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Microemulsion Polymerization for Producing Fluorinated Structured Materials

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Summary: When perfluoropolyether microemulsions are used during polymerization of fluoropolymers, the structure of the reaction environment can be strictly controlled. In particular, the number and size of polymer particles in latexes can be set freely, yielding a number of advantages.

First, as a result of radical segregation, terminations can be decreased without reducing polymerization rate: in this way high molecular weights are easily obtained also with poorly reactive monomers.

Moreover, in combination with a reversible chain transfer mechanism based on iodine, particle segregation allows establishing pseudo-living polymerization conditions. In this situation formation of long branches in the polymer can be controlled by using bifunctional molecules that are able to link two different polymer chains to each other during polymerization. This is the so-called "branching and pseudo-living" technology.

Finally, by co-coagulating latexes of different polymers prepared by microemulsion polymerization, very small particles and, thus, high interface areas are generated. In this way properties of different polymers, such as fluoroelastomers and fluorinated semicrystalline polymers, are matched effectively, generating new nanocomposite materials that exhibit outstanding properties.

In this paper these results are reported and an overview of some novel sophisticated fluoropolymers obtained in microemulsion is given.

Keywords: controlled branching; fluoropolymers; microemulsion; nanocomposites; pseudo-living polymerization

Introduction

Fluoropolymers are characterized by good mechanical properties and excellent chemical and thermal resistance, compared to other classes of polymers. This peculiar stability is related to very strong intra-molecular interactions, in particular the carbon-fluorine bond, combined with rather

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low inter-molecular forces, which diminish swelling by most solvents and, thus, further enhance chemical resistance.

Thanks to their outstanding behavior in hostile environments, fluoropolymers are materials of choice for several demanding applications in various fields, such as automotive, aerospace, oil drilling, pharmaceutical and electronic industry. Intensive research keeps being directed towards meeting the latest industrial needs and high revenues are obtained with rather low market volumes, thus they are normally regarded as chemical specialties.

Fluoropolymers are generally manufactured by free radical polymerization, in most cases in aqueous emulsion. However, in recent years novel technologies have been developed, such as polymerization in supercritical carbon dioxide[1] or in perfluoropolyether (PFPE) microemulsions[2]. In particular, in microemulsion polymerization the reacting system's morphology can be controlled precisely, allowing operation under more efficient conditions and, what is even more important, the preparation of new complex molecular architectures and nanocomposite materials.

Polymerization with Perfluoropolyether Microemulsions

Microemulsions are isotropic, thermodynamically stable mixtures of at least three components (two immiscible liquids and a surfactant), which form spontaneously at certain temperatures and compositions upon contact of the ingredients[3]. They consist of a large number of droplets or micelles of a few nm in size and are homogeneous at macroscopic scale.

In the case of PFPE microemulsions, water and a PFPE oil (Galden®) are the immiscible substances and Galden® carboxylates are used as surfactants. It is worth noticing, that fluorinated ingredients are necessary when polymerizing fluoropolymers, otherwise relevant chain transfer due to hydrogen abstraction would be observed, as C-H bonds are significantly weaker than C-F bonds. In Figure 1 a Galden® / Galden® ammonium carboxylate / water ternary diagram is presented: the gray area indicates compositions leading to a single stable phase, the microemulsion. Compositions outside the gray area lead to two-phase systems, in which besides the microemulsion a second phase is formed, either oil or lamellar liquid crystals.

In the microemulsion polymerization process a rather small amount of microemulsion is diluted in a much larger quantity of water before starting the reaction. In this way the overall composition changes dramatically and the corresponding new point in the ternary diagram in Figure 1 is close to the water vertex, outside the gray area. Under these conditions the microemulsion is no longer stable. However, its decomposition is very slow compared to the polymerization time scale: it has been observed that the number and size of droplets remains unchanged for at least 48 hours, while the polymerization of fluoromonomers requires a few hours only[2]. In other words, even if microemulsions are no longer thermodynamically stable upon dilution, they remain strongly kinetically stable.

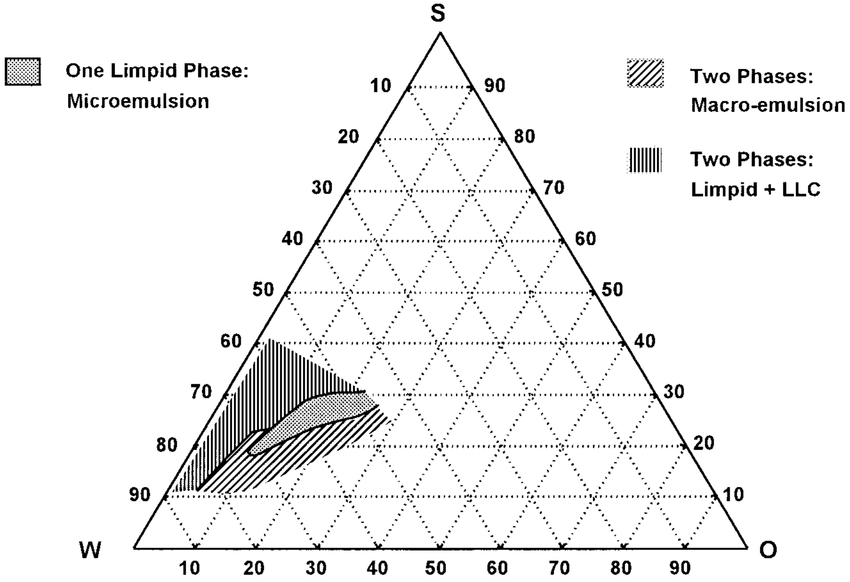

Figure 1. Ternary equilibrium diagram of a PFPE microemulsion at 25°C. O = Galden® oil; S = Galden® ammonium carboxylate; W = water; LLC = lamellar liquid crystals.

Since most fluorinated monomers are gaseous and highly soluble in perfluoropolyethers, they easily dissolve in the microemulsion droplets, which therefore act as polymerization seeds. In this way, polymer chains start growing when a radical enters a droplet and monomer molecules consumed by propagation are replaced by new molecules entering the particle. Hence, the mass of particles increases during polymerization, while the particle number remains constant. This is confirmed as no significant changes are observed by measuring the initial number of micelles by dynamic laser light scattering (DLLS) under reaction conditions and by counting the number of polymer particles by transmission electron microscopy (TEM) in latex samples taken during the reaction and at reaction end[2]. With this respect, it is worth noting that the use of different techniques for measuring particle size leads to different kinds of average. However, this is not expected to heavily influence the results, since the particle size distributions under study are rather monodisperse (polydispersity index around 0.1).

In such a precisely defined system, particle nucleation is instantaneous and particle growth is strictly controlled and reproducible. Accordingly, very narrow particle size distributions (PSDs) are obtained, compared to traditional emulsion systems in which there is a smaller amount of much larger particles stabilized by a surfactant. In Figure 2 typical PSDs of tetrafluoroethylene (TFE) / hexafluoropropylene (HFP) copolymer latexes prepared by microemulsion and by emulsion polymerization with the same amount of surfactant are shown (measurement by TEM): it is seen that when microemulsion is used, PSD is narrow and centered around 40-50 nm (solid line), while when the surfactant only is used to stabilize an emulsion of monomers, particles are significantly larger and their PSD much broader (dashed line)[2]. The dispersing capability of the surfactant is thus greatly enhanced if it is introduced in the reactor in the form of a microemulsion.

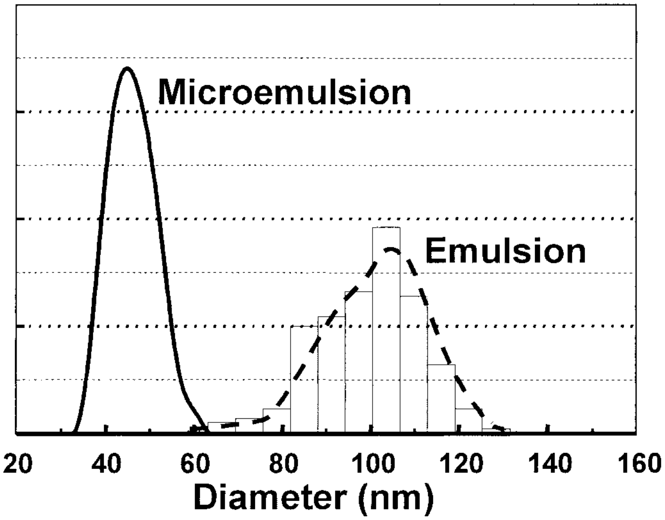

Figure 2. Particle Size Distributions of TFE/HFP latexes measured by TEM .

It is worth recalling that in the emulsion case, even if the constraint of using the same amount of surfactant is removed, above the critical micellar concentration (cmc) the amount of surfactant has only a little effect on the number of polymer particles. On the contrary, in the case of the microemulsions here discussed, the number of polymer particles is linearly dependent on the number of micreoemulsion droplets even well above the surfactant cmc. Thus, when microemulsion is used, the number of particles, N_P, is an independent variable that can be freely chosen to optimize polymerization conditions and product properties. In particular, this major feature of microemulsion polymerizations has been successfully exploited:

- to increase reaction rate, allowing use of poorly reactive monomers,
- to finely control the structure of polymer chains thanks to particle segregation,
- to increase polymer particle surface, thus intensifying interactions between continuous and dispersed phase in fluoropolymer nanocomposites.

These different aspects will be discussed in the next three chapters.

Polymerization of Poorly Reactive Monomers

In emulsion polymerization, if monomers are not very reactive, termination reactions are fast compared to propagation and it is difficult to achieve high molecular weights. Polymer chain length can be increased only by heavily reducing the amount of radicals in the system, as termination rate depends on the square of radical concentration, while propagation depends only linearly on the amount of radicals. Unfortunately, in this way polymerization rate is heavily reduced.

On the other hand, when using microemulsion, strong segregation of growing radicals becomes possible by properly setting size and number of particles. Thus, if particles are small enough and initiator concentration is also rather low, the average number of growing chains per particle turns out to be well below 1. In this situation, since radicals are generated in water by initiator decomposition, the whole polymerization kinetics is controlled by radical entry into particles: propagation starts after entry of a first radical and termination by combination can occur only after entry of a second radical. Nevertheless, the probability of a second radical entry is rather low, hence growing radicals propagate separately one from the other and termination by combination is strongly inhibited.

In addition, it is worth recalling that in emulsion and microemulsion polymerization the propagation rate can be expressed as:

$$R_p = k_p \, M \, n \, N_p / N_A$$

where k_p is the propagation rate constant, M is the monomer concentration within the particles, N_p is the particle number concentration, N_A Avogadro's number and n the average number of growing radicals per particle[4]. When microemulsion is used, N_p is roughly two orders of magnitude larger then in standard emulsion processes. In the case of fluoropolymers transfer to monomer is negligible[5] and radical exit, which might be enhanced by large surface areas, does not play a role. Therefore, even if the overall number of radicals is low, the average number of radicals per particle is small but still significant and propagation rate remains satisfactory. Thus, large molecular weights are easily achieved also when monomer reactivity is modest.

This situation is shown in Figure 3, where conversion is reported as a function of reaction time for three different tetrafluoroethylene (TFE) / perfluoro-methylvinylether (MVE) copolymerization experiments, differing only for the initiator concentration and the use of emulsion or microemulsion. It is seen that in emulsion polymerization initiator concentration must be two orders of magnitude larger to achieve similar reaction rates as in microemulsion polymerization. However, under these conditions, only low molecular weights are obtained with emulsion polymerization, while they are satisfactory when microemulsion is used. Moreover, if initiator concentration is reduced by two orders of magnitude in emulsion polymerization as well, polymerization rate becomes negligible.

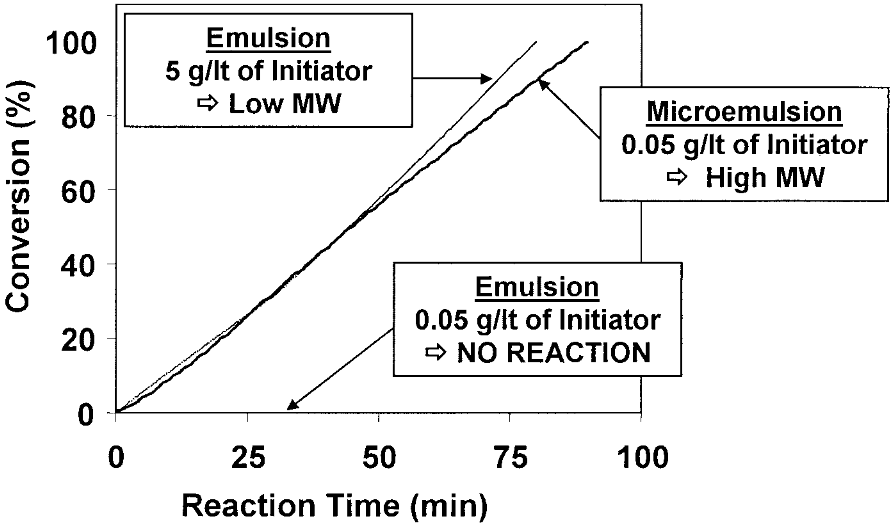

Figure 3. Conversion *vs.* time plots for tetrafluoroethylene (TFE) / perfluoro-methylvinylether (MVE) copolymerizations differing only for the initiator concentration and the use of emulsion or microemulsion.

This situation is frequently encountered when using monomers with rather complex structures, as in the case of polymers developed for special applications, such as methoxydioxole polymers, used for optical applications like plastic optical fibers, or sulphonic vinylether polymers for fuel-cell membranes.

Branching and Pseudo-living Polymerization

Segregation of radicals can be effectively exploited in particular in combination with a "reversible" chain transfer mechanism based on the weakness of the carbon-iodine bond (55 kcal/mol, compared to 130.5 kcal/mol for the C-F bond). If iodine-containing molecules such as I-$(CF_2)_n$-I (with n typically in the range 4-8) are added to the system, iodine is easily abstracted and a new C-I bond is formed on the growing polymer chain, while the molecule originally containing iodine becomes a growing radical. Thanks to the low bond energy, this reaction is rather fast and iodine atoms shift easily from chain to chain, replacing radicals. In this way, when a radical is present on a chain, propagation takes place, while the chain is "dormant" when iodine is present. Under standard process conditions, active and dormant states frequently alternate in the life of a polymer chain, so that a chain with degree of polymerization 10^4 has normally experienced 10^3 activation/deactivation events.

In addition, if termination by combination is inhibited by segregation and low overall radical concentration, as discussed in the previous chapter, polymer chain life becomes virtually longer than the whole process. Such a situation is normally referred to as a pseudo-living polymerization: it is now adopted in industrial practice and has already been deeply analyzed through a detailed mathematical model[6].

Its great advantage is that polymer chains grow gradually, as confirmed by the linear increase of molecular weight with conversion and by the very narrow molecular weight distributions. Since chain ends are reactive at any moment in time, during and after polymerization, it is possible to control the evolution of polymer composition by changing the monomer feed composition or by stopping the reaction and starting a different one afterwards. Consequently, block copolymers are easily generated and the introduction of special comonomers in the polymer chain can be finely controlled.

These outstanding features allow introducing a further tool to control the polymer's microstructure: if a highly reactive polyfunctional fluorinated molecule is added during polymerization, it is possible to link different growing chains to each other, thus creating controlled branches in the polymer. This novel polymerization technology has been named accordingly "branching & pseudo-living" and is now applied industrially by using small amounts of a fluorinated diene such as $CH_2=CH-(CF_2)_n-CH=CH_2$[7]. The reaction mechanism can be described as follows: first, one double bond of the diene undergoes propagation to a growing polymer chain and introduces a pendant double bond in the polymer. Then, the pendant double bond reacts with another polymeric radical, linking two macromolecules into one, as depicted in Figure 4. In this way, the polymer chains are partially crosslinked and the branching degree and distribution is controlled by the diene feeding policy.

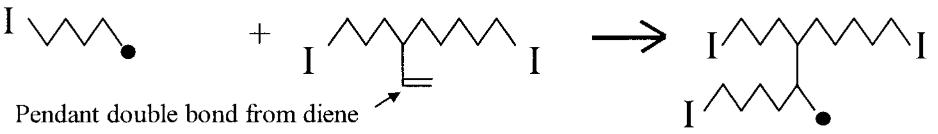

Figure 4. Mechanism of branching & pseudo-living polymerization.

As it is readily clear by looking at the branching mechanism (Figure 4), the polymer structure is heavily modified by it and the average number of iodine chain-end groups per macromolecule becomes much higher. In particular, molecular weight distributions change dramatically: in Figure 5 it is seen that by increasing the amount of diene fed to the reacting system, first a shoulder and then a second peak is formed in the high-molecular-weight range of the distribution, while the position of the original peak remains unchanged. The high-molecular peak corresponds to molecular weights almost two orders of magnitude larger than the original peak and is straightforwardly linked to highly branched or even partially cured polymer chains.

The presence of macromolecules holding many iodine atoms has been successfully applied to improve peroxide-curable fluoroelastomers. Since iodine is susceptible of radical attack, it acts as a cure-site. In standard pseudo-living polymerization, the average number of iodine atoms per molecule is below 2 and is not enough for achieving satisfactory elastic properties upon curing (in particular, low enough compression sets). Thus, it is necessary to add special cure-site monomers to provide additional sites for radical attack during vulcanization. On the contrary, when "branching & pseudo-living" technology is applied, the presence of highly branched species offers a iodine-rich ground for completely curing the remaining polymer chains. As a result, curing properly takes place without requiring additional comonomers and, what is more, scrap during polymer processing is heavily reduced. Thus, nowadays peroxide-curable fluoroelastomers by Solvay Solexis (Tecnoflon® P/PL series) are produced using this technology.

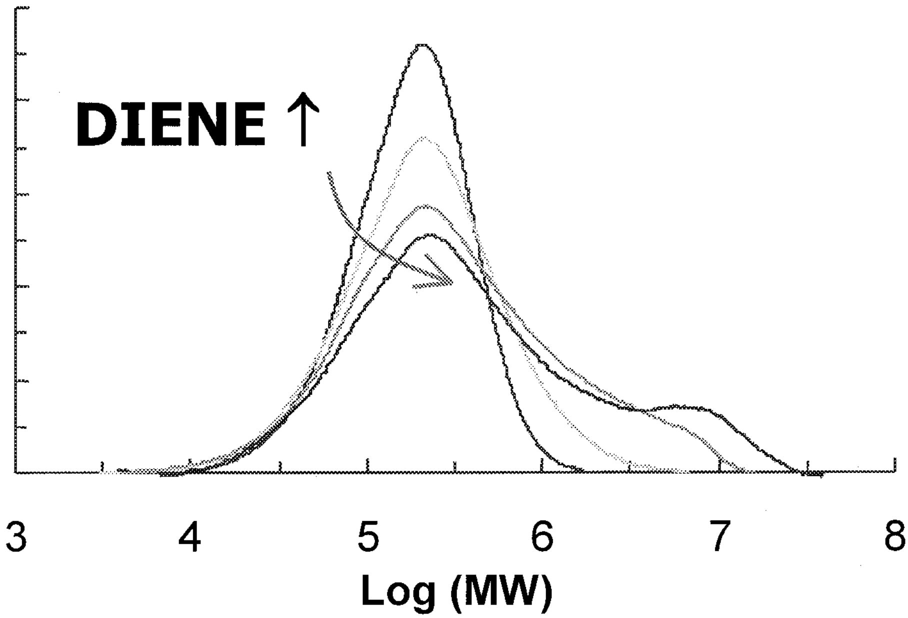

Figure 5. Molecular weight distributions of vinylidene fluoride (VDF) / tetrafluoroethylene (TFE) / hexafluoropropylene (HFP) terpolymers obtained by branching & pseudoliving polymerization with increasing amounts of $CH_2=CH-(CF_2)_6-CH=CH_2$ diene, as indicated by the arrow.

A second important application that has been made possible by "branching and pseudo-living" polymerization is the synthesis of fluorinated thermoplastic elastomers (FTPE). In FTPE ordinary chemical cross-linking is replaced by formation of crystalline regions in the polymer's matrix. Strong intermolecular interactions in crystalline areas provide the desired elastic properties when temperature is low, but upon heating it is possible to melt the polymer, making processing much more flexible.

Thermoplastic fluoroelastomers are block copolymers, prepared through pseudo-living polymerization: first the elastomeric segment is polymerized, then semicrystalline polymer is synthesized on the elastomeric chains that hold iodine terminal groups and hence are still reactive. After processing the polymer, different semicrystalline chains crystallize together, providing a sort of physical cross-linking. Once more, it has been observed, that elastic properties of linear copolymers having semicrystalline/elastomeric/semicrystalline morphology are not satisfactory. On the other hand, if highly branched macromolecules are present elastic properties improve enormously (compression set (24h, 100°C) around 20% instead of 60%), since the average number of physical cross-links per molecule is larger or, in other words, both physical and chemical cross-links are present, as in the scheme reported in Figure 6.

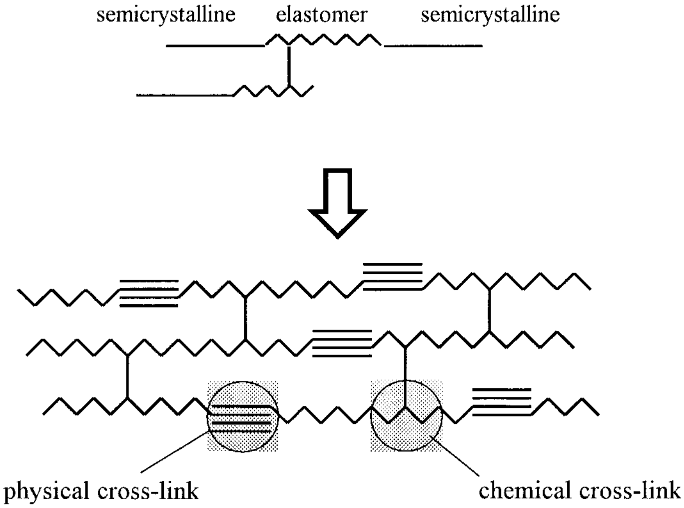

Figure 6. Scheme of the cross-linked structure of a thermoplastic fluoroelastomers synthesized via "branching & pseudo-living" technology.

Fuoropolymer Nanoblends

Polymer blending is an effective technique to achieve particular ranges of properties that cannot be obtained with pure polymers. In the field of fluorinated materials it is particularly interesting to combine the sealing properties of elastomers with the low permeability and high hardness typical of semicrystalline polymers.

Since thermodynamically miscible polymers are very seldom found, polymer blends are normally made of a continuous phase of one polymer and a dispersed phase of the other one. The effectiveness of blending has been found to be strongly dependent on the size of dispersed phase, as interactions between two immiscible phases strongly depend on contact surface. In many cases a critical particle size exists that leads to the optimal combination of properties[8,9]. Due to low inter-molecular forces, fluoropolymers need very large contact surfaces to achieve significant interaction energies. Hence, it is not surprising that the optimal particle size for fluoropolymers is very small, well below 0.1 μm, a range of size that is impossible to reach by standard mechanical mixing techniques[10].

An alternative approach has been developed to tackle this problem: the two polymers to be mixed are prepared separately by microemulsion polymerization. The two latexes are then blended and coagulated simultaneously. The free control of polymer particle size possible with microemulsion polymerization and an accurate choice of degree of conversion allows preparing particles with diameters around 30nm. If the colloidal stability of the two latexes is properly equalized, this size is retained during coagulation and is found in the final polymer, as confirmed by atomic force microscopy measurements[11]. In this way the dispersed phase is one order of magnitude smaller than sizes achievable by mechanical mixing or from co-coagulation of latexes prepared in emulsion. As a matter of fact, nanoblends prepared by microemulsion polymerization are perfectly transparent to visible light, confirming presence of discontinuities only at a much smaller scale than the light's wavelength.

In Table 1 a comparison is presented among three different blends between a standard fluoroelastomer (Tecnoflon® P959) and 30% wt PTFE. Blend 1 was obtained from microemulsion polymerization latexes, as described above, blend 2 was prepared from standard emulsion latexes, while blend 3 results from mechanical mixing in open roll mixer of fluoroelastomer and micronized PTFE powder. Due to low compatibility of the two polymers, preparation of blend 3 was a rather challenging task. These three blends only differ for the particle size of the dispersed phase.

It is readily seen that tensile strength (TS) increases when particle size is reduced: tensile strength of blend 1 is more than 30% higher than the one of blends 2 and 3, which is consistent with the assumption that in nanoblends interactions are stronger. Moreover, modulus and hardness are slightly higher and elongation at break is larger in blend 1 than in blends 2 and 3, which again show similar values, thus confirming that particle size affects mechanical properties independently from the adopted mixing technique.

This is evident also in the toughness data, normalized in Table 1 for better understanding: toughness is the integral of the stress-strain curve and provides a measure of the energy per unit volume adsorbed by the material before it breaks. It is seen than traditional blends are able to absorb only 62-65% of energy absorbed by nanoblends before braking. This value confirms once more that interaction energy between fluoroelastomer and PTFE is higher when dispersed phase particle size is smaller. In addition, it clearly indicates that the overall set of mechanical properties of nanoblends is superior in comparison to standard blends. In particular, the combination of high elongation at break and high hardness is a unique feature which offers great advantages in several applications, above all in oil drilling industry.

Table 1. Effect of dispersed particle diameter on blend mechanical properties. All blends contain 30wt% of dispersed phase. TS: tensile at break. M: modulus. EB: elongation at break. HDS: hardness. TH: toughness (relative values).

Blend	**Mixing technology**	**Diameter** (nm)	**TS** (MPa)	**M** (MPa)	**EB** (%)	**HDS** (ShA)	**TH** (-)
1	Blending of microemulsion latexes	45	21.2	5.6	332	79	1
2	Blending of emulsion latexes	250	15.7	5.2	275	74	0.62
3	Mechanical mixing	300	15.5	4.6	296	76	0.65

Conclusions

The remarkable improvements achieved by using microemulsion when polymerizing fluorinated monomers have been presented and discussed. It has been shown that the use of microemulsion allows free and independent control of the number and size of particles in the reacting system. This is an additional degree of freedom that can be exploited to obtain sufficiently large polymerization rates also in poorly reactive systems, as those involving complex monomers for special applications.

Furthermore, it has been illustrated how the use of a chain transfer agent containing iodine atoms, which are frequently transferred from chain to chain, permits establishing pseudo-living polymerization conditions, thanks to radical segregation in very small particles obtained by using microemulsion. The newly developed "branching and pseudo-living" polymerization technique has also been described and its application to a peroxide-based curing chemistry using iodine chain ends and to prepare melt-processable fluoroelastomers has been introduced.

Finally, blending of latexes prepared separately by using microemulsion to make PTFE-reinforced fluoroelastomers has been proved to be much more effective than mechanical mixing or blending of latexes prepared by standard emulsion polymerization: the use of microemulsion, together with a careful equalization of the stability of different latexes, allows obtaining the smallest particle size among known techniques for preparing polymer blends, thus enhancing interactions between the two phases and leading to the most effective combination of properties.

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