Polymers Processing and Recycling Techniques
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Lecture – 76
PolCoPUS: Crosslinking

Hello welcome to this introductory journey on polymers. We are looking at processing and recycling over quite a few set of lectures. In this lecture, we will look at processes in which crosslinking is involved and we know for example thermosets and rubbers are materials which are processed and during this processing crosslinking is important.

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Overview

1. Crosslinkers
2. Extent of crosslinking

So, keeping some applications in mind, we will discuss some aspects of which type of crosslinkers are used for what type of materials and then importantly for processing what is the amount of crosslinking because crosslinking makes the material undergo liquid to solid transition or gelation, and so all the shaping operations have to finish before that extent of crosslinking is reached at which gel point is observed. So therefore, extent of crosslinking is an important variable for us to know.

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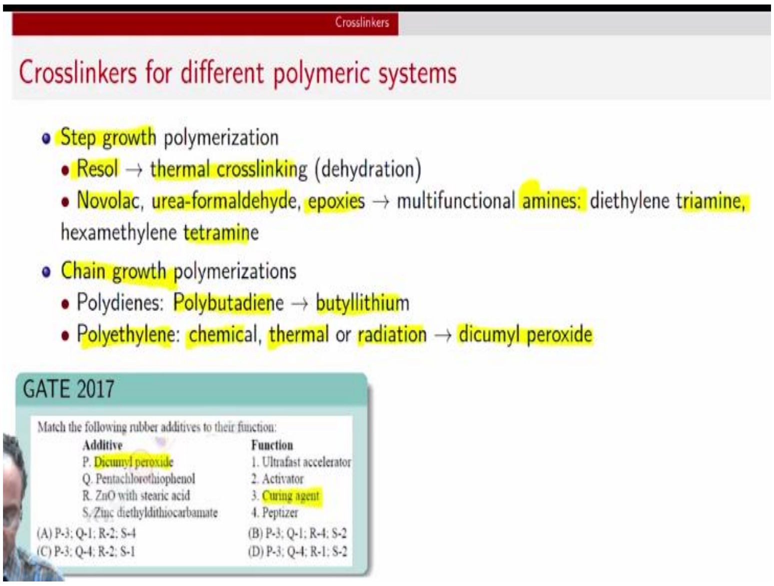

Crosslinkers for different polymeric systems

- Step growth polymerization
  - Resol → thermal crosslinking (dehydration)
  - Novolac, urea-formaldehyde, epoxies → multifunctional amines: diethylene triamine, hexamethylene tetramine
- Chain growth polymerizations
  - Polydienes: Polybutadiene → butyllithium
  - Polyethylene: chemical, thermal or radiation → dicumyl peroxide

GATE 2017

Match the following rubber additives to their function:

Additive	Function
P. Dicumyl peroxide	1. Ultrafast accelerator
Q. Pentachlorothiophenol	2. Activator
R. ZnO with stearic acid	3. Curing agent
S. Zinc diethyldithiocarbamate	4. Peptizer

(A) P-3; Q-1; R-2; S-4
(B) P-3; Q-1; R-4; S-2
(C) P-3; Q-4; R-2; S-1
(D) P-3; Q-4; R-1; S-2

So, crosslinkers are different depending on the different polymeric systems. Of course, for step growth polymerization we have one class and chain growth polymerization given the mechanism itself is different. So for example, Resol is crosslinked using just thermal crosslinking. On the other hand, there are several resins such as urea-formaldehyde or Novolac or epoxies which can be crosslinked using amines.

An amine can also have multiple groups, so tetraamine or triamine and each amine group NH_2 can react twice. So therefore, many of these groups can react four times and additional times and so they are very effective crosslinking agent because as we know more the functionality of a crosslinker more chains it can link. For polybutadiene for example, butyllithium is used and polyethylene which is crosslinked for several applications.

Either for storage tanks or also for wire insulations the crosslinking can be carried out either by chemical means such as use of a peroxide or even thermal or radiative means are possible. So in this exam question, in fact the question is related to you know what are the additives and what is it used for. So of course, as we are seeing the dicumyl peroxide is a curing agent and curing is a word practitioners used to again imply that the transition is happening from a liquid like resin and is getting cured and finally solidified to get the final product.

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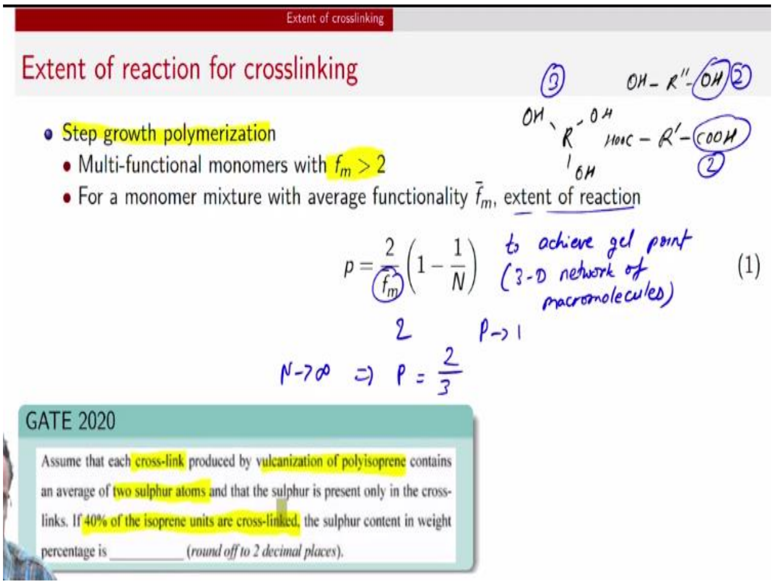

Extent of reaction for crosslinking

- Step growth polymerization
  - Multi-functional monomers with $f_m > 2$
  - For a monomer mixture with average functionality $\bar{f}_m$, extent of reaction

$$p = \frac{2}{\bar{f}_m}\left(1 - \frac{1}{N}\right) \quad (1)$$

to achieve gel point (3-D network of macromolecules)

2 $\quad$ $p \to 1$

$N \to \infty \Rightarrow p = \frac{2}{3}$

GATE 2020

Assume that each cross-link produced by vulcanization of polyisoprene contains an average of two sulphur atoms and that the sulphur is present only in the cross-links. If 40% of the isoprene units are cross-linked, the sulphur content in weight percentage is __________ *(round off to 2 decimal places)*.

So, you can look at some of the other materials which are used for mainly crosslink systems. So if you have a step growth polymerization reactions, then we need basically a multifunctional crosslinker and this could for example be an alcoholic group, if let us say it is reacting with a carbolic carboxylic acid to form polyester. If you have a linear or only difunctional hydroxyl group, then you will get a linear chain.

So, therefore a big requirement in terms of getting a crosslink polymer is that the functionality of the monomer has to be more than 2 and this for example the functionality is 3, while these are all with functionality 2. Given the monomer mixture and given that the functionality is more than 2, then we can have the extent of reaction how many of these carboxylic acid and hydroxyl groups have reacted will tell us what is the overall crosslinking that is reached.

So, for example, this is the extent of reaction to achieve gel point or getting a 3-D network of macromolecules. So if let us say functionality is 2, so if this number is 2**,** then we can see that p has to go to 1 and that is basically saying that if all the monomers combine together in one more macromolecule, then we will have basically a continuously joined macromolecule and that is really a trivial case and it is not ever going to be achieved, but what we do is we put in monomers which have much higher crosslinking.

So for example if fm is let us say 3, then you can see that when n goes to infinity, we will have basically p going to 2/3. So around 66% of extent of reaction we can get the overall gelation. So, you can see that as you increase the functionality, the extent of reaction required for crosslinking is less and generally the crosslink amount can also be estimated. This question for example is looking at the crosslink in case of vulcanization of natural rubber.

And where in fact each crosslink contains certain number of sulphur atoms and so if the percentage of isoprene units which are crosslinked is known, what is the weight percent of sulphur that has to be added? So, given in case of crosslinking we always need to add a crosslinker which is either a higher functionality monomer or a crosslinker which can link different chains, we need to basically estimate the amounts. So, you can look through this question and try to answer the overall amount of sulphur required.

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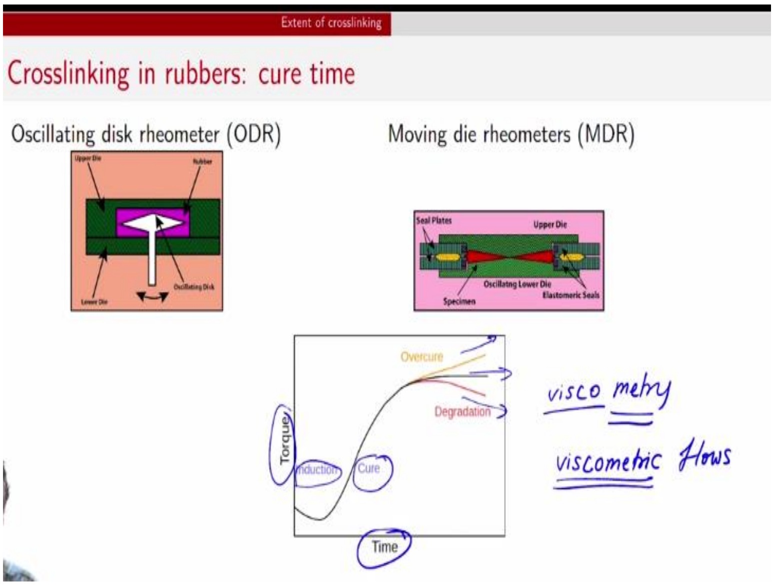

Extent of crosslinking

Crosslinking in rubbers: cure time

Oscillating disk rheometer (ODR)

Moving die rheometers (MDR)

In case of crosslinking of rubbers since we need to finish the shaping operations before the overall gelation sets in or 3-dimensional network is formed, we have several industrial instruments which are quite commonly used. For example, it is called oscillating disk rheometer or moving die rheometers. These try to estimate the overall amount of torque which is required for moving.

In this case it is a disc and this disc is oscillating and then the rubber material is kept or we can have a die, so there is an upper die and then there is a lower die and in between the fluid is kept which is in this case rubber. And then one of them is oscillating, lower die is moving and then therefore what is the amount of torque which is required to make it move and initially when the rubber molecules are smaller molecular weight the torque required is less.

But as crosslinking starts happening the molar mass builds up and the overall torque required to make this motion also increases. So that is what you would see generally when you look at torque as a function of time in one of these instruments. Compared to the rheometers which are generic and used in case of analysis of rheological response, these are more trait tests. So they are very useful in terms of processing of rubbers.

And numbers that are produced in these are very important in terms of making quick decisions in rubber processing industry. However, these cannot be used for any class of materials to just measure a viscosity. So, there is an important word we will see which is related to metry which is the measurement. So, viscometry implies measurement of viscosity and generally for rheology we have what are called viscometric flows.

These viscometric flows will make the rheometers useful for large class of material systems because then the nature of material does not determine the theory which is underlying the analysis of viscometric flows. In oscillating disk rheometer or moving die rheometer on the other hand the nature of materials is interwoven together with whatever are the numbers that are being generated.

So, these are trait tests as opposed to a generic instrument which can analyze flow behavior of large class of materials. However, from a practical point of view the data that is generated in terms of torque versus time is very useful in terms of decision making. So generally, you can see that initially the torque would remain constant or decrease as temperature is changing and then curing or crosslinking starts occurring.

And then the expectation is that beyond a certain point when crosslinking is complete the overall torque required does not change much with time, but depending on what is going on in the sample there could be additional crosslinking which is not desired or there could also be degradation due to the thermal energy and temperatures which are involved. So therefore, such a set of data is useful in terms of deciding the molding conditions and deciding the overall temperature and pressure which are to be utilized for several processing operations related to rubbers.

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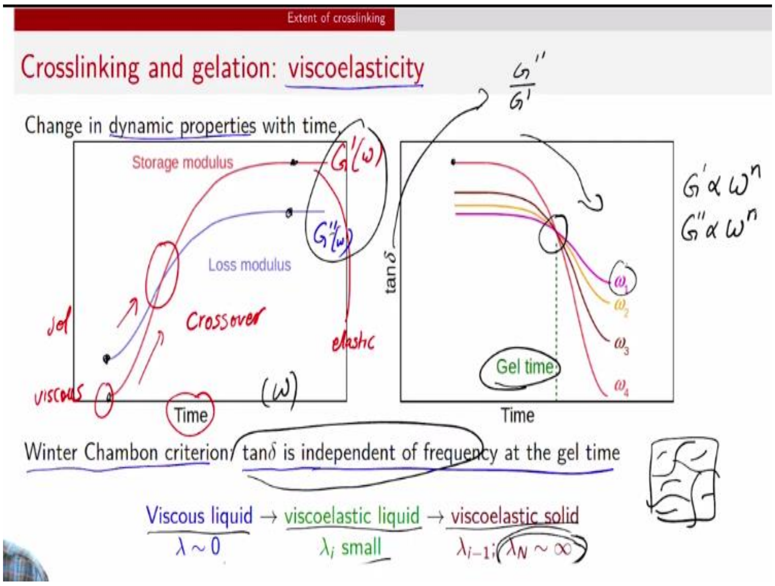

Extent of crosslinking

Crosslinking and gelation: viscoelasticity

Change in dynamic properties with time

Winter Chambon criterion: $\tan\delta$ is independent of frequency at the gel time

Viscous liquid → viscoelastic liquid → viscoelastic solid

$\lambda \sim 0$ — λ_i small — $\lambda_{i-1}; \lambda_N \sim \infty$

So, the other measurement of gelation that can be done on an overall rheometer itself, a generic rheometer is basically measurement of dynamic properties with time. So given that material becomes more and more viscoelastic when gelation happens, we start with a monomer solution or we start with a resin which is completely Newtonian fluid and then with crosslinking it transforms into more elastic crosslink network.

So this viscoelasticity increases or elasticity increases as gelation happens and that can be analyzed by looking at G' and G". So, we could look at the variation of what happens to G" and what happens to G'. So as macromolecular molar mass builds up with crosslinking, both of them increase. However, the G' which indicates the elasticity or the storage modulus that increases much more rapidly.

And you can see that there is a certain point at a certain time we can see that the elastic behavior starts dominating with respect to the viscous behavior. When we have the monomer stage or sol state, in the sol state we have the viscous behavior dominating, while in the gel state we have the elastic behavior dominating. So, therefore material transforms from being a largely viscous material to a largely elastic material.

So this crossover, so many times you would hear people talk about crossover where G' crosses over G" can be used as an indication of gelation because whenever there is a 3-dimensional network formed, the elasticity of the network kicks in and therefore G' is more than the G". However, if you remember G" and G' are both functions of frequency.

So in effect this crossover will also depend on frequency itself and if it is a fundamental property of the reactants which are reacting to form this 3-dimensional network, then the gel time should not depend on the measurement condition which in this case happens to be frequency. So, to evaluate the gel time in crosslink system, there is a Winter Chambon criteria which states that tanδ is independent of frequency at the gel time.

So if you do the same set of experiments but rather than looking at G' and G" individually, what you could do is you can look at tan delta which is nothing but ratio of G" to G'. So initially of course tanδ is high because G" dominates, so since we have G" higher than G' we have tanδ very high and later on what happens is G' dominates over G", so tanδ has decreased.

So, generally there is a decreasing tendency and this is again expected because as crosslinking happens molar mass builds up and elasticity increases, storage capability increases, the dissipation capability comes down. Now if we do this tanδ measurement at different frequencies instead of a single frequency the way it is done here, we can plot all tanδ versus frequency.

And what we will see is at one frequency the tanδ is independent of frequency and this is the gel time. Therefore, in this overall transition, what we see is there is a viscous liquid for which relaxation time is very low or practically 0, then we have a viscoelastic liquid for which relaxation times are small so that dissipation still dominates but there is some amount of elasticity to a viscoelastic solid where there is at least one relaxation time which is infinite.

That relaxation time is associated with the crosslinked network given that we have basically 3-dimensional spanning network though there are some smaller sol still remaining in the material. So, this relaxation time diverging is an indication of the gel time and that is why at that point there is a percolated network formed and then Winter Chambon theoretically showed that therefore gel time will be independent of frequency.

Because G' will be a function of frequency and G" will be also same function of frequency. So, when you take their ratio, the frequency dependence will fall out and therefore the ratio is independent of frequency at the gel time. So, this kind of measurements are useful to determine the gel time in case of crosslink systems.

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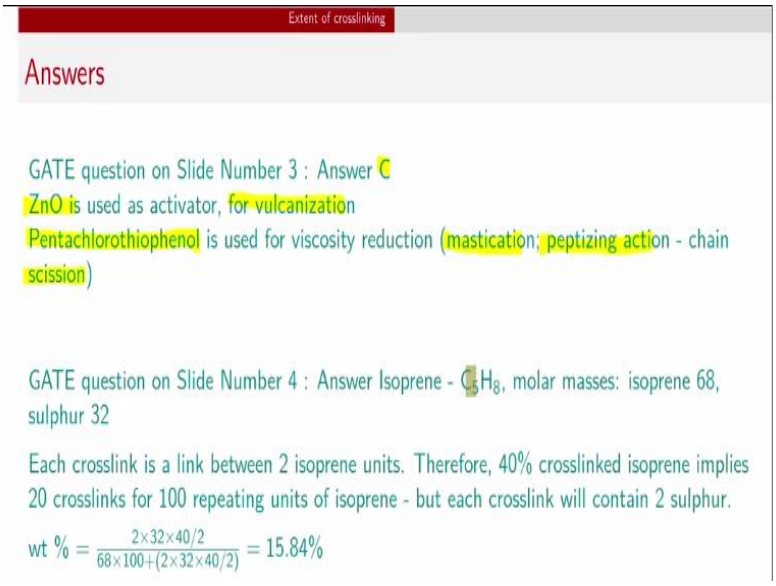

Extent of crosslinking

Answers

GATE question on Slide Number 3 : Answer C

ZnO is used as activator, for vulcanization

Pentachlorothiophenol is used for viscosity reduction (mastication; peptizing action - chain scission)

GATE question on Slide Number 4 : Answer Isoprene - C_5H_8, molar masses: isoprene 68, sulphur 32

Each crosslink is a link between 2 isoprene units. Therefore, 40% crosslinked isoprene implies 20 crosslinks for 100 repeating units of isoprene - but each crosslink will contain 2 sulphur.

$$\text{wt }\% = \frac{2\times32\times40/2}{68\times100+(2\times32\times40/2)} = 15.84\%$$

The questions that we discussed were related to what are the different additives and for example zinc oxide is used for vulcanization as an activator and also depending on the process involved we could use an additive to decrease the viscosity for ease of processing and mixing, it is also called mastication or peptizing action which leads to chain cessation and therefore reduction in molar mass.

So different additives are added in overall rubber formulation depending on the requirement and the other question which was related to the sulfur and isoprene crosslink is just dependent on you know what is the number of groups it is basically accounting of how many sulphur atoms are there and how many groups of isoprene is there. So you can look at this and arrive at the answer. So with this, we will close the lecture and discussion on crosslinking. Thank you.