THE UNINTENDED CONSEQUENCES OF TRACE IMPURITIES IN POLYMER PRODUCT DEVELOPMENT

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Introduction

The chemistry of many types of polymer-based systems (adhesives, coatings, plastics, etc.) is often tightly controlled and orchestrated by the presence or absence of seemingly minor trace-components. Ideally, a polymer chemist or formulator attempts to precisely specify and control the concentrations and structures of each and every one of these components. In reality, however, trace-components are often inadvertently and unknowingly added to polymer formulations. They are usually introduced through the incorporation of commercially available raw materials, which are typically used to create formulated products. For example, a commercial monomer may carry free radical scavengers for shelf stability; extruded polymer pellets may come with antioxidants; and certain polymers may carry trace metal ions (residual catalysts or derivatives thereof). The uncontrolled presence of trace additives like these can sometimes lead to a cascade of unintended consequences.

The structures and concentrations of trace ingredients typically vary from manufacturer to manufacturer. Thus, even a seemingly benign change in the commercial source for a raw material can have a dramatic impact on end-use properties and product performance. In cases involving curable adhesives or coatings, the chemical nature of these additives may differentially affect shelf-life and efficacy (i.e., the heat of reaction, green strength, cure rate, shear strength, tensile strength, peel strength, burst strength, etc.). Under the best circumstances, the property-impact of a trace additive might fall within the acceptable window of "normal" variability for a process or product. A trace additive might even be the primary contributing factor behind the inherent breadth of a "normal" operating window. However, under the worst circumstances, a small variance in the concentration or chemical structure of a trace additive could have a significant impact on product properties. Thus, ignorance of such additives and their effects could expose a company to the potential liability of a catastrophic product failure.

Trace components – underlying factors behind "normal variability"

In general, any compositional change that affects the rate of polymerization and/or the rate of chain termination can have a dramatic impact on the physical properties of thermosetting formulations – both during the building of green strength, and after the cure reaction is complete.

When a thermosetting formulation is initially designed, the formulator may add known concentrations and types of initiators and inhibitors to control the overall rate of polymerization, and the shelf-life of the product. The concentrations of these additives are usually tightly controlled to achieve optimum product performance. In addition, the formulator may specify other key ingredients (i.e., monomers), several of which may already contain inhibitors that have been added by suppliers. The presence of these additional inhibitors (together with derivatives that have formed as a result of the supplier's processes) may also contribute to the observed rate of polymerization of the formulator's final formulation. Thus, any variance in the supplier's additives will have a direct impact on the efficacy of the final formula.

Compositional changes may happen by design, but more often than not, they occur when a formulator sources a key ingredient from a new supplier, or when he/she fails to know what attributes need to be specified from existing suppliers. For example, when sourced from different suppliers, a key monomer ingredient might contain different levels and types of trace additives (compounds that are purposely added such as inhibitors, stabilizers, etc.); trace impurities (i.e., contaminates whose presence may or may not be known, including cross-contaminates from prior manufacturing campaigns, from shipping, from storage, etc.); and chemically transformed trace additives (i.e., trace compounds such as inhibitors of known chemical composition that undergo chemical transformations during the lifespan of the monomer). Compositional variations of these types may affect the cure-chemistry and hence the final physical properties of any addition-polymer system.

The polymer applications literature is full of examples of curable thermosetting systems whose end-use properties can be easily influenced by minor compositional variations. A few examples include acrylates for coating and ophthalmic lens applications, as well as cyanaoacrylates for tissue adhesive applications. In each of these examples, a seemingly simple variation in a supplier's manufacturing procedures (a variation that may be unknown to the formulator, or a variation that may be unrecognized as important by all parties) may have a dramatic impact on the final physical properties of the formulator's finished product. Moreover, the sourcing of a seemingly identical raw material from an alternative supplier may have an unanticipated and sometimes devastating impact on performance. The following discussions will provide examples to illustrate both the chemistry and the importance of variations that may arise as a result of manufacturer-to-manufacturer differences in trace impurities, trace additives, and chemically transformed trace additives.

Cross-contamination and the potential impact of substituting raw materials from different suppliers

There are many compositional and manufacturing variables that are known to influence the cure rate, shelf-life, and efficacy of polymer products and adhesives. In the scheme of things, switching to a nominally "identical" commercial ingredient from an alternative supplier might seem like a minor change. The more the formulator knows, the more likely this is to be true. However, a seemingly innocuous change such as this can sometimes lead to uncontrolled variations in the compositions and levels of trace impurities, trace additives, and chemically transformed trace additives, all of which can have a significant impact on physical properties, cure rates, shelf-life, and efficacy.

For example, samples of a type of monomer from two different suppliers may appear to be nominally identical, but they may actually contain different types and levels of cross-contaminates. If cross-contaminates exist, their structures will likely be unique to each manufacturer, and their identities will depend on specific manufacturing procedures, and on the nature of the other monomer products that are produced at the manufacturer's facility. Therefore, if left unchecked, the substitution of one monomer source for another may lead to differences in cross-contaminates, which in turn may affect polymerization rates and physical properties in end-use formulations.

In one example, the rate of polymerization and the ultimate physical properties of a free-radically cured polyurethane acrylate coating were observed to vary when the coating composition was exposed to certain types of acrylic monomers [1]. Specifically, the exposure of the uncured coating formula (the formula was predominately comprised of aliphatic acrylic esters) to an aromatic acrylic ester was reported to decrease the rate of polymerization. The slower rate of polymerization was used to induce differential shrinkage along the z-axis of the coating, which in turn affected the specular reflection characteristics (gloss) of the finished product. Although this phenomenon was controlled for the benefit of achieving a desired property (i.e., controlled gloss was one object of the invention), it is clear that if left uncontrolled, the presence or absence of small amounts of such monomers could have had deleterious effects on the end-use properties.

In another example, the rate of polymerization and the ultimate physical properties of a free radically cured ophthalmic lens formulation (the formula was also predominately comprised of aliphatic acrylic esters) were controlled via the incorporation of aromatic acrylic monomers [2]. The inventors in this application recognized that the polymerization temperature was critical to the achievement of desirable end-use properties, and that the polymerization temperature was affected by the degree of exotherm, which scaled with the rate of the reaction. They found that they could slow the rate of polymerization by incorporating an aromatic acrylic monomer into their formulation. The monomers that were used in this patent were all obtained from the same supplier. As in the prior example, this phenomenon was controlled for the benefit of achieving a desired property. However, it is clear that if left uncontrolled, the presence or absence of small amounts of such monomers could potentially have had deleterious effects on end-use properties.

If the inventors in these applications had no knowledge of the effects of aromatic monomers on their cure rates, the potential for product variability would have been high, particularly if cross-contamination were to occur either in the supplier's location, or in the end-user's location. Cross-contamination can occur as a result of transfer procedures that are used when a manufacturer transfers materials (via pipes, hoses, pumps, etc.) from its inventory to a reactor, or from a reactor to storage vessels (i.e., totes, drums, truck, etc.). When a company manufactures multiple varieties of monomers (as some do), its reactors are often used to process multiple batches of different products. The length of a production campaign (the number of batches) for any one product typically depends on commercial demand. If demand is high for a certain monomer, it may be economically justifiable to dedicate a reactor to that product. In such a case, the potential for cross-contamination would be minimized. However, in many cases, a single reactor is often used to produce multiple products, in which case the potential for cross-contamination arises both before and after each production changeover.

In some cases, products are scheduled for sequential campaigns based on their mutual compatibility with one another. This is done to minimize the amount of lost production time that would be required for extensive clean-ups during changeovers. If the monomer is intended to be sold as a "general purpose" monomer, a certain degree of cross-contamination may be tolerated for the sake of economics. In many cases, the formulators (those who purchase the monomers) may unknowingly end up formulating their products with monomers that contain varying levels and types of cross-contaminates.

In cases where the formulator desires a specific rate of polymerization (i.e., for a coating or adhesive application), he/she may adjust the initiator or inhibitor levels accordingly to compensate not only for the reaction chemistry of the nominal monomer, but also for the chemistry that is unknowingly imparted by the cross contaminate (i.e., a cross-contaminating monomer may have a reactivity ratio that slows the overall observed rate of polymerization, or it may serve as a chain transfer agent which changes the final molecular weight). Hence, unbeknownst to the formulator, he or she may end up adjusting the formula to compensate for the presence or absence of cross-contaminates, which may or may not be present in the next batch of monomer product that is procured by his or her company. Consequently, if no formulation changes are made to compensate for these differences (i.e., one might have to change the initiator level), then the resulting performance of the polymer system might be drastically altered.

Trace additives: components that are intentionally added to industrial grade monomers

Unlike cross-contaminates, certain trace additives such as inhibitors and stabilizers are intentionally added by the manufacturer. These compounds are usually added both during the production of the monomer (pre-addition for in-process stability), and after the manufacturing process (post-addition for shelf stability).

"Inhibitors" such as quinones are typically added during the manufacture of acrylic ester monomers so as to prevent premature radical polymerization reactions between the acrylic moieties (acrylic esters are often formed via a thermally induced esterification reaction between an acrylic acid compound and an alcohol). During this process, the chemical composition of an inhibitor can actually be transformed via a series of side reactions either with oxygen, with acrylic moieties, or with other sources of free radicals that may be present (this topic will be discussed in more detail in the next section).

The chemical compositions and reactivities of transformed inhibitor species are usually not known, but they generally retain their ability to influence reaction rates. Given that different manufacturers employ different conditions during the production of a monomer (i.e., different reaction temperatures, different reaction times, different atmospheric conditions, different head space volumes, etc.), the chemical nature of these transformed inhibitor species will likely vary from manufacturer to manufacturer – even when the nominal composition of each manufacturer's primary monomer is the same. Thus, a nominally identical monomer that is obtained from two different suppliers may produce finished formulations with completely

different rates of polymerization. This difference would likely lead to unanticipated variations in the efficacy of a formulated product.

Like the pre-addition inhibitors, post-addition inhibitors are also sometimes added to guard against similar types of unwanted side reactions. These compounds are usually added for the purpose of enhancing the shelf-life of a monomer, or for controlling an end-user's induction period (if the end-user has specified this). The chemical transformation of these additives will occur over longer periods of time, typically throughout the storage history of the monomer product. The chemical nature and concentrations of these transformed species will depend on the storage conditions (i.e., storage time, storage temperature, atmospheric exposure to oxygen, atmospheric exposure to moisture, chemical nature of the storage container, shipping conditions, etc.). Given that storage histories will likely vary from manufacturer to manufacturer, and from facility to facility, it follows that even a simple change in storage conditions can result in a finished formulation with altered cure characteristics.

Although it is possible in theory to specify the compositions and concentrations of post-addition inhibitors (assuming that one is skilled enough to know which additives need to be specified, and which analytical procedures would be required to insure that their concentrations fall within specified limits), it is usually difficult to specify the chemical nature of pre-addition inhibitors, primarily because this knowledge is often considered to be proprietary and specific to a given manufacturer's process. Moreover, it would be nearly impossible to specify the chemical compositions of transformed additives, mainly because the in-process chemical transformations will inevitably vary from manufacturer to manufacturer.

Of equal importance, the impact of a transformed trace-additive on cure-chemistry may go completely unrecognized by both the monomer manufacturer and by the end user. Moreover, the implementation of analytical protocols for the detection of pre-addition and post-addition trace additives may not be sufficient to facilitate the detection of their chemically transformed counterparts, primarily because the identities and spectroscopic characteristics of these species are typically unknown and highly variable. To further complicate the matter, trace additives from a supplier's monomer may also be prone to undergo chemical transformations after they have been incorporated into a finished adhesive formulation. This could also alter the cure characteristics of the adhesive in potentially unpredictable ways. Thus, to reiterate, a nominally identical ingredient from two different commercial suppliers may actually contain different types and levels of trace additives and transformed trace-additives, any or all of which could influence the cure-chemistry, and hence the shelf-life and efficacy of the entire formulation.

Inhibitor reaction chemistry

As noted in the prior section, inhibitors are added to acrylic and vinyl monomers to prevent premature polymerization reactions during manufacture and storage [3]. Many inhibitors perform this function by reacting with oxygen and carbon-centered radicals to form stable free radical intermediates (their stability is attributed to resonance stabilization, and to steric hindrance from bulky aromatic substituents – depending on structure) [3,4]. In turn, these intermediates are not capable of initiating free radical polymerizations by themselves. However,

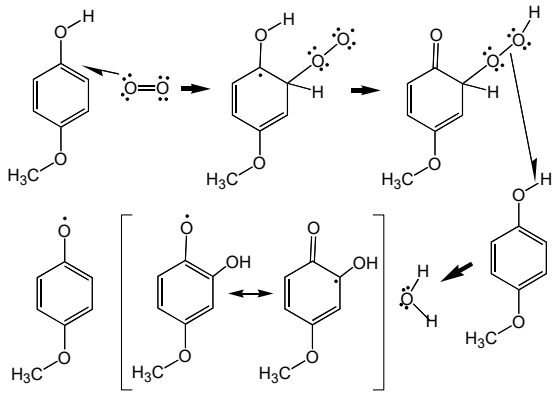
inhibitors do influence the course of polymerization reactions, particularly at the onset where they may react with initiators and/or with growing chain ends to inhibit chain growth.

Independent of whether inhibitors are knowingly used (by design), or unknowingly used (by default), their presence or absence can influence the physical properties of resultant polymers. Depending on the nature of the polymerization reaction (i.e., the type and level of initiator, the presence or absence of oxygen, the source of initiation, etc.), the presence or absence of inhibitors may affect molecular weight distributions, cross-link densities, shrinkage, gloss, color, strength, modulus, impact resistance, and even adhesion.

Inhibitors for acrylic monomers are typically chosen from a broad class of hydroxyaromatic compounds [3], including compounds like hydroquinone (HQ), 4-methoxyphenol (MEHQ), butylated hydroxytoluene (BHT), di-tertbutylhydroquinone, tertbutylhydroquinone, and others. In the presence of oxidizing agents (i.e., oxygen, carbon-centered and oxygen-centered free radicals, certain metal ions, etc.), these compounds can be reversibly oxidized to yield quinones [3,4,5,6,7].

Figure 1 illustrates a potential reaction pathway involving 2 equivalents of MEHQ and atmospheric oxygen to yield two types of resonance stabilized, radical intermediates.

Figure 1



Radical intermediates like those shown in Figure 1 are eventually terminated through several possible coupling and/or disproportionation reactions, including reactions with growing radical chains, reactions with other quinone/hydroquinone radicals, reactions with oxygen, or reactions with monomeric acrylic radicals [3].

Quinones (the oxidized forms of hydroxyaromatic compounds) are strong chromophores, and they are often responsible for the discoloration of monomers (i.e., yellowing). These compounds are more efficient at quenching chain polymerization reactions than their reduced-state, hydroquinone counterparts [3,8]. Consequently, the inhibition efficiency of hydroxyaromatics can be greatly altered by the presence of oxygen. Although the mechanisms are not completely understood, oxygen can play at least two roles in inhibition chemistry. In one case,

hydroxyaromatics can be oxidized to yield quinones, which then preferentially react with growing polymer chains [3]. In a second case, a growing radical chain can react with oxygen to form a peroxide, which can then react with a hydroxyaromatic compound to yield a hydroxyaromatic radical and a fairly stable hydroperoxide [3]. Note that in the later case, the hydroxyaromatic radical may go on to react in other ways, including: 1) through coupling reactions with monomeric, dimeric, oligomeric or polymeric radicals to yield ethers (via reaction with the oxygen centered radical); 2) through coupling reactions with other similar radicals to yield quinones (via reaction with the aromatic ring); or 3) through methyl hydrogen abstraction and disproportionation with growing radical chains [3].

Quinones can also interact with hydroquinones to form stable charge-transfer complexes [7]. Thus, it is sometimes important to control the molar ratio of the two species. In addition, quinones and hydroquinones can participate in redox reactions with certain metals. Thus, the chemical nature of a metal transfer container is also an important consideration when dealing with certain types of monomers.

From these discussions, it should be apparent that the transformation products of inhibitors are affected by a variety of process and storage-related variables. It is therefore expected that the composition of a nominally identical monomer from two different commercial suppliers may contain different types and levels of trace additives and transformed trace-additives. These differences may impact the cure-chemistry, the shelf-life, and the efficacy of comparative formulations that contains them.

Case Study: The Effects of Trace Additives (and Transformed Trace Additives) on Cyanoacrylate Chemistry

Like other types of acrylic-based curing systems, the end-use performance characteristics of cyanoacrylate soft tissue adhesives are potentially vulnerable to minor variations in composition [9]. As noted earlier, a simple supplier substitution for a key monomer ingredient could result in an unanticipated change in the polymerization rate (i.e., due to differences in the types and concentrations of cross contaminates, trace additives, and chemically transformed trace additives).

As with other types of acrylates, the cure characteristics of cyanoacrylates are susceptible to variations in ingredients that affect free radical reaction chemistry. However, in addition, the cure-chemistry of cyanoacrylates is also susceptible to variations in ingredients that affect anionic polymerizations (cyanoacrylates cure by both free radical and anionic polymerization mechanisms).

As noted by Azevedo [10], cyanoacrylates are purposely formulated with two principal groups of stabilizers: those that prevent free radical polymerization, and those that inhibit anionic polymerization. According to Wojciak [11], several protic and/or Lewis acids are useful as anionic polymerization inhibitors. Wojciak also noted that certain impurities (the nature of which was not specified) should be avoided since they may potentially catalyze the hydrolysis of cyanoacrylate esters to yield carboxylic acids, which in turn would inhibit polymerization and have a detrimental impact on the physical properties of the cured adhesive. Like Azevedo,

Wojciak also noted that cyanoacrylates are also formulated with free radical scavengers of the phenolic type, such as quinone, hydroquinone, t-butyl catechol, p-methoxy-phenol, and others. Importantly, the preferred inhibitor of Wojciak was hydroquinone at a level of about 0.02% to about 1.0% by weight.

It is interesting to note that both inventors, although skilled in the art, have made a distinction between compounds that are capable of imparting free radical stabilizing functions, and those that are capable of imparting anionic stabilizing functions. This distinction implies that those skilled in the art of formulating cyanoacrylate adhesives may not necessarily realize that certain free radical stabilizers may also function as protic acids. In fact, hydroxyaromatic compounds of the type specified by Wojciak (hydroquinone is his case) are actually weak acids [7]. Furthermore, the pKa's (and hence reactivity) of these types of compounds would vary depending upon the nature of the chemical transformations that the compounds undergo when they are incorporated into the monomers (i.e., the reactivity of a hydroxyaromatic compound can be altered by aromatic substitution).

Thus, aside from the potential variability that is possible via free-radical reaction pathways (as was discussed in prior sections), the polymerization rates of cyanoacrylates adhesives, by virtue of their ability to polymerize anionically, are susceptible to variations in the types and concentrations of protic acids that are incorporated into the adhesive formulation. Ironically, certain free radical inhibitors may also serve as protic acids, and as such, they have the potential to perform additional chemistry in cyanoacrylate systems (the acidities of these compounds will scale with their anionic inhibition potentials). Furthermore, it follows that the relative acidities of these compounds would depend on their chemical structures (i.e., both the structures of trace additives as well as the structures of their transformed counterparts).

The following hypothetical example illustrates how the presence or absence of these structures can have an unanticipated impact on end-use performance. Let's assume that Company A's monomer was stored in a warehouse for six months before it was procured by a formulator. Furthermore, during the six-month storage period, a fraction of the hydroquinone inhibitor molecules have reacted with atmospheric oxygen to yield quinones. By the time the formulator receives the monomer it will contain some ratio of the two species – call it x. Suppose that the formulator prepares his/her adhesive formula with this aliquot of Company A's monomer, and that the formula meets its specified property targets. The formulator then sells a large amount of adhesive and now needs to produce a new batch. Company A no longer makes the monomer, so the formulator procures the same monomer from Company B. Company B uses the same procedures and the same inhibitors as Company A (this is not likely, but we'll assume it is true for this example). The formulator needs to make adhesive quickly, so he/she requests immediate shipment. Company B ships the product within 2 days of its manufacture. Consequently, and unbeknownst to either party, there is a much higher level of hydroquinone in this monomer than in the monomer from Company B – not because more was added, but because less has been oxidized to yield quinone. Remember, a higher level of hydroquinone equates to a change in the protic acid concentration, because hydroquinone is itself a weak protic acid. The formulator now makes the adhesive, packages it, and ships it to distributors. A customer purchases a quantity of the new batch, and then discovers that the adhesive does not work – it does not cure quickly

enough, it has poor green strength, and it cracks before it sets. Does this sound like a problem that you have experienced?

Conclusions

The physical properties of polymer products, particularly those that cure through addition polymerization mechanisms (i.e., free radical, radical-cation, and anionic polymerization mechanisms) are generally susceptible to seemingly minor, yet inordinately complex, compositional variations that can arise (either by design or by chance) from even the simplest manufacturing changes (i.e., from a change in the source of a raw material, or from a change in a manufacturing process procedure, etc.). For example, a simple change in the supplier of a key monomer ingredient can lead to a cascade of unforeseen chemical compositional changes, any one of which may impact the rate of polymerization, the shelf-life, and the end-use properties (efficacy) of thermosetting addition polymer systems.

Each supplier of a nominally identical product has its own unique set of manufacturing procedures, raw material sources, additives, storage conditions, and shipping conditions. In turn, each of these factors has the potential to influence the chemical structures and concentrations of minor compositional components, including trace additives (i.e., inhibitors, stabilizers, etc.); trace impurities (i.e., contaminates from prior manufacturing campaigns, from shipping, from storage, etc.); and transformed trace additives. The concentrations and chemical identities of these minor components will likely vary from manufacturer to manufacturer, even when the primary components are nominally the same. Moreover, even if a formulator were able to specify the tolerable limits and structures of specific trace additives, it is unlikely that he/she would ever have control over the compositions of chemically transformed additives, mainly because the nature of these species would be specific to both the monomer's process history, and to the manufacturer's synthetic procedures, which are usually proprietary.

In some end-use applications, the windows of tolerance for physical property and cure rate variations may be relatively high. In such cases, variations that are induced by minor manufacturing changes may be insignificant. However, in many applications (i.e., those discussed in this paper), the windows of tolerance for cure rate and physical property variations are either small or unknown. In these cases, it is critical to scrutinize all manufacturing changes before they are implemented.

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