

Why synthetic rubber has such a high molecular weight?

This monthly column is all about openly sharing expertise and knowhow with our readers, regardless of industry, product or service. The aim is to plant the seeds of inspiration, strengthen the knowledge base, and hopefully, lead to new opportunities and innovations.

While the column is being rolled out with the ideas of Prof. V.C. Malshe, an academician, researcher, innovator, consultant and businessman, it is open to one all. Simply write to editorial@chemicalweekly.com.

In 1995, I was new to the job as Professor in UDCT. I had only a couple of Ph.D. students, just four to five lectures every week and few consultancies. In short, I had lots of free time, and able to accept whatever work came my way.

At such a time, one of my friends working in a petrochemical industry asked me about the use of alpha-methylstyrene (AMS) dimer for molecular weight control of vinylic polymers. I told him what I knew, which was not a whole lot. Then I came to know that his employer was getting about 150-tonnes of AMS as a by-product, which they were selling at a price cheaper than of styrene monomer. AMS does not homopolymerise and acts as an inhibitor for vinylic polymerisation by formation of stable free radicals. AMS dimer, which is a mixture of two dissimilar structures, had been reported for molecular weight control of vinylic polymers, but exact details were not known. On his request, I gave him a research proposal to study the effect of AMS dimer on the molecular weight of acrylic and styrenic emulsion polymers.

The then Paints, Pigments and Var-nishes (PPV) Section of the Plastics and PPV Department at UDCT had a Gel

Permeation Chromatograph (GPC) as also lab facilities required for prepar-ing emulsion polymers. One student who had finished her Ph.D. work but not finished her viva-voce was available for four to six months. Since I wanted work badly, I made a proposal that my friend could not refuse. I only asked for 5 litres of several monomers, a monthly stipend for the student, and some funds for other consumables. In those days, a research guide could not include consultancy fees in the research proposal (now it can be done); so, my services were available for free!

It was agreed that several polymers and copolymers of acrylic monomers would be prepared by emulsion poly-merisation using AMS dimer as chain transfer agent at various concentrations and without it; the polymers would then be isolated, purified by repeated precipitation; and the molecular weight and molecular weight distribution determined by GPC.

The project was finished on time, a report was prepared, and several copies were handed over to the sponsor. They used it to promote use of AMS dimer to regulate molecular weight of emulsion polymers.

As per the contract with them, we could not publish that work. I did not even keep a copy for future use.

Controlling the molecular weight of synthetic rubber

For next several years they did not raise the subject. But sometime in 2002, the company proposed to increase their AMS dimer capacity. So, a delegation met me to find out avenues for increas-ing the market for AMS dimer. I gave them several ideas. One possibility was for controlling the molecular weight of synthetic rubber.



I knew something about rubber compounding and processing. I knew that the first step of rubber compounding was to masticate rubber with a free radical generator to reduce the mole-cular weight, so that mixing of the various components to the formulation becomes easy. Rubber compounding is relatively simple – rubber, carbon black, silica, and other additives such as masticating agents, vulcanising agent, antioxidants, antiozonants, sulphur, lubricants, zinc oxide, stearic acid, rosin esters, etc. are mixed in 30:30:30:10 (the last being all the additives put together), though there are some minor variations to this composition.

The first step of processing all rub-bers is mastication with free radical gen-erators. The purpose is to bring down the molecular weight. Most rubbers as pro-duced have very high molecular weight. Natural rubber has a molecular weight in the range of 5-6 million Dalton. Synthetic varieties are about a million; give or take a few thousand.

This first step is energy intensive. Typically, in a high shear mixer, 2,700-kWh of energy is required to masticate one tonne of rubber to make it process-

able. More than an hour is needed, besides very heavy machinery, which is expensive because of the rugged construction. Since a large quantity of carbon black is required to be dispersed in rubber, the latter needs to be of sufficiently low viscosity to be able to mix efficiently. Additives like oils, resins, antioxidants help to reduce viscosity further.

I suggested to the client that if we can use AMS dimer to regulate the molecular weight of rubber, we may be able to save significant amount of electricity in rubber processing. They liked the idea and asked me to give a proposal. Since the process would have involved emulsion polymerisation of styrene and butadiene, facilities to handle gaseous monomers would be required. UDCT's Polymer Department did not have these facilities. So, the proposal ran into a few lakhs of Rupees, as high pressure reactors, and equipment for recovery of unused monomers would have to be installed. The client unfortunately thought the cost was high and I did not get the project.

Why high molecular weight rubbers in the first place?

But the question remained unanswered in my mind. Regulating molecular weight of synthetic rubbers like SBR, NBR, SNR, and polychloroprene, which are manufactured by emulsion techniques at low temperature using special initiators is not difficult. Why then did everyone produce a million molecular weight rubber in the first place? The answer was not easy to find. I spoke to several rubber technologists known to me. No one had any satisfactory answers. I happened to visit USA in 2003 and met scientists of a large multinational. All of them sounded very knowledgeable about the subject of rubber compounding but were clueless as to why the first synthetic rubber was manufactured with a million molecular weight when the desirable molecular weight was only about

30,000. Someone thought the additional double bonds formed by the breakdown of the chains would help crosslinking reactions. But this argument had no substance because there are residual double bonds from the diene and are quite abundant because the unit molecular weight of the diene is just about 60-70 in most cases.

On my return I had to figure out the reasons for manufacture of a million molecular weight rubber. For any polymer chemist, it is very easy to change the molecular weight by adjusting the process parameters – initiator concentration, reaction temperature, chain transfer agent, etc. Polymer chemistry at the time of the Second World War was developed enough to achieve any desired molecular weight.

India was once the primary source of natural rubber in the world (it was even called India Rubber). Other Asian countries like Thailand, Indonesia and Vietnam also supplied natural rubber. During Second World War, the need for rubber tyres increased many folds. Availability from India became difficult because India was a British colony. Substitutes were urgently required and that is when SBR was born in early 1940s in United States.

The manufacturing process of rubber tyres was well established. Process steps like mastication and mixing with other ingredients was the norm. The US administration might have wanted to substitute one-for-one so that the production process could continue unhindered. If the workers were using X quantity of natural rubber, they would use same quantity of synthetic rubber and produce tyres of all description. Such might have been the urgency of the war. By the time the war ended, this had become an established procedure. So, no one has questioned it in last 85 years.

Today, I am throwing open this idea to the synthetic rubber manufacturers of

the world and urge them to take up this challenge. The annual world synthetic rubber production is about 16-mt, while that of natural rubber is about 10-mt. So there is a challenge for polymer chemists to save 70-billion kWh of electrical energy annually and for biochemical engineers to genetically modify the natural rubber plant so that the molecular weight of the rubber from the latex is reduced to about 30,000 from the present 5-6 million. This could be a great green initiative.

Substantial savings

As I said earlier, for polymer chemists this would be a relatively simpler job – increase reaction temperature, increase catalyst concentration and add a chain transfer agent. Molecular weight of about 30,000 would be easily achievable for the standard SBR composition. SNR, polyisobutylene, nitrile, chloroprene, and EPDM could all follow. The cost of tyres manufactured from this rubber will be lower to the extent of saving in electricity, as well as labour in the operation and maintenance of the heavy machinery. These could easily amount to about 20% of the tyre cost.

India uses about 2-mt of rubber annually currently. Of this, about 90% is used for tyre manufacture. A 20% saving could significantly contribute to the profits of tyre manufacturing companies. With increasing cost of electricity (recently my electricity bill went up by 20%) it would be a great advantage to the manufacturing sector.

India has only three synthetic rubber manufacturers. They might initiate the development, but very likely they would not be the first to do this, as Indian entrepreneurs are very good followers.

This development may not be patentable, as I have disclosed enough to be cited as prior knowledge.

Still, I wish good luck to the local rubber manufacturing industry. **V.C. Malshe**