

peroxide curing

ways to manipulate and improve peroxide-cured rubber

Peroxide curing of rubber continues to increase as higher performance requirements necessitate the use of more durable rubber. And in the case of sealing and heat aging, peroxide cures are about the best that a compounder can provide his customer. Many compounders have an aversion to peroxide cures. They are reluctant to go beyond sulfur cures, often due to a lack of familiarity with peroxides. This Solution will cover many of the well-known properties of peroxides and will try to acquaint you with ways to tweak and improve your peroxide cures.

Crosslinking (curing) elastomers with peroxides was first notably mentioned by scientists in the early 1900s. Natural Rubber in combination with benzoyl peroxide produced the first peroxide-cured elastomer. But when compared to its counterpart, sulfur-cured natural rubber, this peroxide-cured network produced inferior room temperature and heat-aged properties. It was not until the 1950s, when other more stable peroxides, di-tert-butyl and dicumyl, did rubber compounders start to investigate the true benefits of peroxide-curing natural rubber. Then in the 1960s, with the commercialization of EPDM and the fully saturated (no double bonds) EPR, peroxide-curing investigation increased and the full benefits of this chemical reaction started to be discovered. Today there are some 100 different types and forms of peroxides for rubber compounders to choose from. The task is choosing the best-suited peroxide which is dependent on curing temperatures and physical properties needed within the elastomeric application.

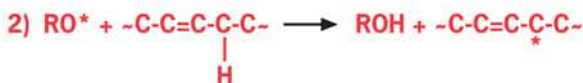
The peroxide manufacturers have done a competent job issuing technical literature concerning peroxide curing. Every ACS Rubber Show has 6-8 technical papers, especially if you include coagent use. This literature will summarize all the information out there, review some of the peroxide benefits and deficiencies, and finally go over a few of the lesser known ways of manipulating peroxide cures. At the same time, you can become familiar with Akrochem's peroxide line-up. We carry most of the primary rubber peroxides in use today.

How Peroxides Crosslink Elastomers:

The chemistry of peroxides cross-linking is relatively simple and well documented. Peroxides are chemical compounds that contain oxygen-to-oxygen (O-O) bonds. These bonds are broken or "cleaved" when exposed to heat (Δ):

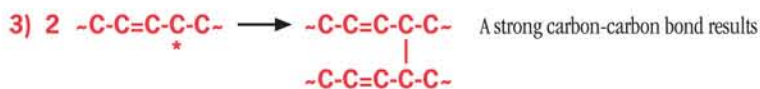


The products of this reaction are two radicals (*). For those interested in chemistry, the * denotes an unshared, unpaired electron. These radicals are highly reactive (unstable) and desperately want to react with something. When these radicals are exposed to elastomers, like EPDM, NR, SBR, NBR, etc., they react and easily extract weakly bonded hydrogens from the elastomeric chain:



Peroxide Radical Elastomer (NR) with vulnerable hydrogen \longrightarrow simple alcohol + polymer chain with radical

This reaction produces polymer chain radicals and now these polymer radicals are highly reactive and unstable and want to react with something quickly. They easily find other polymer radicals and create chemical crosslinks:



Note: The covalent bond between the carbons of the polymer chains is stronger (350kJ) than the sulfur-carbon bond (285kJ) formed by EV sulfur cures and much stronger than the sulfur-sulfur bonds (varies from 155 to 270kJ) formed from normal sulfur cures. The higher bond strength means the heat needed to break them is greater and thus the resistance to heat and compression set is better in elastomers with peroxide cures.

The part about heat being needed to start a peroxide reaction is crucial to understanding peroxides. The more stable a peroxide is, the more it resists separation and the higher the temperature must be to get this reaction going. To the compounder, the higher temperatures needed mean that curing temperatures must be higher and congruently, processing or scorch time will be proportionally longer. This is a constant trade-off with peroxides: you can improve the safety of the compound by going to a higher-temperature peroxide, but a higher molding temperature will be required (or a longer cure time at lower temperatures is needed). Thus, peroxides are heat-driven. Unlike sulfur cures where additives can be used to manipulate the cure rate, peroxide cures are almost solely dependent on the heat delivered to the system. They don't start reacting until they reach a particular minimum temperature. By comparison, most sulfur cures have shelf lives limited to the fact that crosslinking reactions are occurring all the time. Typical peroxide-cured rubbers have outstanding shelf lives as long as storage temperatures stay below the minimum needed to start the peroxide reaction. That's why you often see very long peroxide scorches at processing temperatures (Mooney at 250°F) where the heat is barely enough to start only a few peroxide reactions and very short scorches at curing temperatures (rheometer) when the heat is sufficient to open the peroxide immediately.

choosing a peroxide based on halflife and reactivity

Usually a major reason for choosing a particular peroxide is its reactivity or expected curing temperature. Reactivity, and thus optimum cure temperature, is measured by peroxide "half-life." Half-life is a somewhat confusing term when trying to apply to rubber curing. It is the time and/or temperature needed to consume, or open, half of the peroxide available. It is typically presented as the temperature at which the half-life requires 0.1 hrs, 1 hr or 10 hrs. For dicumyl peroxide, these temperatures are 185°C, 140°C, and 120°C, respectively. As is true with all chemical reactions, as the temperature gets higher it takes less time to use up the peroxide. At 185°C, it takes 6 minutes (0.1 hr.) to use up half the dicumyl peroxide. After a further 6 minutes, half of what was left will have been consumed. And so forth. Somewhere between 5 and 7 half-lives have to pass in order to consume enough peroxide to achieve a thorough cure (comparable to a T90). The table at right synthesizes this.

HALFLIFE vs. % OF PEROXIDE CONSUMED	
Number of half-lives	% of Original peroxide consumed or opened
1	50
2	75
3	87.5
4	93.7
5	96.9
6	98.4
7	99.2
8	99.6
9	99.8
10	99.9

It's not often that enough mold time is available to do a really totally thorough cure (10 half-lives). That's why many peroxide cures include a post-cure to exhaust all the available peroxide and maximize the number of crosslinks. *However, as a caveat of postcuring, typically you will get a better quality part with a long cure in a mold than you do with a short cure followed by a post-cure in an oven.*

A compounder had a peroxide-cured EPDM part to mold with severe undercuts. A fully cured part gave outstanding compression set results but hot tear was very poor. By undercuring the part, the tear was better but no amount of postcure ever gave equal set quality. Sometimes it is just not feasible to do a full mold cure on a part. You can postcure under nitrogen to overcome this deficiency but that is not possible for most shops.

So how does one use this curious half-life information? Below, you can see the most often used peroxides in rubber (excluding silicones); the temperature at which their half-life is 1 hour; the safe processing temperature of this peroxide; and finally, the typical curing temperature of this peroxide. You can see the temperatures for each individual peroxide are all relative to one another. While sophisticated mathematics can be performed on half-life numbers, the rubber chemist has to keep only the processing and curing temperatures in mind.

Akrochem Peroxide	Chemical Name	°C where half-life is 1 hour	Safe Processing Temp ($t_c > 20$ min)	Typical Cure Temp ($t_{90} = 12'$)
2,5 Tri	2,5 Dimethyl -2,5-di-(t-butylperoxy) hexyne-3	149	145	185
DDPH	2,5 Dimethyl-2,5-di-(t-butylperoxy) hexane	142	135	175
VC	Di-(2-t-butylperoxy-isopropyl) benzene	142	135	175
DC	Dicumyl	136	130	170
VAL	Butyl 4,4-di-(t-butylperoxy) valerate	131	125	160
TMC	1,1-Di(t-butylperoxy)-3,3,5-trimethylcyclohexane	117	114	145

Pure (near 100% activity) and cut (typically 40% active) versions of Akrochem peroxides are available as powders and/or EPR-rubber bound products.

Examining the foregoing temperatures, you can see some rhyme and reason. The first column is the temperature at which half the peroxides will open up in an hour's time. If you are processing the rubber, you don't want half your peroxides to open, so the safe processing temperature (second column) is below this hour half-life temperature. On the other hand, during cures, you don't want to wait 3-4 half-life hours. Most of the common cure temperatures are about 30°C higher than the one-hour half-life, or roughly 12 minutes of curing time.

When choosing a peroxide, the first question to consider is, what are the curing conditions needed to make an economical part without excess scrap? Is it an injection mold with a long runner system or a large transfer part that will require a lot of time to fill the cavity? Best to use one of the higher-temperature peroxides. But if it is a compression molded O-ring with minimal heat during the processing stage, you may want to use a low-temperature peroxide.

After looking into the processing and curing requirements in order to choose the peroxide you are going to use, what other issues might come into play that lead to the choosing of a peroxide? Let's examine some choices:

- **Odor** – As anyone who has worked with dicumyl peroxide can tell you, the by-products (specifically acetophenone) of dicumyl reaction are extremely pungent. Some people say the odor is sickeningly sweet, but tolerable. Others say it is too nauseating to use. In short, you have to decide if you want to deal with the odor. Most people become used to it quickly and after the initial complaints, will learn to work with it. Some people absolutely will resist working with the dicumyl. If the odor might be a problem, use a different peroxide. You will not be able to mask the dicumyl odor; reodorants and post-curing fall short in eliminating the odor issue. Although it may be inconvenient, it's better to use an alternate if odor is a potential issue.
- **FDA Status** – This can be a bit tricky. FDA regulations (177.2600) for rubber allow for the use of either dicumyl or 1,1,4,4-tetramethyltetramethylenebis[t-butyl peroxide] among the commonly used rubber peroxides. The latter is the Akrochem DDPH material although the FDA uses a different naming system than just about anybody else. These fall under the accelerator category so by this regulation only 1.5% of a permitted peroxide can be used. This is a potentially severe limitation. For example, if you have an EPDM with 200 phr total, the pure peroxide can only be 3 phr of that ($3/200 = 1.5\%$). In addition, any co-agent like TAC (triallyl cyanurate) must be included as well, in that 1.5%. This limitation is repeatedly overlooked by many compounders. It is best to use DDPH which supplies about 50% more crosslinks part-for-part compared to dicumyl (thus you can use less) and to load your compound up with inactive fillers as much as possible to raise the total phr and thus raise the allowable peroxide/co-agent level. Certain co-agents have somewhat nebulous FDA approval under different categories other than accelerators. This can save some phr for more peroxide.
- **Bloom** – Normally bloom is not an issue with peroxides. This is one of the best attributes of peroxides. However, many compounders do not realize that the VC-type peroxide will bloom. It's not a heavy bloom but if a customer wants a "shiny black" rubber part, the VC peroxide should not be used.
- **Cost** – Some compounders (and nearly all purchasing managers) prefer to choose DC (dicumyl) first, due to its low per-pound cost. However, on a usage basis, VC-peroxide is often less expensive since 62.5% as much VC compared to DC has to be used to achieve the same crosslink density. If 10 phr of DC-40K is used at \$3.00/lb. and 6.25 phr of VC-40K is used at \$4.00/lb., the lowest material cost on paper is clear. One still has to consider the higher curing temperature of VC compared to DC peroxide.

ADVANTAGES OF PEROXIDE CURING

- Compression Set
- Heat Aging
- Electrical Properties
- Color
- Metal Stains
- Non-blooming
- Non-nitrosamine
- High durometer

Outstanding Compression Set: Sulfur cures cannot come close in most cases to the excellent set that results from peroxide cures. And if a lower set is needed, one only has to add more peroxide to the compound. Unlike sulfur, a peroxide crosslink is essentially of only one type (carbon-to-carbon). Thus the more the crosslinks, the higher the rheometer torque, the better the set will be. Of course, this eventually reaches a point of diminishing returns where little additional set can be gained by adding peroxide. Physical properties degrade as excessive crosslinks are used.

Outstanding Heat Aging: This is certainly true of saturated (no double bonds) polymer backbones. The C-C bond created is as strong as the C-C bonds between the polymer chain's ethylene carbons or propylene carbons. *However, an overlooked fact is that peroxides do not really supply any better heat aging in nitrile, natural and SBR than does a high-thiuram sulfur cure.* This is due to the huge number of double bonds present in the backbone of these polymers. The fact the peroxide bond is more stable does not prevent the double bonds from promoting radicals and oxidative crosslinking. In some cases, a sulfur cure can be made to age better at 125°C than peroxide in NBR and SBR. Plus, ozone protection is less complicated (see peroxide curing interference). But, if the polymer is saturated, do not try to get 150°C aging from sulfur cures.

Good Electrical Properties: Virtually all high voltage rubber will be cured with peroxides due to their resistance to heat and their electrical stability in wet environments. All electrical-grade clay products that are intended for high voltage applications are treated solely with vinyl silane (a silane for peroxides) due to peroxides being the primary curing method in most electrical goods.

Good Color: Peroxides improve on sulfur's color in two broad areas. First, the cured color is better. Sulfur will show a distinct yellowing upon cure. It takes 4–5 times as much titanium dioxide to make a white sulfur cure than a white peroxide cure. This follows through to other colors. Sulfur cures will leave the uncolored compound dirty so that bright colors are harder (thus more expensive) to produce. Secondly, once a colored product is in use, peroxides will discolor much less than a sulfur cure (primarily in sunlight but indoor lighting can be a factor). Thus peroxides not only cure to a cleaner color but also stay cleaner longer.

No Metal Stains: Sulfur reacts with many metal types from silver to copper to zinc. This can cause simple discoloration or a more drastic loss of electrode function. There are ways to compound around the sulfur problem and peroxides are the easiest and most certain way.

Most are Non-blooming: Most peroxide cures are bloom-free and result in black, shiny parts that are cosmetically desirable (the one exception being VC peroxide). There is perhaps nothing more frustrating to a compounder than fighting an unknown bloom that is usually due to the sulfur curatives. We spoke earlier about the good heat aging of high-thiuram sulfur cures but you may also have to battle a bloom problem with this type of cure.

Non-nitrosamine-containing: Nitrosoamines generated by sulfur cures continue to be an increasing issue in rubber compounding. There are no nitrosoamines whatsoever in a peroxide cure. This eliminates the concern about whether a nitrosoamine is regulated (that is, harmful) or is a "safe" nitrosoamine.

High durometer parts: It is difficult to make good-processing, high-durometer (60-80 Shore D) parts. Various ways include ebonite (very slow cures are needed in any thicker cross-sections due to the exothermic reaction of ebonites); high plastic or curing resin can be added to the rubber. These have issues with high initial viscosities and short scorch for the curable phenolics. Plastic has poor set, poor hot tear. A peroxide cured in combination with high levels of acrylic resins will provide excellent properties while permitting a very processable compound. The acrylic resin (best to use a scorch-retarded version) will function as a plasticizer until cure kicks in.

DISADVANTAGES OF PEROXIDE CURING

- Cure interference
- Exposure to Oxygen
- Non-Curable Polymers
- Flex Cracking
- pH problems
- Colorants
- Hot Tear
- Scorch

Cure interference: Any material in a peroxide-cured compound that competes with the polymer chain for donating hydrogen to the peroxide radical will compete with the peroxide's curing ability and must be taken into account. Among these are p-phenylene diamine antioxidants or PPD's; phenolic resins; aromatic and to some extent, naphthenic oils (paraffinic oils and most esters are acceptable for peroxide curing). You can use small amounts of these materials, but more peroxide must be added to get back the same crosslink density. Large amounts of peroxide are not reasonable to use. However, in unsaturated polymers, the peroxide need is substantially less; such that some usage of aromatic oils or resins can be tolerated.

Antioxidants have to be paid some attention when peroxide curing. After all, the reason for antioxidants being present in rubber is to soak up radicals generated by oxidation. And antioxidants should be included in peroxide cures as it will improve aging particularly at, or above, 150°C (rule-of-thumb is no antioxidant is needed to pass 125-135°C aging in EPDM's with peroxides but above that, AO's will help). The best antioxidant for peroxide cures is polymerized dihydroquinoline (Akrochem Antioxidant DQ). An even better antioxidant combination for peroxides is DQ in synergism with Antioxidant 58 or 60 (respectively, ZnMMBI and MMBI). If color is important, replace the DQ with Antioxidant 358-SWC (p-TBp14) or Antioxidant 1010 (the well-known tetrakis phenolic). These will boost non-black peroxide's heat resistance.

Acidic pH problems: Air-floated clays (so-called soft and hard clays) have a pH of around 4.7 and if high loadings are used, can kill a peroxide cure. Compounders trying to reduce cost of a non-black, peroxide-cured rubber will use these acidic clays and find their cure curves flat-lined. The acid will alter the normal opening of a peroxide and the preferred radical is not formed. Few, if any, crosslinks are formed. To avoid this, use a water-washed clay with a neutral (6-8) pH. Other ways of dealing with acidic clays and peroxide cures are to add TEA (triethanolamine) and MgO to the mix to offset the pH problem.

Exposure to Oxygen During Cure: If air is present (in an oven-cure or flash in a molded part) during a peroxide cure, oxygen will react with the elastomer radicals formed and depolymerize the rubber. The result is a sticky, undercured product. There is no magic additive that will easily get rid of this problem. You can reduce the extent of the problem by using a high level of co-agent along with a low level of peroxide. The idea is to form a minimum number of radicals but to capture those radicals with the co-agent and turn them into a crosslink. By adding a co-agent like TAC (triallyl cyanurate), the number of crosslinks grows enormously as the radicals formed are "directed" by the co-agent to form crosslinks rather than re-arranging and scissioning the polymer chain.

Peroxide Influence on Colorants: Peroxides can destroy certain color pigments. The result can vary from a weakening of the color all the way to a total burnout. Sometimes there is only a minor color alteration and the formula color can be controlled. Other times a whole new colorant has to be used. Pigments Red 38, Orange 13, and Violet 23 are susceptible with Red 38 being most vulnerable. On the other hand, fluorescent pigments will not develop their full, bright colors *unless a peroxide cure is used*. Sulfur reacts adversely with fluorescents and results in a very dirty fluorescent color.

Polymers that Peroxides Don't Cure: Butyl, ECO and PP will not peroxide-cure. In fact, butyl is chain-scissioned and peroxides are sometimes used to peptize the polymer. The halobutyls stabilize the radical enough to allow peroxide cures. For ECO, an additional monomer is grafted into the backbone to allow it to be peroxide-cured.

Peroxide-Cured Performance “Problems”

Sometimes compounders avoid using peroxides because of certain functional deficiencies that peroxide has that sulfur doesn't (or sulfur exhibits less of the problem). Here are a few of the things to watch out for in peroxide cures and some suggestions to counter the problem.

- **Poor Hot Tear:** Because peroxide cures with short, often high modulus crosslinks, parts are sometimes hard to demold without tearing. First, make sure the tearing is due to actual rubber tear and not sticking in the mold. Peroxides will sometimes stick (often, the co-agent is a big factor) in a cavity and tear upon demolding. There are excellent semi-permanent mold releases available from Akrochem to aid peroxide molding. Also, internal compound release aids can be added.

If hot tear really is an issue, there are a few things you can try. Reduce the peroxide to the minimum needed to get the required physical properties. Add high surface area silicas to the formula. With silica addition, do not add oil to compensate for durometer; tear will get worse with more oil. Reduce other fillers, preferably the least reinforcing ones.

- **Flex-cracking resistance:** Just as single sulfur crosslinks flex poorer than multiple sulfur links, a peroxide-generated crosslink limits polymer flexibility. Flexing of a peroxide cure is difficult to match a sulfur cure but the better heat aging is sometimes desirable. Minimizing the amount of peroxide used to just the minimum needed will help flex. Recent studies have shown metal methacrylates as coagents to provide a flexible crosslink that flexes surprisingly well.
- **Scorchy stock at curing temperatures:** Since you cure at temperatures meant to open the peroxide, there is typically little scorch remaining when trying to fill a mold cavity. A slight delay is needed but going to a higher temperature peroxide may not be economically feasible, i.e., longer T90. One way to delay the onset of crosslinking is to soak up the first radicals formed with a highly active antioxidant like BHT. 0.25 to 0.50 phr of BHT will delay the scorch but also the T90 cure time.

Other Peroxide Issues

Coagents: Most compounders know that coagents are used with peroxides. But I find many incorrect usages of co-agents. Co-agents make peroxides more efficient. They trap the peroxide radical formed and convert the radical to a crosslink. Without a coagent, many more undesirable reactions occur limiting the desirable polymer-to-polymer crosslink. Here are a few tips for coagent usage:

- Highly unsaturated polymers (NBR, SBR, NR, PBD) typically don't need a coagent or need very little in demanding applications. The presence of the double bonds is, in essence, a built-in

co-agent. The allylic carbon (that is next to the double-bond carbons) is an excellent site for a radical that results in a crosslink. Coagent use in unsaturated polymers may be useful if an acrylic resin is used at high levels in order to both harden the end rubber as well as plasticize the uncured rubber. Sulfur is sometimes added at 0.25 phr to peroxide-cured unsaturated polymers to improve the elongation, tensile, and tear of the product (watch out for occasional strong odors from this combination). Do not add sulfur to peroxide-cured, saturated polymers. The set and heat-resistance will suffer when sulfur is added.

- Don't use TAC, TAIC, or polybutadiene in unsaturated polymers like NBR or SBR. They will have little or no effect on the peroxide cure. Think of them as double-bond donors, which are fine in a saturated or nearly saturated (EPDM, CPE, HNBR, etc.) polymer system. But in NBR and SBR, there are plenty of double bonds already, so the co-agent adds nothing to the mix. Use acrylics or maleimides with unsaturated polymers.

This Solution insert reviewed many well-known pieces of literature concerning peroxides. Most of the literature typically concentrates on just one or two of the many subjects covered here. Better-known information was presented while including some lesser-known compounding tips or suggestions. Akrochem hopes this piece of literature will be helpful and kept in safe keeping for reference in your peroxide compounding work.



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