperature on the FP, along with comparison of FP with BP.

Experimental Section

Materials. PPG (hydroxyl number of 56 mg KOH/g, average molecule weight of 2000) was acquired from Dow Co. The E44 ([epoxy value] = 0.41–0.47 equiv/100 g), stannous caprylate, TDI, BD, and toluene were supplied by Aldrich and used as received.

FP. For the synthesis of the EP/PU hybrid networks by FP (shown in Figure 1a), the appropriate amounts of E44, TDI, PPG, BD, and stannous caprylate (as the catalyst) were mixed together at ambient temperature in toluene in a flask. A typical molar composition was TDI/PPG/BD = 2.8:1:1 mol/mol. The flask was shaken vigorously to obtain a homogeneous mixture. Then, the solution was poured into a 10 mL ($D = 15$ mm) test tube, and a K-type thermocouple, connected to a digital thermometer, was utilized to monitor the temperature change. The junction was immersed at about 1.0 cm from the free surface of the liquid. The upper layer of the mixture was then heated by a soldering iron bar until the formation of a hot propagating front.

The front velocities were determined by measuring the distance that the front traveled as a function of time. When pure FP occurred, a constant velocity front propagated with almost no bubbles. Temperature profiles and the maximum temperature (T_{\max}) of the front were measured by using a K-type thermocouple by measuring the temperature at a fixed point as a function of time. Subsequently, they were converted to spatial profiles using the front velocity.

BP. Several batch runs had been performed to compare the resultant samples with the corresponding ones obtained by FP. In a typical run, the same amounts of each component as quoted above were mixed with vigorous stirring in a reaction vessel and immersed in a thermostatic oil bath set at 85 °C for 3 h. Then the mixture was cooled back to ambient temperature and stirred for 1 h.

Characterization. The chemical structure of EP/PU hybrid networks was analyzed by Fourier transform infrared (FT-IR) spectroscopy in the range 450–4000 cm^{-1} using an AVATAR-360 (KBr disk, 64 scans, 4 cm^{-1} resolution). The weight loss of the EP/PU hybrid networks on heating was studied by thermogravimetric analysis (TGA) using a thermogravimetric apparatus Shimadzu-TGA 50 in a nitrogen atmosphere. Measurements were taken with a heating rate of 10 °C/min from 30 to 600 °C. The surface morphology of EP/PU hybrid networks coated with Au was investigated by scanning electron microscopy (SEM) using a QUANTA 200. SEM samples were prepared by applying drops of hybrids onto hot aluminum SEM stubs, followed by drying at ambient temperature.

Results and Discussion

Preliminary Experiments. We have performed several preliminary experiments to find a suitable route for obtaining PU by FP.²⁹ Usually, the pot life is an important factor for FP. We evaluated the pot life via mixing the reactants, leaving them at ambient temperature, and visually determining at what time they could spontaneously polymerized. On the basis of this point, we employ the same method to examine the pot life in preparing EP/PU hybrid networks by FP. We found that a solution of E44, PPG, BD, TDI, stannous caprylate ([NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol, [catalyst]/[TDI] = 1.0×10^{-3} mol/mol), and toluene (10 wt %) exhibited a pot life of more than 3 h at the ambient temperature (30 °C), and instantaneous spontaneous polymerization (SP) does not occur. Some litera-

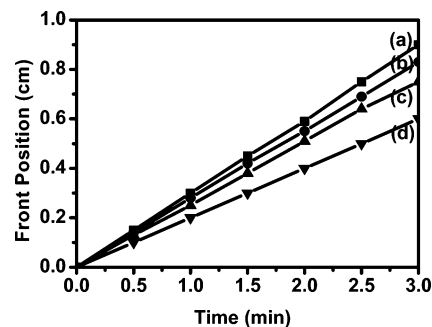


Figure 2. Front position vs time for typical runs (a–d). (a) Pure PU prepared by FP, [NCO]/[OH] = 1.4:1 mol/mol; [catalyst]/[TDI] = 1.0×10^{-3} mol/mol; toluene = 10 wt %. (b) EP/PU hybrid networks prepared by FP, E44 = 5 wt %; [NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol; [catalyst]/[TDI] = 1.0×10^{-3} mol/mol; toluene = 10 wt %. (c) EP/PU hybrid networks prepared by FP, E44 = 10 wt %; [NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol; [catalyst]/[TDI] = 1.0×10^{-3} mol/mol; toluene = 10 wt %. (d) EP/PU hybrid networks prepared by FP, E44 = 15 wt %; [NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol; [catalyst]/[TDI] = 1.0×10^{-3} mol/mol; toluene = 10 wt %.

ture^{27,41} reported that an extended pot life in the synthesis of PUs can be achieved by adding suitable amounts of additive (pyrocatechol) to depress the activity of dibutyltin dilaurate (DBTDL, as the catalyst) at ambient temperature. However, by pyrocatechol addition a pot life could be only achieved to 25 min. We have found that stannous caprylate catalyst is better than DBTDL for preparing PU by FP. It can be attributed to the fact that the catalyst, stannous caprylate, has the lower activity than that of DBTDL,⁴² which could obtain a longer pot life for FP. This finding allowed us to perform pure FP runs without simultaneous occurrence of SP.

Effect of the Relative Parameters Relating to FP. One of the key features of pure FP is that all data on front velocity versus reaction time are well-described by a straight and linear fit. Moreover, there is a T_{\max} value in the function of front temperature and front position during the FP. Conversely, SP may occur simultaneously.

The position of the thermal front as a function of time is given in Figure 2 for (a) pure PU and EP/PU hybrid networks with (b) 5 wt % E44, (c) 10 wt % E44, and (d) 15 wt % E44. As shown in Figure 2, the experimental data for all sets of experiments are well-fitted by straight lines, meaning that the propagation of the polymerization front moves at a constant velocity. This is the first strong evidence that pure FP is occurring. Also, the velocity of the EP/PU hybrid networks front decreases with an increase of the E44 concentration. This can be explained by the fact that the viscosity of hybrids increases as a result of the reaction between the E44 and isocyanate in EP/PU hybrid networks, which can decrease the convection conduct caused by buoyancy. Fiori and Mariani²⁷ have reported that deviations from the linearity are generally observed when a simultaneous SP is occurring due to heat dispersion caused by the monomer fraction polymerized by SP and to the related change of medium viscosity.

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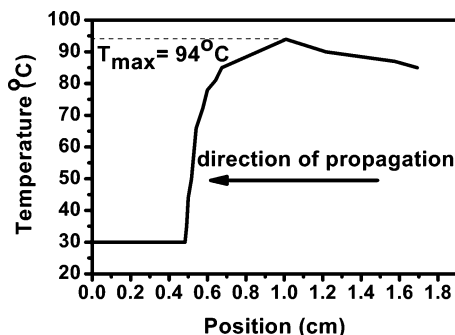


Figure 3. Typical front temperature profile of EP/PU hybrid networks prepared by FP. E44 = 10 wt %; [NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol; [catalyst]/[TDI] = 1.0×10^{-3} mol/mol; toluene = 10 wt %.

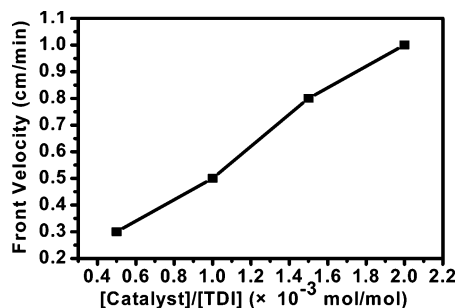


Figure 4. Frontal velocity of EP/PU hybrid networks prepared vs [catalyst]/[TDI] ratio. E44 = 10 wt %; [NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol; toluene = 10 wt %.

Further evidence to support pure FP is the temperature profile. A typical temperature profile of EP/PU hybrid networks is shown in Figure 3. This experiment was done with E44 = 10 wt %, [NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol, [catalyst]/[TDI] = 1.0×10^{-3} mol/mol, and toluene = 10 wt %. A temperature increase can be observed on account of the highly exothermic reaction, and the T_{\max} is 94 °C. As a result of the constant temperature value in zones far from the incoming hot front, there is a horizontal part of the curve, meaning that SP is not occurring. The front temperature profile is more evidence to reveal that only pure FP occurs.

We studied the front velocity dependence on the catalyst concentration with a constant concentration of E44 (10 wt %) and [NCO]/[OH]/[epoxy value] (1.4:1:1, mol/mol). Figure 4 is the curve of front velocity of EP/PU hybrid networks versus catalyst concentration by FP. As expected, the front velocity increases with higher concentrations of catalyst. FP could be observed for [catalyst]/[TDI] between 0.5×10^{-3} and 2.0×10^{-3} mol/mol. For lower catalyst concentrations ([catalyst]/[TDI] less than 0.5×10^{-3} mol/mol), no propagating front could be achieved because of heat loss. Conversely, for [catalyst]/[TDI] $> 2.0 \times 10^{-3}$ mol/mol, SP occurred.

Figure 5 is the curve of T_{\max} of EP/PU hybrid networks by FP versus catalyst concentrations. An increase of [catalyst]/[TDI] from 0.5×10^{-3} to 2.0×10^{-3} mol/mol caused an increase of T_{\max} from 86 to 105 °C. Our experiments were performed under nonadiabatic conditions; for this reason, the increased front velocity reduced the time for heat loss.

Characterization Data and Comparison between Samples Prepared by FP and Samples Prepared by BP. The polymer structure of EP/PU hybrid networks is ascertained from FT-IR spectra. Figure 6 shows FT-IR spectra of

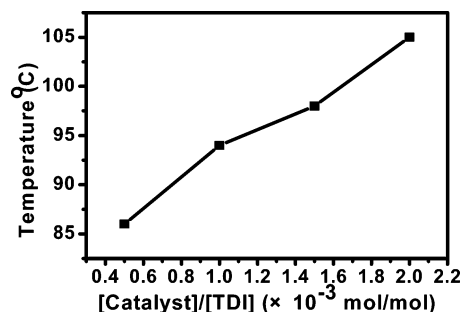


Figure 5. T_{\max} of EP/PU hybrid networks front prepared vs [catalyst]/[TDI] ratio. E44 = 10 wt %; [NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol; toluene = 10 wt %.

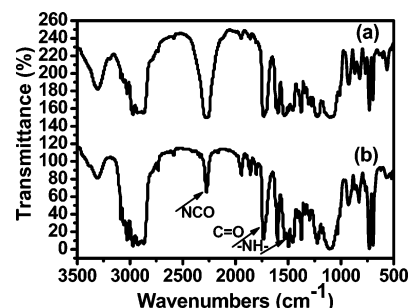


Figure 6. FT-IR spectra ($500\text{--}3500\text{ cm}^{-1}$) of EP/PU hybrid networks. (a) EP/PU hybrid networks synthesized by FP, E44 = 10 wt %; [NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol; [catalyst]/[TDI] = 1.0×10^{-3} mol/mol; toluene = 10 wt %. (b) EP/PU hybrid networks synthesized by BP, E44 = 10 wt %; [NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol; [catalyst]/[TDI] = 1.0×10^{-3} mol/mol; toluene = 70 wt %.

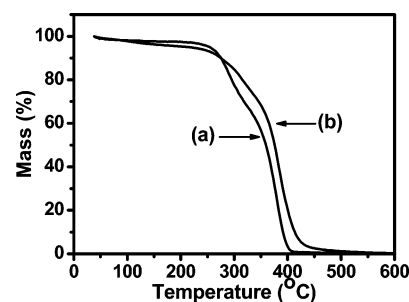


Figure 7. TGA spectra of pure PU and EP/PU hybrid networks prepared by FP. (a) Pure PU prepared by FP, [NCO]/[OH] = 1.4:1 mol/mol; [catalyst]/[TDI] = 1.0×10^{-3} mol/mol; toluene = 10 wt %. (b) EP/PU hybrid networks prepared by FP, E44 = 15 wt %; [NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol; [catalyst]/[TDI] = 1.0×10^{-3} mol/mol; toluene = 10 wt %.

EP/PU hybrid networks prepared by FP and BP respectively, with [NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol, E44 = 10 wt %, and [catalyst]/[TDI] = 1.0×10^{-3} mol/mol. As is seen in Figure 6, the bending vibration absorption peaks of the N—H group at 1535 cm^{-1} and the stretching vibration absorption peaks of the C=O group at 1730 cm^{-1} can be observed. However, the stretching vibration absorption peaks of the isocyanate group at 2356 cm^{-1} can also be observed because of excessive concentration of TDI. This all strongly indicates that the products by FP have chemical structures similar to those obtained by BP.⁴⁰

Typical TGA spectra for samples of pure PU and EP/PU hybrid networks prepared by FP are shown in Figure 7, each of them keeping constant a specific [NCO]/[OH] = 1.4:1 mol/mol, [catalyst]/[TDI] = 1.0×10^{-3} mol/mol, and toluene = 10 wt %. By comparison, in the temperature range of the first degradation step ($113\text{--}270\text{ °C}$ at a heating rate of 10

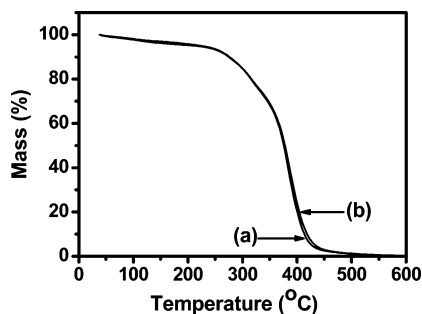


Figure 8. TGA spectra of EP/PU hybrid networks synthesized by (a) FP and (b) BP. (a) EP/PU hybrid networks synthesized by FP, E44 = 15 wt %; [NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol; [catalyst]/[TDI] = 1.0×10^{-3} mol/mol; toluene = 10 wt %. (b) EP/PU hybrid networks synthesized by BP, E44 = 15 wt %; [NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol; [catalyst]/[TDI] = 1.0×10^{-3} mol/mol; toluene = 70 wt %.

°C/min), the EP/PU hybrid networks degrade slightly faster than pure PU because of the degradation of some unconverted E44 present in the hybrids. As a matter of fact, the onset temperature of decomposition (113 °C) of E44 was reported in the literature.³⁹ The small organic molecules tend to degrade before the PU polymer, causing a slight weight loss in the hybrids. However, the EP/PU hybrid networks show higher thermal resistance than that of pure PU in the temperature range of the degradation step (above 270 °C at a heating rate of 10 °C/min), which might be attributed to the presence of cross-linking structures through covalent bonds between PU chains and EP chains. It clearly shows that the EP incorporated in the PU matrix provides higher thermal stabilities of EP/PU hybrid networks ascribed to the intermolecular hydrogen bonds of EP, which improve cohesion force and high regular soft segments. Figure 8 is a TGA thermogram spectra comparison of the spectrum of EP/PU hybrid networks prepared by FP compared with that of the networks prepared by BP. The TGA spectra result allows us to conclude that both front and batch samples show similar thermal stabilities.

SEM images are used to investigate the surface morphology of the PU and EP/PU hybrid networks all synthesized by FP. Figure 9 presents the surface morphology of the PU and EP/PU hybrid networks with different E44 concentrations (5, 10, and 15 wt %). Figure 9a is the surface of the pure PU. From Figure 9b–d we can see that both the black PU phase and the white EP phase constitute a distinct “net” structure. They show isotropic and well-pronounced homogeneous networks of two-dimensional platelets of similar dimensions owing to covalent cross-linking between EP chains and PU chains. The SEM micrographs of EP/PU hybrid networks also reveal that the hybrid domain sizes changed with the E44 concentration. As can be seen from the images, the domain size of the sample with 15 wt % E44 is smaller than that with 5 wt % E44. It can be concluded that the cross-linking density of EP/PU hybrid networks increases with the concentration of E44. These micrographs provide more direct evidence that the E44 uniformly disperses in PU matrix and forms a network structure even though no stirring is performed in this case.

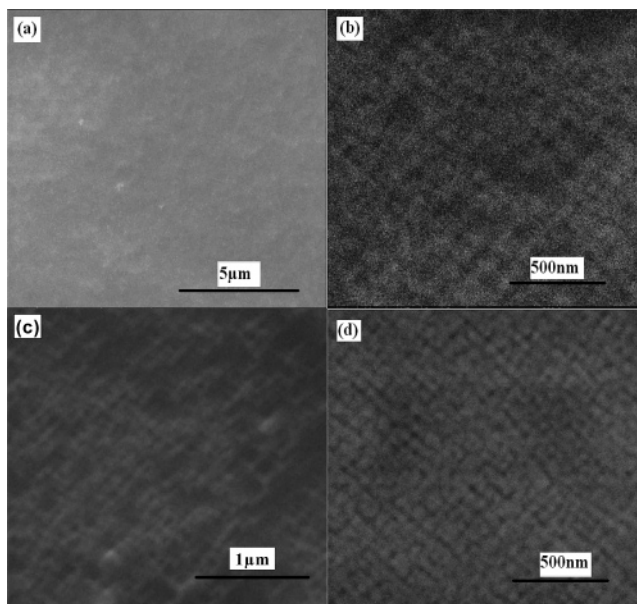


Figure 9. SEM images of the surface morphologies of pure PU and EP/PU hybrid networks all synthesized by FP. (a) Pure PU prepared by FP, [NCO]/[OH] = 1.4:1 mol/mol; [catalyst]/[TDI] = 1.0×10^{-3} mol/mol; toluene = 10 wt %. (b) EP/PU hybrid networks prepared by FP, E44 = 5 wt %; [NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol; [catalyst]/[TDI] = 1.0×10^{-3} mol/mol; toluene = 10 wt %. (c) EP/PU hybrid networks prepared by FP, E44 = 10 wt %; [NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol; [catalyst]/[TDI] = 1.0×10^{-3} mol/mol; toluene = 10 wt %. (d) EP/PU hybrid networks prepared by FP, E44 = 15 wt %; [NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol; [catalyst]/[TDI] = 1.0×10^{-3} mol/mol; toluene = 10 wt %.

Conclusions

The first synthesis of EP/PU hybrid networks by FP has been successfully carried out. We have found that a solution of E44, PPG, BD, TDI, stannous caprylate ([NCO]/[OH]/[epoxy value] = 1.4:1:1 mol/mol, [catalyst]/[TDI] = 1.0×10^{-3} mol/mol), and toluene (10 wt %) exhibited a pot life of more than 3 h at the ambient temperature (30 °C), and instantaneous SP does not occur. In agreement with data of other published FP systems, the experimental data for all FP experiments are well-fitted by straight lines, meaning that the fronts propagate with constant velocities. The features of EP/PU hybrid networks prepared frontally were similar to those obtained by BP but were achieved in a shorter reaction time. FT-IR spectra of EP/PU hybrid networks by FP displays the characteristic absorption peaks, which are almost the same as those of EP/PU hybrid networks by BP. TGA characterization indicates that both front and batch samples had similar thermal stabilities. SEM images provide direct evidence that the EP uniformly disperses in the PU matrix and formed a cross-linking network structure even without stirring. The above results allow us to conclude that FP can be exploited as an alternative means for preparation of EP/PU hybrid networks with the additional advantages of high velocity, low cost, and low energy as compared with traditional batch methods.