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Nano-scale phenomena and applications in polymer processing

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Abstract

A broad range of scientific and technological problems involves multi-scales and complex systems. This paper reviews some of unique and interesting nano-scale phenomena and applications relevant to polymer processing. It addresses four subjects. The first one is concerned with the dynamics of polymer chains in confined geometries. In contrary to intuition one may have, polymer chains may diffuse much faster in confined geometries than in the bulk. The second subject deals with extruder processing of polymer nanocomposites. Understanding of the dynamics of polymer chains in confined geometries helps shade light on how nanoparticles may be dispersed in polymer matrices in a nanometer scale. The third one is on the use of nano-objects as nano-reactors. An example is given to show how one may take the advantage of nano-reactors to improve reaction yield and/or reaction selectivity. The last subject deals with reaction kinetics at polymer-polymer interfaces of a few nanometers in thickness, a very important issue in reactive polymer blending processes.

Introduction

By their nature, all industrial processes involve multiple scales and complex systems [Charpentier and McKenna, 2004; Li, 2004; Ottino, 2003; Wintermantel, 1999; Ma, 2005]. Optimisation and control of such a process or system call upon multi-scale methodology. They go through clear identification of scales relevant to the process and deep understanding of phenomena occurring at each of these relevant scales and their coupling. The concept of relevant scales is important because for a given process, not

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all scales are relevant. Traditional scales considered in chemical engineering are atomic, microscopic and/or macroscopic scales.

Over the last two decades, much hope has been placed on the nanometer scale, to the point that nowadays “nano” can be found almost anywhere and has become a suffix of many scientific disciplines and terms including polymer related processes. However, while the nanometer scale may be present in almost all polymer related processes, it may not always be relevant. In other words, the nanometer scale may not always be one at which unique and non-linear phenomena take place and are able to significantly influence the performance of the process or product. As a matter of fact, polymer related processes to which the nanometer scale is relevant are still scarce. This paper aims at reviewing some of the nano-scale phenomena and applications relevant to polymer processing.

Dynamics of polymer chains in confined geometries

Over the last two decades, polymer nanocomposites have gained much attention. A polymer nanocomposite is a polymer composite, i.e., an integrated mixture of polymers and fillers, in which at least one of the dimensions of the latter is below 100 nm. In other words, the very difference between a conventional polymer composite and a polymer nanocomposite lies in the size of fillers. The size of fillers in nanocomposites can be one to five orders of magnitude smaller than that in conventional micrometer scale composites. Such fillers may be called nano-fillers. As a result of the size difference, polymer nanocomposites may have very different properties from those of conventional ones. Their compounding process may not face the same challenges either.

Among nano-fillers (nano-particles), montmorillonite (MMT) has attracted the greatest attention. MMT is a 2:1 layered silicate, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet. Particles are composed of layers (a layer is a combination of sheets in 2:1 assembly) with an average diameter of 100 to 1000 nm and a thickness of about 1 nm. The interlayer distance may vary from 1 to 3 nm. In fact, MMT particles exist in multiple-scale structures [Homminga et al., 2006]. At a macroscopic scale, MMT consists of individual agglomerates of the order of 0.1 mm in size. An agglomerate may consist of many primary particles of 1 to 10 μm in size that in turn may be composed of compact tactoids (crystallinites) of 0.1 to 1 μm in size.

When foreign objects such as polymer chains diffuse into or intercalate these tactoids, silicate layers may be intercalated or exfoliated (delaminated).

The diffusion/intercalation of polymer chains inside MMT galleries is a crucial step in nanocomposite compounding. It may also be a rate-limiting step, as will be further discussed later. The dynamics of polymers confined in spaces comparable to or smaller than their dimensions are expected to be drastically different than in their equivalent bulk. This is because the chain conformations are significantly deformed due to geometric constraints (confinements), as shown in **Figure 1**. Polymer diffusion can also be much affected by the layer surface-polymer interactions [Cacciuto and Luijten, 2006; Sakaue and Raphaël, 2006].

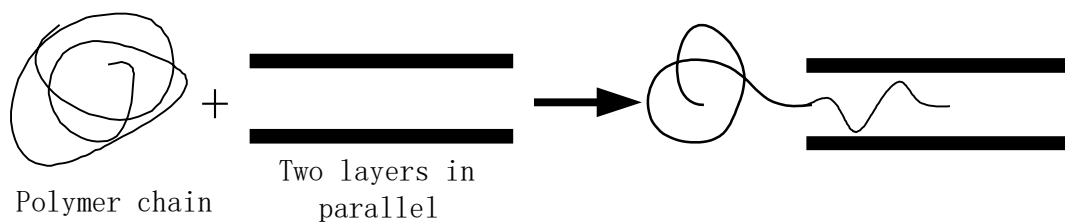


Figure 1. A schematic of an initially coiled polymer chain diffusing into a confined geometry composed of two layers in parallel.

The driving force for the diffusion is the difference in free energy between the polymer outside and inside the silicate gallery, ΔF . The force that resists to the diffusion is the friction coefficient for polymer motion inside the gallery, ξ . The effective diffusion constant is related to the ratio between the two and can be expressed by [Manias et al, 2000]:

$$D_{eff} \approx \frac{\Delta F}{\xi} \quad (1)$$

Manias et al. [Manias et al, 2000] studied experimentally the motion of monodispersed polystyrene in alkylammonium modified fluorohectorite (FH), a synthetic 2:1 silicate that is parallel and atomically smooth solid surfaces separated by 2 nm, as shown in **Figure 2**.

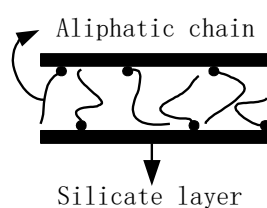


Figure 2. A schematic of alkylammonium modified fluohectorite (FH) used for assessing dynamics of polystyrene in confined geometries. The number of the alkyl group, n , is 12, 14, 16 or 18.

The main results are summarized below:

- (a) Polymer chains diffuse in the silicate galleries 10 to 100 times faster than if they do in the bulk (see **Figure 3**). This might appear very surprising. Indeed one might argue that while the gap between two adjacent layers is 2 nm, the radius of gyration of a Gaussian polystyrene chain used in the work is much larger (100 to 500 nm). Thus one would expect that such a polymer chain diffuses more slowly in the confined geometry than if it was in the bulk without confinement.
- (b) D_{eff} follows approximately the Rouse model, namely, it decreases more or less as N^{-1} , where N is the degree of polymerization of the polymer and spans a range between 2 and 52 entanglement lengths. This is in contrast to the reptation model which predicts that D_{eff} scales as N^{-2} in the bulk. This is a very interesting finding. It seems to infer that unlike in the bulk in which polymer chains are entangled, in order for polymers chains to diffuse in the confined geometry they may have to disentangle first and then stretch themselves. Thus their diffusion process does not follow the reptation model but the Rouse model. Since polymer chains are not entangled in the confined geometry, they are able to diffuse faster than if they were in the bulk in which they are entangled.
- (c) D_{eff} decreases with increasing the interaction between the polymer and the silicate surfaces. Increased interaction can be promoted either by decreasing the alkylammonium length or by adding Br groups along the polymer chains. **Figure 4** shows that D_{eff} increases with the alkylammonium length to the $2/3$ power ($n^{2/3}$). **Figure 5** shows that there is a systematic decrease of D_{eff} with increasing bromination level. The decrease is much more dramatic for surfaces bearing shorter surfactants, where more of the silicate surface is exposed to interact with the bromine groups.

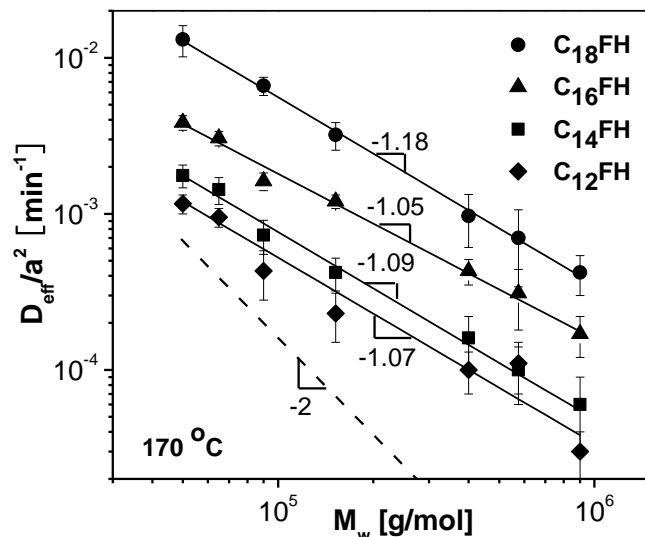


Figure 3. Effect of the polymer molar mass on $D_{\text{eff}}/a^2 = 1/\tau_{\text{diffusion}}$ inside four different FH surfaces separated by 2 nm and modified with alkylammonium of different alkyl length (C12, C14, C16 or C18) at 170 °C. D_{eff} and a are the effective diffusion constant and the mean silicate size, respectively. The slopes are from the best fits to the experimental data. The self-diffusion coefficient/($a = 5 \mu\text{m}$) at the same temperature is shown as a dashed line [Green et al., 1985]. After [Manias et al., 2000].

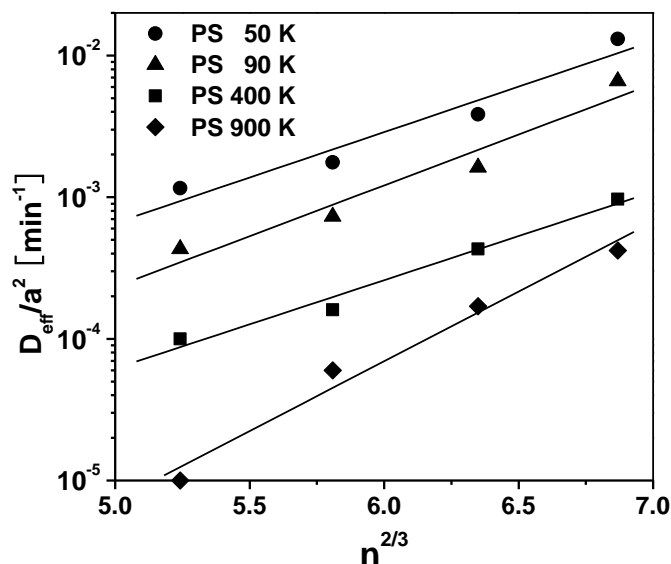


Figure 4. D_{eff}/a^2 as a function of the alkylammonium length to the 2/3 power ($n^{2/3}$) for polystyrene of four different molar masses at 170 °C. After [Manias et al., 2000].

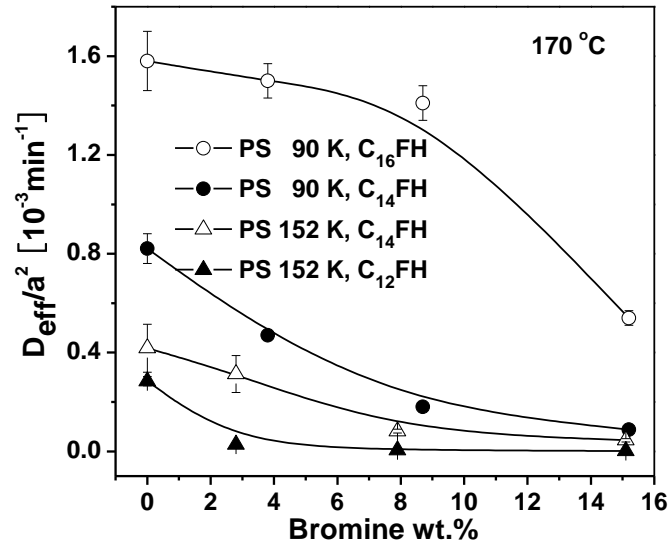


Figure 5. Effect of the bromination level on D_{eff}/a^2 at 170 °C. After [Manias et al., 2000].

Extruder compounding processes for polymer nanocomposites

The preceding section on the dynamics of polymer chains in confined geometries will help understand the underlying mechanisms of the dispersion process of nanoparticles like MMT in a polymer matrix during an extruder nanocomposite compounding process.

An extruder polymer nanocomposite compounding process aims at using a screw extruder to disperse MMT agglomerates of the order of 0.1 mm in size into nanometer-scale intercalated layer stacks (intercalated morphology) of 10 to 100 nm or exfoliated individual layers (exfoliated morphology) of 1 nm and to uniformly distribute them in the polymer matrix. It is a very challenging operation. This is because reaching that scale of dispersion amounts to increasing the number of particles by a factor of 10^9 to 10^{11} and the interfacial area between the MMT and the polymer by a factor of 10^5 . Quantitative models describing extruder nanocomposite compounding processes are still unavailable. Nevertheless, qualitatively speaking it may be envisioned as being composed of two main consecutive steps: dispersion and intercalation/exfoliation. This is shown in **Figure 6**. Initial MMT particles are big. Thus dispersion by stress dominates the process. When they are reduced to tactoids, stress may no longer be strong enough compared to the cohesive strength of the tactoids to break them further down. Then polymer chain diffusion toward the layered stacks and inside the galleries will take over, leading to intercalation and possibly exfoliation.

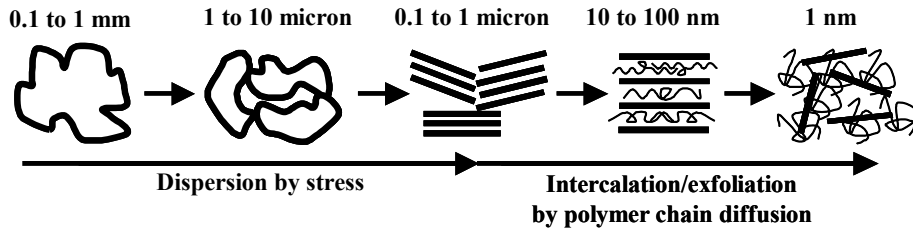


Figure 6. A schematic of the two consecutive steps involved in a polymer nanocomposite compounding process in an extruder: dispersion by stress and intercalation/exfoliation by polymer chain diffusion.

Whether or not an intercalated or exfoliated morphology is obtained depends on the interplay between enthalpy and entropy. It has been shown that the net entropy change associated with intercalation is close to zero because the entropy loss associated with the confinement of polymer chains is compensated for by the entropy gain associated with layer separation [Vaia and Giannelis, 1997]. Thus, if the compatibility or interactions between MMT layers and the polymer are favourable, then exfoliation is possible. In other words, there are four fundamental variables that dictate a nanocomposite compounding process and the ultimate morphology of the nanocomposite: cohesive strength of MMT, applied stress, polymer diffusivity inside MMT galleries and compatibility between MMT and polymer.

The dynamics of polymer chains in confined geometries described in the preceding section show that intercalation of layered silicates with polymers is possible within a time scale that is compatible with extruder compounding processes because polymer chains may diffuse much more rapidly in confined spaces than in the bulk. Based on the dynamics of polymer chains in the bulk, intercalation or exfoliation will likely be impossible within the typical average residence time of an extruder compounding process. Parameters that one may play with to increase the diffusion coefficient in confined spaces are: temperature, polymer chain length and interactions between the polymer and silicate surfaces. The diffusion coefficient increases with increasing temperature, decreasing the polymer chain length or decreasing the interactions between the polymer and silicate surfaces. It should be noted that decreasing the interactions between the polymer and silicate surfaces amounts to decreasing the compatibility between them, which is unfavourable for exfoliation. Thus very good compatibility between the polymer and MMT and sufficiently long

process time are two necessary and likely sufficient conditions for obtaining exfoliated morphologies. The process time is likely longer for exfoliated morphologies than intercalated ones because the former requires better compatibility. Better compatibility may slow down polymer diffusion inside the silicate layers.

Stress serves to largely shorten the diffusion time necessary for reaching the final morphology by reducing the size of MMT particles and therefore the diffusion path. But it likely does not alter the ultimate morphology. In other words, one may always reach the ultimate morphology corresponding to given compatibility. It is only a question of time [Giannelis, 1996; Dennis et al., 2001].

Nano-objects as nano-reactors

Recent years have seen rapid development and increasing applications of the concept of nano-reactor. Many chemical reactions have been successfully carried out in nano-sized reactors to obtain nano-sized products such as nano-crystals (Djalali et al., 2004) and nano-tubes (Lu et. al., 2004).

There are mainly two types of potential nano-reactors. One is made of the self-assembly of molecules such as micelles and vesicles. Another one is composed of natural or synthetic objects such as zeolites, layered silicates, nanotubes and dendrimers. Till now, most of the works use synthetic materials as nano-reactors, such as self-assembly of block copolymers or micelles formed by surfactants in solvent. A few of them use, however, natural materials such as layered silicates.

In what follows, an example is given to show that appropriate use of nano-reactors may greatly help control the selectivity of complex reactions without having to modify existing equipment and process conditions. It deals with the free radical grafting of maleic anhydride (MAH) onto polypropylene (PP) in the melt by reactive extrusion, a very important industrial process. A major problem facing this melt grafting process that has still not been well solved is PP chain scission. In other words, an increase in the amount of MAH grafted onto PP necessarily leads to an increase in the extent of the molar mass reduction of PP. This can be shown with a simplified reaction scheme involved in the free radical grafting process (**Figure 7**).

According to the simplified free radical grafting scheme in **Figure 7**, increasing the local concentration ratio of the grafting monomer to the macroradical is expected to increase the selectivity of the grafting reaction and limit side reactions (β -scission for PP and crosslinking for PE). The use of the concept of nano-reactor may allow putting

this idea into practice. A nano-reactor could be of any geometry with one of the characteristic dimensions being of the order of a few nanometers. **Figure 8** shows a simplified reaction scheme of the free radical grafting system of which the peroxide is initially confined in a nano-reactor.

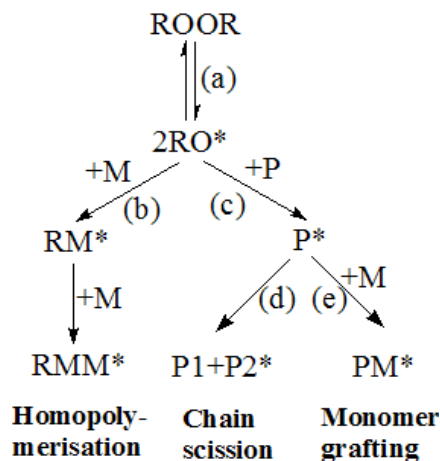


Figure 7. A simplified scheme of the free radical grafting process of an unsaturated monomer M onto a polymer backbone P such as PP. Note that there are three main reactions (homo-polymerisation, chain scission and monomer grafting) involved in the process and that they compete among them. The first two are undesired and the last one is desired. After [Shi et al., 2006a, 2006b].

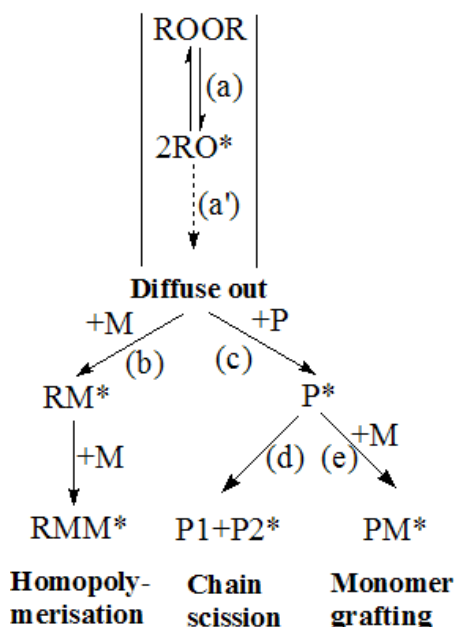


Figure 8. A simplified scheme of the free radical grafting process with ROOR being confined in a nano-reactors. Note that RO* primary free radicals generated inside a nano-reactor have to diffuse out (step a') from there before they can be in contact with M or P and then react with. After [Shi et al., 2006a, 2006b].

An important difference between the conventional free radical grafting process and the one with nano-reactors is that in the first case, RO* primary radicals are formed evenly over the entire reacting volume if ROOR is evenly distributed therein too (**Figure 7**). Once formed, they are in direct and immediate contact with M and/or P. In the second one, since ROOR molecules are initially confined in the nano-reactors, RO* primary radicals are formed therein and will have to diffuse out from there before they can encounter and then react with M and/or P. Since the decomposition of ROOR to RO* is a reversible reaction and the RO* primary free radicals initially located in confined spaces, the rate of formation of RO* primary radicals is obviously higher in the first free radical grafting system than in the second one. In other words, unlike in a non-confined situation where the peroxide decomposes into primary radicals following Arrhenius' law, in a confined situation the free radical generation is controlled both by Arrhenius' law and diffusion. Thus the rate of release of RO* primary free radicals to the space occupied by M and P is significantly slowed down and is more even over time. It is similar to that of encapsulation of active species. A lower and more even rate of RO* primary free radical release is believed to increase the initiator efficiency, favour the selectivity of the monomer grafting and disfavour that of the chain scission.

Since a peroxide molecule like dicumyl peroxide (DCP) is of the order of 1 nm in size, nano-objects like MMT may be suitable for its confinement. Indeed, DCP is like the letter Z and has a length of 1.20 nm, a width of 0.69 nm and a thickness of 0.59 nm [Shi et al., 2006b]. **Figure 9** is a schematic of DCP confined in a gallery of MMT.

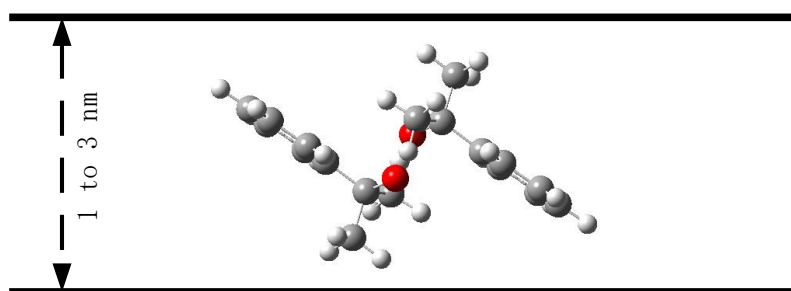


Figure 9. A schematic of DCP confined in a gallery of MMT.

Figure 10a compares the evolution of the grafting yield of MA as a function of the amount of DCP between a conventional PP/DCP/MA grafting system and that in which

DCP is confined in an organically modified MMT (o-MMT). The amount of MA is fixed at 2 wt.% with respect to PP. The values of the grafting yields of MA obtained with the pre-confinement of DCP in o-MMT are significantly and systematically higher than those without. **Figure 10b** shows the evolution of the number average molar mass of the corresponding PP as a function of the amount of DCP. The values of the number average molar mass of the PP obtained with the pre-confinement of DCP in o-MMT are also significantly and systematically higher than those of the conventional grafting process.

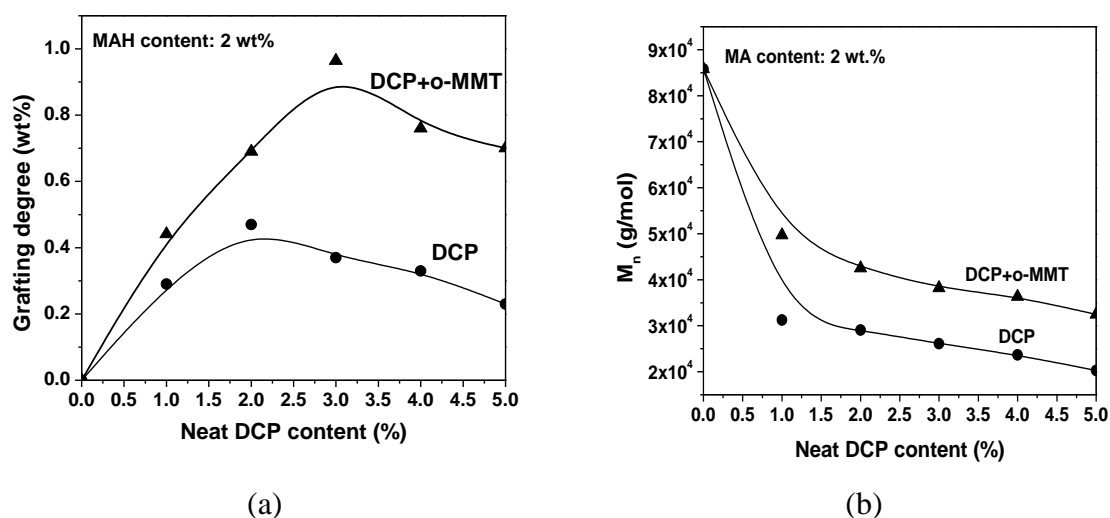


Figure 10. Comparison of the evolution of the grafting yield of MA (a) and that of the molar mass of the PP-g-MA (b) as a function of the amount of DCP between the classical PP/DCP/MA grafting system and the one in which DCP is pre-confined in o-MMT, PP/MA/(DCP+o-MMT). The amount of MA is fixed at 2 wt.% with respect to the PP. After [Shi et al., 2006a, 2006b].

It should be emphasized that the key to the above success is that DCP is effectively confined in the o-MMT layers. Otherwise, it is expected that results in terms of the grafting degree of MAH and the molar mass of the grafted PP would not be different from the conventional PP/MAH/DCP grafting system. This expectation is confirmed experimentally by substituting o-MMT with pristine MMT. The latter is not subjected to any organic modification. The absence of the effect of p-MMT could be explained as follows. The pristine MMT is hydrophilic in nature whereas DCP is hydrophobic. Moreover, the interlayer distance of p-MMT is 1.2 nm, which is much smaller than that of o-MMT (2.4 nm). For those two reasons it would be much more difficult for DCP molecules to intercalate the galleries of p-MMT layers than those of o-MMT.

Reaction kinetics at polymer-polymer nano-meter scale interfaces

During the last three decades, blending existing polymers has become a very important approach to tailoring compositions to meet specific end use requirements without creating new molecules. However, most polymer pairs are immiscible. Therefore the presence of a copolymer is often required in an immiscible polymer blend in order to control its morphology and interfaces and consequently its end-use properties. Such a copolymer can be prepared separately and then added to the polymer blend during the blending process. It may also be generated in-situ during the blending process by directly reacting mutually reactive polymers. The latter is practiced the most for the reasons outlined in a book entitled “Reactive Polymer Blending” [Baker et al., 2001].

Chemical reactions at polymer-polymer interfaces are a very important issue of reactive polymer blending. **Figure 11** is a schematic of complementary functional groups located inside an interface formed by two immiscible polymers A and B. An interface between two immiscible polymers is typically of the order of 1 to 5 nm. The reaction kinetics in this nano-meter scale interface may behave very differently, as will be discussed below.

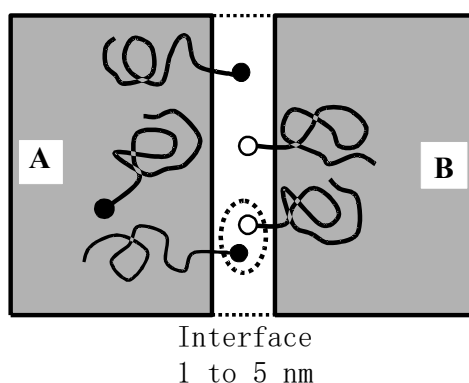


Figure 11. A schematic of reaction between complementary functional groups near or in an interface formed by two immiscible polymers A and B. Of the two pairs of the complementary functional groups inside the interface, one is located within a “capture radius” and the other one separated by a distance much greater than the capture radius. After [Feng and Hu, 2004].

For given nominal molar concentrations in complementary functional groups, it is believed that the reaction rate of those attached to polymer chains never exceeds that of

small molecule analogues. In other words, the latter is the upper bound of the former. They are at best equal. Equality is possible when reacting systems are homogeneous at a molecular level and the intrinsic reactivity of the functional groups is independent of molecular size. For example, Bhide and Sudborough (1925) studied the kinetics of the esterification of a series of homologous carboxylic acids of type $\text{H}(\text{CH}_2)_x\text{CO}_2\text{H}$ with ethanol:



Those homologous carboxylic acids differed only in molecular size. The latter was characterized by the number of the CH_2 repeating unit, x , in the molecule. They found that although there was a decrease in reactivity with increased molecular size, the effect was only significant at a very small size. The reaction rate constant very quickly reached a limiting value at $x = 3$. It then remained constant and independent of molecular size (**Figure 12**). Analogous results were found for the polyesterification of sebacyl chloride with a series of homologous α,ω -alkane diols of type $\text{HO}(\text{CH}_2)_x\text{OH}$ (Ueberreiter and Engel, 1977):

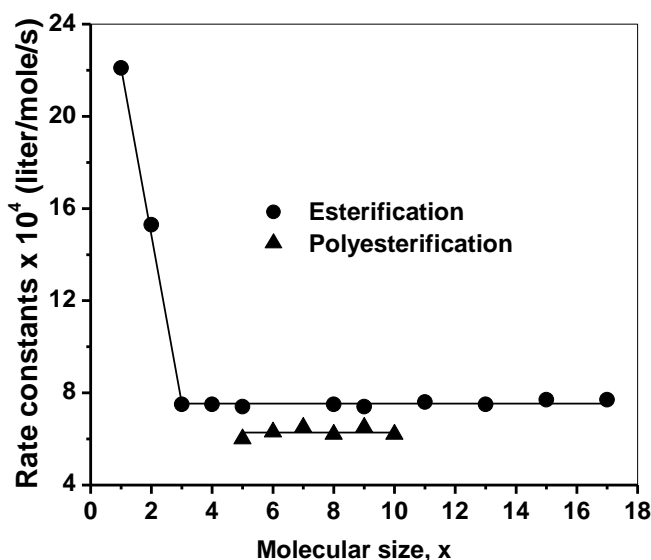
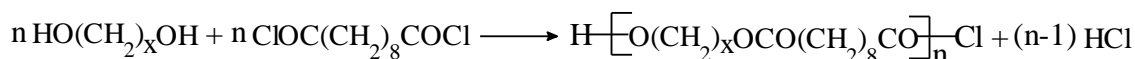


Figure 12. (●) Rate constants for the esterification of a series of homologous carboxylic acids of type $\text{H}(\text{CH}_2)_x\text{CO}_2\text{H}$ with ethanol at 25°C . Note that the rate constant reaches a limiting value and remains constant for $x = 3$; (▲) Rate constants for the polyesterification of sebacyl chloride with a series of homologous α, ω -alkane diols of

type $\text{HO}(\text{CH}_2)_x\text{OH}$ at 26.9°C . Note that the rate constant is the same for $5 \leq x \leq 10$. After [Feng and Hu, 2004].

There are two scenarios where the reaction rate may no longer remain constant but decrease significantly with increased molecule size. First, the reactivity of the functional groups is so high and/or the polymer is so big that the bulk diffusion of the polymer chains becomes the limiting step of the reaction rate. Second, polymers to which complementary functional groups are attached are immiscible at a chain level and their mixture phase-separates. This is often the case for two dissimilar polymers because of the very small entropy of mixing compared to that of small molecule analogues. In such a phase-separated polymer reacting system, complementary functional groups from the two phases can only meet and react in the interfacial regions, as shown in **Figure 11**. Thus, only small fractions of them may have opportunities to collide and react and the rest of them may be excluded from such opportunities.

In what follows, it will be shown that if polymer chains to which complementary functional groups are attached are immiscible and mixing to which the system is subjected is strong enough, the reaction kinetics may be significantly faster than that of small molecule analogues. For that purpose, one may compare the kinetics of four reactive systems, all containing the same numbers of A and B functional groups. In system (a), molecules bearing A and B functional groups are small and mutually miscible. System (b) differs from system (a) in that B functional group is attached to a polymer. Nevertheless, they remain miscible. In system (c), both A and B functional groups are attached to a polymer of the same chemical nature. The system is thus miscible. In system (d), A and B functional groups are attached to polymers of different chemical natures that are immiscible. In other words, in the first three miscible systems, the A and B functional groups are randomly distributed over the entire reaction volume at the scale of their size. In the last immiscible system, since A-bearing polymer and B-bearing polymer are immiscible, most of the A and B functional groups are located in their respective polymer phases. Only small fractions of them are located in the interfaces between the two polymer bulk phases. The interfaces are the only locations where they can collide and react. If the nominal molar concentrations of the reacting functional groups in the above four reactive systems are equivalent, the common wisdom regarding their reaction rates follows the order: $(a) \geq (b) \geq (c) \gg (d)$. This is

true *under static conditions*, i.e., *without mixing*. However, *under mixing* the situation can be completely reversed to the point that the reaction rate of system (d) may significantly exceed that of system (a), (b) or (c).

Consider two reactive systems based on the alcohol/isocyanate chemistry. One is Ph-(CH₂)₃-OH/(PMMA+PMMA-r-NCO) where Ph-(CH₂)₃-OH is a small molecule alcohol, PMMA is poly(methyl methacrylate) and is chemically inert and PMMA-r-NCO is a PMMA that contains isocyanate groups along its chain in a random manner. The other reactive system is (PS+PS-(CH₂)₂-OH)/(PMMA+ PMMA-r-NCO) (60/40 by weight), where PS is a chemically inert polystyrene and PS-(CH₂)₂-OH is a polystyrene terminated with an hydroxyl group. The former is a miscible system like system (b) mentioned above and the second is an immiscible one like system (d) mentioned above. They both contain the same molar numbers of hydroxyl and isocyanate groups. Moreover the molar ratio between the two functional groups is unity.

A batch mixer of type Haake equipped with a pair of rotators is used to study the kinetics of the above two reactive systems. **Figure 13** compares the conversion of the isocyanate group as a function of time under one of the following three mixing conditions: (a) continuous mixing at 64 or 84 revolutions per minute (rpm) for the entire reaction time; (b) step-wise mixing with the rotation speed alternating between 0 at 64 rpm; (c) without mixing, except for the very first minute during which the rotation speed is 64 rpm to ensure melting and a certain degree of homogenization of the reacting systems. In the case of the miscible small alcohol reactive system, mixing has little effect on the reaction rate because the conversion follows the same pace, regardless of the mixing condition. This implies that in the miscible system, the bulk diffusion of the reactive molecules is most likely not the rate-limiting step of the reaction rate. By contrast, the reaction rate of the immiscible macromolecular alcohol system depends very strongly on the mixing condition. The conversion increases more rapidly at 84 rpm than at 64 rpm, especially in the very early stage of mixing. Without mixing (the rotation speed being zero), the reaction rate is zero. This is further corroborated by the experiment carried out under the step-wise mixing condition. In stage I (0 to 1 min) in which the mixing speed is 64 rpm, the conversion increases very rapidly. In stage II, mixing is stopped and the reaction stops to proceed. Once mixing is resumed, the reaction starts to proceed again (stage III). It stops again in stage IV where

there is no mixing. It quickly starts to proceed again under mixing (stage V). These results show that the reaction rate of the immiscible macromolecular alcohol system is controlled by the rate of mixing or the rate of interfacial area generation. Comparison of the kinetic data shows that under the specified continuous mixing conditions, while both the miscible and immiscible reactive systems contain equivalent nominal concentrations in the hydroxyl and isocyanate groups, the overall reaction rate, defined as the slope of a conversion-time curve, of the immiscible one is much faster than that of the miscible, at least in the first 5 - 10 minutes of the reaction. Since these mixing conditions are easily met in practical reactive polymer blending processes, it is expected that on the basis of equal molar concentrations in reacting functional groups, the reaction rates of immiscible reactive polymer systems can be significantly higher than those of small molecule analogues.

The above finding is not only scientifically interesting and challenging but is also technologically relevant. It indicates that kinetic data obtained from miscible reactive systems may not always be the upper limits of immiscible ones. It may also explain why some not-very-fast chemical reaction systems have had success with reactive blending process whose average residence time is typically of the order of a minute or less.

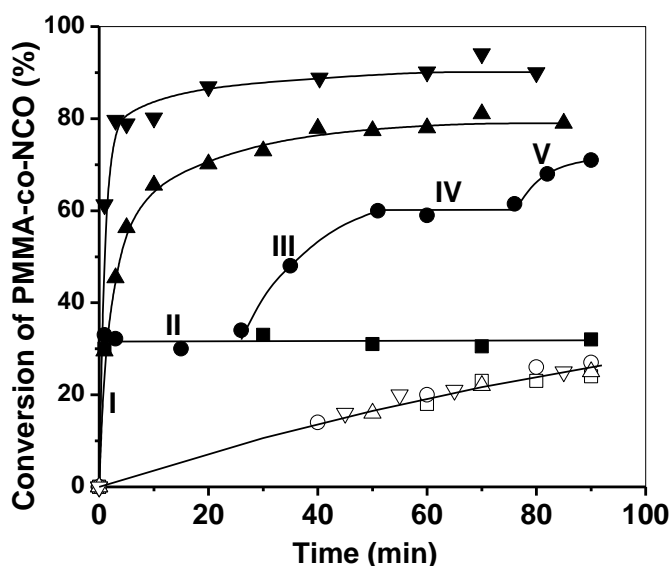


Figure 13. Time dependency of the conversion for the Ph-(CH₂)₃-OH/(PMMA+PMMA-r-NCO) miscible and small molecule alcohol reactive system (open symbols) and the (PS+PS-(CH₂)₂-OH)/(PMMA+PMMA-r-NCO) (60/40) immiscible macromolecular alcohol reactive system (closed symbols) under three mixing conditions. (▼, ▽): continuous mixing at 84 rpm; (▲, △): continuous mixing

at 64 rpm; (■, □): step-wise mixing with the rotation speed alternating between 0 at 64 rpm; (●, ○): without mixing, except for the very first minute during which the rotation speed was 64 rpm to ensure melting and a certain degree of homogenization of both reactive systems. After [Feng and Hu, 2004].

The two complementary functional groups involved in the miscible small molecule alcohol reacting system are distributed randomly at the scale of their size over the entire volume of the reactive system. The reaction between them is a product of their random collisions occurring over that volume. The fact that the reaction rate of the miscible small alcohol reactive system is not mixing-controlled implies that mixing most likely does not alter the random distribution feature of the functional groups nor their collision mode and frequency. The latter refers to the number of collisions per unit time. By contrast, the two complementary functional groups involved in the immiscible macromolecular alcohol reactive system are no longer distributed randomly at the scale of their size over the entire reactive volume. Instead, they are highly segregated. The hydroxyl and isocyanate groups are located primarily in the PS and PMMA bulk phases, respectively. The interfacial regions between both phases are the only locations where the two complementary functional groups can meet, collide and react. This is demonstrated unambiguously by the kinetic results shown in **Figure 13**. The fact that the rate of reaction is entirely controlled by the rate of mixing implies that the collision frequency of the functional groups increases with increasing mixing rate.

How does mixing increase the collision frequency of the complementary functional groups in the immiscible macromolecular alcohol reacting system? Mixing is expected to play two positive roles in promoting collision of functional groups in an immiscible reactive polymer blend. The very first, obvious and likely the most important one is to increase the interfacial area. An increase in interfacial area increases the number of contacts and collisions between the two complementary reacting functional groups.

The second effect of mixing is to accelerate the process of copolymer pull-out from the interfaces (Charoensirisomboon et al., 2000; Lyu et al., 1999), generating additional fresh interfaces free of copolymer coverage. This mixing process may be called interfacial mixing. A copolymer chain formed in-situ at an interface may leave the interface for thermodynamic and/or hydrodynamic reasons. The degree to which

copolymer chains can be pulled out off interfaces by mixing depends, among other factors, on their architecture, the areal density of copolymer chains at the interfaces and mixing condition.

It is straightforward to understand that the overall reaction rate between two immiscible reactive polymers is promoted by mixing through interfacial area generation and/or copolymer pull-out creating additional interfacial area. However, these two mixing-induced interfacial area generation mechanisms do not seem to be enough to explain the above finding that under mixing and with equivalent nominal molar concentrations in functional groups, the reaction rate of the immiscible macromolecular alcohol reacting system is significantly faster than that of the miscible small alcohol analogue. This is because under the specified conditions, the two immiscible reacting polymer phases involved in the immiscible macromolecular alcohol reacting system are not mixed at the polymer chain level but remain segregated at a sub-micrometer scale. Thus, at a first glance, large fractions of functional groups are still excluded from collisions and reaction. This argument together with the experimental fact that the overall reaction rate of the immiscible reactive system is even much faster than the miscible reactive analogue suggests that the reaction rate in the interfacial regions be much higher than that would be expected from the miscible reactive analogous system. If this assumption is valid, one could then explain another experimental fact that the reaction kinetics of the miscible small alcohol systems is reaction controlled, whereas that of the immiscible macromolecular alcohol homologue is interfacial-area-generation controlled.

The validity of this assumption is seemingly supported by the dynamics of polymer chains at an interface. Consider an end-functionalized polymer chain whose reactive end is in an interface and main body in the bulk phase (Figure 11). Because of highly anisotropic friction with the neighboring chains, the relaxation (or snakelike motion) of the main body is a slow process whereas that of the reactive end is a rapid one (Welp et al., 1999; Russell et al., 1993). As such, when two complementary functional groups are located within a “capture radius” (De Gennes, 1982a; De Gennes, 1982b), the probability for them to collide is much higher than that for small molecule analogues because the much slower relaxation process of the main bodies holds them close to one another for a much longer period of time than small molecule counterparts. Relaxation of polymer chains depends very much on their molar masses. It will be much slower

when full entanglement dynamics are operative. The latter require that the molar masses of the polymers be higher than 10 times their respective entanglement molar masses. The reactive polymers used in this work are about 3 times their entanglement molar masses, implying that the dynamics of the immiscible reactive system is likely somewhere between Rouse regime and full entanglement regime

It should be noted that the above mentioned collision probability increase is only limited to complementary functional groups which are located within the capture radius. Those located outside the capture radius, which are in very large quantities, will either "never" be able to approach one another to within the capture radius or need very long time. This is why without mixing the reaction rate is virtually zero and why mixing is crucial for interfacial reactions. In addition to generating interfaces by the two mechanisms mentioned above, under certain circumstances mixing may cause relative displacement between the two phases of an interface – interfacial slip (Brochard-Wyart et al., 1990; Govas and Fredrickson, 1998; Barsky and Robbins, 2002; Zhao and Macosko, 2002), which allows complementary functional groups located outside the capture radius approaching each other and then reacting. For a system composed of two immiscible polymers, the interfacial slip is related to the fact that the viscosity of the interfacial region (interfacial viscosity) can be much smaller than that of each of the two bulk polymers phases (bulk viscosity). This viscosity difference is attributed to the fact that chains located in the interfacial regions are much less entangled than in the bulk phases. However, it should be noted that the presence of a copolymer in the system, even in small amounts, can significantly reduce interfacial slip. This implies that the effect of interfacial slip may come into play only in the early stage of mixing where the copolymer areal density is low.

It is worthy noting that in a system composed of two immiscible polymers, there are more chain ends in the interface than in the bulk phases due to entropic adsorption (Reiter and Steiner, 1993; Zhao et al., 1993). If complementary functional groups like hydroxyl and isocyanate are attached to the chain ends, enrichment in functional groups in the interfaces is expected to be more important. This is because interactions between functional groups and polymer segments are often repulsive, and those between complementary functional groups are necessarily attractive. This enrichment also favours interfacial reactions.

In summary, under mixing the reaction kinetics of immiscible reactive polymer

systems may significantly exceed that of miscible small molecule analogues. This may be attributed to an increased collision frequency resulting not only from mixing-induced interfacial area generation and interfacial copolymer pull-out, but also from slow relaxation process of reactive polymer chains, interfacial enrichment in functional groups and eventually interfacial slip.

Concluding remarks

This paper has reviewed a few unique and challenging nano-scale phenomena and applications relevant to polymer processing. It has started with the dynamics of polymer chains in confined geometries. As opposed to intuition one might have, confined polymer chains may diffuse much more rapidly than if there are in the bulk. For a given chain length, polymer chains may be less entangled when confined compared to the situation where they are in the bulk. The dynamics of confined polymer chains helps understand why dispersion of nano-particles like montmorillonite (MMT) in polymer matrices at a nanometer scale through polymer chain intercalation is possible within the typical residence time of an extruder nanocomposite compounding process. Appropriate use of nano-objects like MMT as nano-reactors may help control the selectivity of complex reaction processes. This has been illustrated with the free radical grafting of maleic anhydride onto polypropylene, an important industrial process. The confinement of the peroxide with MMT significantly alters its decomposition kinetics and the rate with which it releases primary free radicals. This results in significant improvement in peroxide efficiency and the selectivity of the grafting reaction (the desired one) against side reactions. Under mixing the reaction kinetics of immiscible reactive polymer systems may significantly exceed that of miscible small molecule analogues. This may offer an explanation to the fact that homogeneous kinetic data may not always be used as the upper limits for designing reactive blending processes. Some not-very-fast reactions have been used in reactive blending processes with success.

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