A Quicker Method for Blending Polyethylenes

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When was the last time you didn't use a polymer? Chances are, you are reading this on a screen, which is made out of light emitting diodes (LEDs) or is a liquid-crystal display (LCD) – both full of millions of tiny bits of special is edpolymers. In case you have a printout that paper have multitudes of microscopic cellulose fibres running through it. All around us, humans are dependent on things made from polymers – from the bristles of our toothbrushes, to the insulation on space rockets – synthetic polymeric materials can be considered as the literal building blocks of our civilization for over the last one hundred years. Indeed, in 1980 when the Nobel Prize winning biochemist Alexander Todd was asked the question, 'What is chemistry's biggest contribution to science and society?' he replied, 'The development of polymerization.' Polymers come in all shapes and sizes – both at the molecular level and on the macroscopic scale. But here I will be talking about the work that we have done using the simplest polymers of all – polyethylene.

Picture two carbon atoms bonded, with two hydrogen atoms connected to each of them. Now imagine this simple system repeat itself hundreds and thousands of times in a chain. That is the nature of the simplicity of this material, first synthesized in 1898 by accident, which today is the polymer with the largest consumption by volume worldwide. We all have heard of polyethylene; also known as polythene, and often colloquially what we mean when we say 'plastic'. If we look carefully at the various bags, sheets, boxes, wrappers, and pipes that are made of polyethylene, we might see indexes and codes like HDPE, LDPE, LLDPE, MDPE, UHMWPE, and so on. But

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what do these abbreviations mean? These are just the different grades of polyethylene, differing only in their arrangement of carbon and hydrogen bunches on the long chain that I wrote about earlier. For example, LDPE is Low Density Polyethylene, where the main chain of carbon and hydrogen, sometimes has branches as well of the same elements. Our work, in particular, focuses on two other grades from the list above – High Density Polyethylene (HDPE) and Ultra High Molecular Weight Polyethylene (UHMWPE). These two species have little or no branching, which makes their molecules essentially long, linear chains. However, UHMWPE chains are much longer than HDPE ones – almost 100 times longer – which makes their properties and applications immensely different from each other. For example, HDPE is lightweight and can be used to make pipes to carry fluids like water, oil or gas. On the other hand, UHMWPE is extremely strong and is used to make artificial joints that are inserted into the skeletal system of human bodies.

For the last thirty years or so, industries and researchers have tried to blend these two polyethylene grades in varying ratios. The reason behind this is to get the strength and durability of UHMWPE combined with the versatility and process ability of HDPE in the same material. Now the problem that we had taken up was "Can these two polyethylene grades be blended easily and effectively?" The scenario appears to be very simple – in a mixer at high temperatures, you take a lot of HDPE and a little amount of UHMWPE powders, and throw them in. Chemically, there is no difference between them – as they are both polyethylene species. So, after a short amount of time, the UHMWPE should be well-mixed with the HDPE, the former's strength and durability getting imparted to the versatility of the latter, thus giving us the best of both worlds. But does this happen so easily? Unfortunately no, there are a few pitfalls along the way.

Long, linear polymers like these, in the hot melted state, are essentially like a cluster of worms in the soil – piled up, constantly moving, and crucially, entangled with each other trying to slide away. How easily they can slide away depends on how long each worm is. Let us move away from garden animals to the more appetising analogy of food. Molten commercial UHMWPE is like a bowl of cooked noodles – if you try to pull out one noodle, it is quite difficult to because the other strands won't let you. This is because the long noodle twists and turns through all the others and everywhere it touches, the net friction on it adds up, making it more difficult to untangle from this "network" of noodles. Similarly, each UHMWPE chain forms innumerable "entanglements" with all the others due to their long length. This problem doesn't appear as much in molten HDPE because its chains are much shorter. So, when a grain of UHMWPE starts melting in an ocean of molten HDPE, these entanglements hinder these chains from diffusing out into the surroundings, thus delaying the blending process. In the polymer processing industry, economic feasibility dictates that these blending processes should occur in a matter of few minutes. But the aforementioned delay in blending takes the process up to several hours to complete – which is unacceptable.

In order to tackle this issue, we have experimented with using a different type of UHMWPE than the commercially available one. This type, known as "disentangled" UHMWPE (dPE), is made using special polymerization techniques which prevent the chains from getting quickly entangled in the molten state. Nevertheless, they will eventually entangle like the commercial UHMWPE chains – but this will happen after a certain period of time, within which, the requisite dissolution

in HDPE will have occurred. Thus, by delaying the dPE chains to entangle with themselves, we have given them an opportunity to simultaneously escape their own network and blend with the surrounding HDPE environment. The remarkable aspect of using the "disentangled" dPE is that the entire blending process now occurs in a matter of a few minutes, instead of the several hours using commercial UHMWPE.

But how did we verify, or even estimate the extent of this dissolution? The answer lies in the field of rheology. Rheology literally means "the study of flow", and it is used to measure the response of a material to a physical stimulus. All matter flows under some natural force, for example, consider a rubber ball getting squeezed between your fingers. Your fingers exert a force, which changes the shape of the ball, and the ball experiences some forces on it. Once you release the ball, the forces get dissipated, and the ball relaxes. Using highly sophisticated instruments, we can apply an exact amount of deformation to a material, and then accurately measure the response of the material towards it. Quick, rapid, deformations allow us to probe the effect of the shorter chains in the mixture, i.e., the HDPE, while slower deformations let us study the same due to the dPE in the blend. This is known as oscillatory rheology. From these experiments we can distinctly understand the structure and properties of the material. In the context of our work, rheology on our dPE-HDPE blends sheds light on the nature of how well these two polyethylenes have mixed. By comparing with commercial blends, rheological studies have demonstrated the need to make the UHMWPE "disentangled", in order to get quick and effective mixing. The next step would be use theories of mathematics and physics to try an explain the phenomena observed.

We believe the outcome of our research will be valuable to the polymer processing industry. Not only have we showed that it is possible to quickly blend UHMWPE and HDPE using a simple tweak, but we have also discovered new applications of these blends. These blends could be used for application where previously pure HDPE could not be employed because of its limitations. Now with the added UHMWPE, there are several new possibilities where the cheap and easily processible HDPE can be utilized effectively. This work also emphasizes the efficacy of the field of rheology in order to ascertain the nature of complex materials.