

CHEMICAL COMPATIBILITY OF POLYMERIC MATERIALS

Some Simple Guidelines

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THE AUTHORS PRESENT here some principles for specifying general classes of polymers to be used in contact with acids, bases, oxidants, certain other common antagonists, and specific solvents. These principles are appropriate for an undergraduate chemical engineering general course in materials, where extensive detail and discussion about a myriad of chemical reactions and polymer variations cannot be treated.

Many chemical engineers face the problem of selecting equipment made from or lined with polymers, and the compatibility of the equipment surface with the chemical to be handled is a significant consideration. It is obviously important to know whether chemical reactions will occur between the chemical and the polymer walls and whether solvent effects will cause polymer swelling, dissolution, or alterations in mechanical properties. Yet, our chemical engineering department, like many others, can afford only one re-

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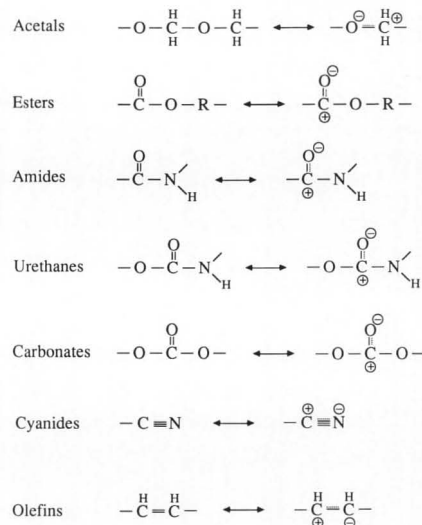
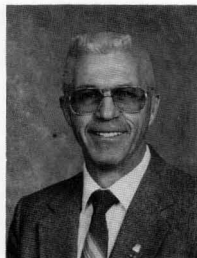


FIGURE 1. Dipole resonant forms in some common classes of polymers.

quired undergraduate course in engineering materials. The course is based on one of the popular general textbooks on engineering materials which covers a wide spectrum of topics including metallurgy, ceramics, semiconductor materials, and polymers. However, the polymer treatment is limited and focuses largely on forming and molding the polymers (*i.e.*, mechanisms and kinetics of polymer formation and rheology of polymer melts) and on physical properties. Thus, we felt that supplementary coverage was necessary.

Our goal is to explain polymer-chemical compatibility, as much as possible, in terms of unifying principles. The alternative would be to memorize extensive information about the very large number of specific reactions encountered between nearly-infinite combinations of polymers and chemicals. Even with the application of some central principles, the number of exceptions and variations would require significant discussion and tabulation. Such a treatment is attempted in a few books dedicated to the description of polymers

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(see references 1-3 for example), but general textbooks about engineering materials can hardly begin such coverage. Further, while the vendors of polymer equipment provide "technical specifications" about chemical compatibility, those specifications are typically tables of chemicals matched against their products with empirical recommendations such as "good," "fair," and "not recommended." Other tables specify the maximum usable temperature recommended for each chemical-polymer pair, but do so also in an empirical fashion. A further complication is that each manufacturer adds specific agents to its polymer formulations to modify the properties of the final product, thereby adding even greater uncertainty to the application of general principles. However, chemical engineers, with their background in organic and physical chemistry, should know some basic rules which will allow at least preliminary selection of polymer types and evaluation of vendor claims for a particular application.

This paper summarizes some basic principles for predicting relative chemical attack from acids, bases, oxidants, and certain other common antagonists and also for predicting relative solvent effects in polymers. This material is presented in two or three lectures in our chemical engineering materials course after reviewing with the students the structures and names of common polymers, discussing structural characteristics (density, crystallinity, *etc.*), and comparing the properties of thermoplastic and thermosetting polymers. The brief treatment described below provides some understanding (as opposed to memorization) which will allow preliminary evaluation of polymer equipment for handling chemicals and which

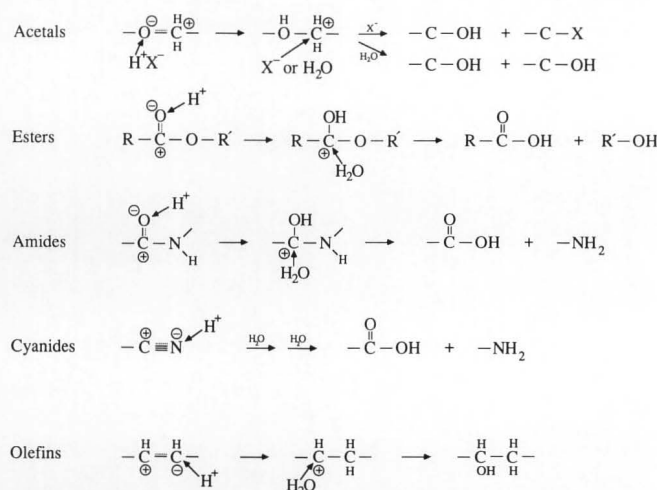


FIGURE 2. Examples of the attack of dipolar resonance forms of polymers by acids.

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will also serve as a framework upon which information about specific reactions and cases can later be added.

UNDESIRABLE CHEMICAL REACTIONS

Acid-Base Attack

The susceptibility of many polymers to attack by surrounding acids and bases is related to the degree of "charged dipole formation within the polymer structure. A review of atomic structure will convince the student that the relative electronegativities of C, N, and O are in the order $O > N > C$. This helps to explain that the combination of these elements in a polymer structure results in the distortion of electron clouds away from carbon atoms, with a resultant dipole as one resonant form (Figure 1). The student should also be aware, however, that even olefinic double bonds have resonant dipole forms. Non-oxidizing acids generally attack by attraction of the H^+ ion to the negative side of the dipole resonant structure and formation of a complex. The unstable complex then further reacts with the negative ion of the acid or with water (in the case of aqueous solutions) to split the polymer chain at that point (Figure 2). The attack of a polymer by a base proceeds in a similar fashion, with the initial attraction of the OH^- and complex formation at the positive site of the resonant dipole and then subsequent resolution of the unstable complex (Figure 3).

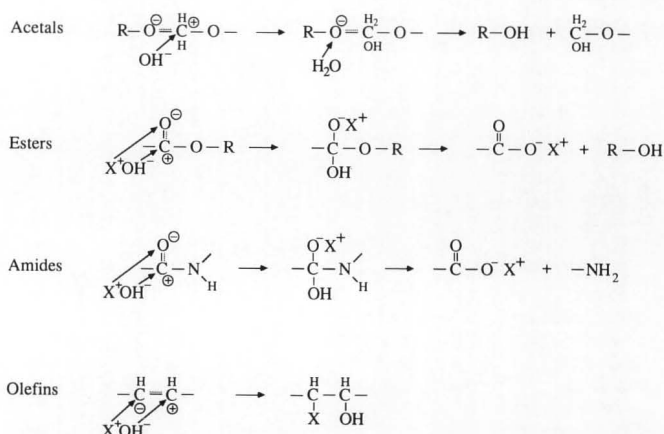


FIGURE 3. Examples of the attack of dipolar resonance forms of polymers by bases.

In our materials course, the emphasis is not so much on the reaction mechanisms as on the principle that more polar resonant forms will cause greater attack in general. Hence, polyamides (*e.g.*, nylon), olefins (*e.g.*, natural rubber and styrene butadiene), and polyesters (*e.g.*, polymethylmethacrylate, PMMA) will be relatively susceptible to acid-base attack. Examples include the partial hydrolysis of poly(methylacrylamide) in base to the free acid form, the conversion of acetals by alkali and acid to produce alcohols, the cleavage of polyester chains by hot alkali treatment, *etc.* Polyurethanes are not quite as susceptible, because the urethane nitrogen atom stabilizes the resonant form and reduces the polarity. At the other extreme, polyethylene (PE), with no polar resonance, will generally not be attacked by acids and bases (which explains why acids and bases can be stored in polyethylene containers).

Of course, very strong acids and bases (especially oxidizing acids) can attack even polyethylene or polypropylene (PP) by directly attacking the C-H bonds, especially the weaker bonds on the methyl side groups of the PP. Where these very strong reagents are to

TABLE 1
Relative Rates of Oxidation Versus Structure [4]

<u>Structure</u>	<u>Relative Rate of Oxidation</u>
$\begin{array}{c} \text{CH}_3 \\ \\ (-\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2-) \\ \uparrow \qquad \qquad \qquad \uparrow \end{array}$	10
$\begin{array}{c} \text{CH}_3 \\ \\ (-\text{CH}_2-\text{CH}-\text{O}-) \\ \uparrow \end{array}$	9
$\begin{array}{c} \text{CH}_3 \\ \\ (-\text{CH}_2-\text{CH}-) \\ \uparrow \end{array}$	6.5
$\begin{array}{c} \text{CH}_3 \\ \\ \text{O} \\ \\ (-\text{CH}_2-\text{CH}-) \\ \uparrow \end{array}$	2.8
$\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{O} \\ \\ \text{C}=\text{O} \\ \\ -\text{CH}_2-\text{CH}- \\ \uparrow \end{array}$	1.4

be encountered, the PE chain is used with fluorine substituted for both of the hydrogens on every other carbon atom (polyvinylidene fluoride, PVDF) or on every carbon atom (polytetrafluoroethylene, PTFE) to reduce such attack. The electron-rich fluorine acts by stabilizing the polar resonant forms.

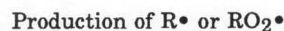
Chlorine is also used for a replacement for hydrogen on every other carbon, either substituted for one of the hydrogen atoms on that carbon (polyvinylchloride, PVC) or for both hydrogen atoms of that carbon (polyvinylidene chloride, PVDC). However, the larger chlorine atom creates some steric stress because of its size and has a greater tendency to be removed. Hence, its resistance to acid-base attack is limited.

Oxidation

Synthetic polymers are oxidized by oxygen in the atmosphere, particularly in the presence of light (in the absence of light the reaction is relatively slow) and by liquid oxidants, such as permanganate, peroxides, epoxides, oxidizing acids (*e.g.*, nitric, sulfuric, and chromic), and even water. The resulting changes in polymer chemistry yield a more brittle polymer with corresponding loss of strength.

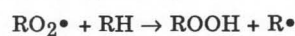
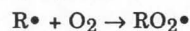
Oxidation of polymers can be generalized into the following reactions (4):

Initiation:

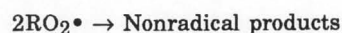


(where R is some portion of the hydrocarbon chain)

Propagation:



Termination:



Particularly susceptible locations include carbon atoms which are 1) adjacent to double-bond carbon atoms (polymers such as polyisoprene or polybutadiene that contain unsaturated linkage are susceptible to attack by ozone as well as oxygen), 2) connected to ether oxygen atoms, and 3) tertiary carbons (Table 1, poly(vinylchloride) is very susceptible to oxidation, and, of the major polymer systems, polypropylene is more susceptible than polyethylene).

Oxidation can be reduced by adding inhibitors or by altering polymer structure. UV screeners are

added to all polymer formulations for equipment use. The substitution of fluorine in place of hydrogen (PVDF, PTFE, etc.) significantly reduces susceptibility to oxidation, because the electronegative fluorine causes charge repulsion of the oxidant. Also, polystyrene, with its electron-rich aromatic ring to protect potential oxidation sites, is less susceptible to oxidation than is polyethylene.

Special Addition/Substitution Reactions

Several chemical agents add to the double bonds of unsaturated polymers, and some may even attack saturated compounds. The most common of these are:

CHLORINATION: Chlorine gas, hydrochloric acid, chlorosulfonic acid, and phosphorus-containing chlorides are among the agents which will cause chlorine attack of polymers. Not only will chlorine be added to unsaturated bonds (e.g., conversion of PVC to a dichloride), but polyethylene can also be chlorinated. Chlorination of natural rubber involves a complex series of addition, substitution, crosslinking, and cyclization reactions.

HYDROGENATION: Polymers with unsaturated bonds may be subject to hydrogenation, particularly at high temperatures in the presence of high-pressure hydrogen gas. For example, polyisoprene can be hydrogenated to yield poly-isopentane, and polystyrene can be converted to poly-vinylcyclohexane.

NITRATION: Nitric acid is the most common source of this attack. Polymers with aromatic groups are susceptible to nitration reactions on the aromatic ring. For example, polystyrene in the presence of both nitric and sulfuric acids yields the corresponding poly(nitrostyrene). With aliphatic polymers, the nitro group attaches to the chain or to a suitable substituent on the chain.

Many additional specific reactions could be included, but only a few of the more common ones are described, and the students are warned that they must do their own homework on the job for each application which presents itself.

High-Temperature Effects

In addition to the fact that high temperatures cause softening (loss of strength) of polymers, organic polymers are unstable at temperatures above 150-200 degrees centigrade and undergo some chemical reactions. The kinds of reactions include:

ISOMERIZATION: Polymers containing certain side chains such as cyano(nitrile), chloro, carboxylic acid, or ester groups, when subjected to high temperatures, undergo isomerization to yield new products. A classic example is the cyclization of natural rubber to produce cyclohexane rings in the polymer chain. (This reaction is exploited by the Goodyear Tire and Rubber Com-

pany to produce Pliolite rubber using chlorostannic acid as a reagent.)

DEPOLYMERIZATION: High temperatures can cause depolymerization to yield the monomer or chain cleavage to yield low molecular weight products or degradation of side chains. The result is a general breakdown of the polymer. For example, poly(tetrafluoroethylene), poly(methyl methacrylate) and poly(alpha-methyl styrene) undergo complete conversion to the monomer when heated to high temperatures.

The students should be alerted to the possibility of polymer degradation from factors other than contact with reactive chemicals. Such factors include X-ray irradiation, electric discharge, ultra-violet radiation, etc., which may result in cleavage and reformation of the polymer chains. However, no simple theories are available to predict the effects of such phenomena.

With this background, the students are prepared to understand some of the general trends seen in the empirical tables provided by the polymer vendors. For example, the extracted information in Table 2 shows that polyamides, polyesters, and rubber are not good candidates for use in the presence of acids and bases, while PE and PVDF are much better candidates.

TABLE 2
Selected Data on Chemical Resistance at 70°F
from Gates Rubber Co.
Chemical Resistance for Industrial Hose Stocks

	Nat. Rubber & Styrene But.	Cross-linked PE (Gatlon)	PVDF + HFPP (Viton)	Polyester Elastomer (Hytel)	Polyamide (Nylon)
Acetic Acid (25%-50%)	N	G	N	G	N
Agua Regia	N	G	G	N	N
Chromic Acid (10%)	N	E	E	N	N
Chromic Acid (25%)	N	G	E	N	N
Chromic Acid (50%)	N	N	E	N	N
HCl(15-37%)	G	G	E	N	N
Nitric Acid (10-60%)	N	G	E	N	N
Sulfuric Acid (10%)	E	E	E	N	N
Sulfuric Acid (30%)	G	E	E	N	N
Sulfuric Acid (50%)	N	E	E	N	N
Sulfuric Acid (93%)	N	E	E	N	N
Sodium Hydroxide (40%)	E	E	G	G	N
" (50,115°F)	E	G	N	-	N
" (50,180°F)	N	N	N	-	N
" (60%)	G	-	N	-	N
Potass. Hydroxide (30%)	G	G	G	N	N
Potass. Permanganate	N	E	G	-	N

E = Excellent: G = Good: N = Not Recommended: - = Insufficient Data

SOLVENT EFFECTS

Solvents interrupt the weak, secondary bonds between polymer chains. With thermosetting polymers, this can result in swelling of the polymer. In thermoplastic polymers, where chains are not necessarily covalently attached to each other, solvent effects can include the "dissolving" of some polymer material (*i.e.*, liquifying and removing it from the original bulk of polymer). Obviously, the extent of the solvent effects is influenced by the access of the solvent to the polymer chains, so amorphous, low-density (loosely-packed) polymers with minimal cross-linking or with long cross-links will be more susceptible.

To actually dissolve a polymer, the solvent must completely surround the chains, so short-chain polymers are more susceptible. For example, foams typically have very low molecular weights, are very amorphous, and dissolve relatively easily (a good demonstration here is to compare the effects of a mild acid on a styrofoam cup versus a polystyrene beaker). This principle is used to good advantage by manufacturers who solvent-treat polymer formulations to carry away low-molecular weight chains to produce high-molecular weight products.

The prediction of which solvents will be more effective with a given polymer begins with the hypothesis that solvents must compete with the cohesive forces between polymer chains. Such forces can be characterized by the "cohesive energy density" which, for liquids, can be defined as the energy needed to vaporize a certain volume of the liquid. Thus

$$\text{Cohesive Energy Density} = \delta^2 = E_0/V_0$$

where

$$E_0 = \text{latent energy of vaporization of volume } V_0$$

$$\delta = \text{"solubility parameter"}$$

The hypothesis is that a solvent with an energy density similar to that of the polymer will be able to exchange weak bonds with the polymer molecules (chains) and to disrupt the polymer. This is presumably the reason for observation of the "like-attracts-like" relationship (polar solvents attack polar polymers, aromatic solvents attack aromatic polymers, alkane solvents attack alkane polymers, *etc.*). If the hypothesis is correct, a value of δ exists for the polymer (determined from exposure to solvents, since polymers are not volatile) at which a maximum solvent effect will be achieved (*i.e.*, when $\delta_{\text{solvent}} \approx \delta_{\text{polymer}}$). In fact, swelling and/or dissolution in most polymers is observed when δ_{solvent} is within $\pm \approx 2\text{-}3$ (cal/cm³)^{1/2} of a central value, which is then reported as δ_{polymer} (examples of this effect are given in references 4 and

5). Values of δ for polymers and solvents are tabulated in several references (4, 6), and it is instructive to have the students plot a vendor's recommendations of solvents for a polymer against the values of δ_{solvent} , such as illustrated in Figure 4 for a PVDC formulation from Dow Chemical Company.

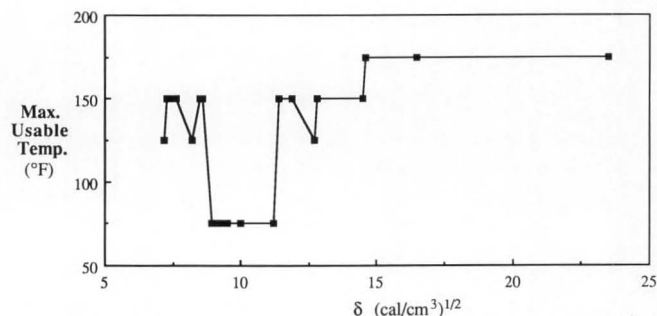


FIGURE 4. Recommended maximum usable temperatures of solvents with PVDC (Saran®) extracted from Dow Chemical Company "Chemical Resistance Guide for Systems Using Plastic Lined Piping Products" (values of δ were compiled from reference 4).

The value here is that for a particular polymer, given the value of δ for that polymer or given a table with recommendations for a few solvents, the student will be able to quickly guess if a particular solvent is safe or questionable by referring to the value of δ for that solvent. For example, suppose that an engineer wishes to know if dimethyl sulfoxide will cause serious swelling and/or dissolution with the PVDC from Dow Chemical Company. First of all, a dilemma arises, because the value of δ for PBDC is reported by Hall (6) as 9.8 (cal/cm³)^{1/2} and by Rodriguez (4) as 12.2 (cal/cm³)^{1/2}. From Figure 4, it is obvious that the formulation from Dow Chemical Company is closer to the material reported by Hall, and that dimethyl sulfoxide ($\delta = 13.0$ (cal/cm³)^{1/2}) will probably not induce significant solvent effects with this polymer.

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