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Sample Pages

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Plastics Failure Guide

Cause and Prevention

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2.6.3 Orientation Due to Processing

Many molded products have at least some orientation resulting from processing. In some cases, orientation is intentional and is required for the product to perform. Fibers and heat shrink tubing are examples. Much of the time, however, orientation is not wanted, and processing is carried out so as to minimize it. Frozen-in stress in a plastic product is the result of such orientation. In their normal state, most polymer molecules are random coils with no particular shape, physically intertwined with each other (Figs. 2.1 and 2.2). Processing at high speed and high shear rate extends these random coils into an oriented configuration like a stretched rubber band. Rapid cooling during processing does not allow enough time for complete relaxation, leaving a substantial amount of orientation and resultant frozen-in stress in the part. Picture the coiled, partially relaxed product as in Figures 2.1 and 2.2, but with much less randomness, and with some elongated portions. The higher the MW, the longer it takes for the oriented molecules to relax at any given temperature. With time or temperature, this stress can be relieved, allowing the molecules to become more like their original relaxed, coiled configuration.

The oriented condition may be likened to that of a spring that is stretched and not allowed to go all the way back to its unstretched or relaxed state. If the mechanical restraint on the spring is removed, it will snap back. If the restraint on the molded plastic is removed, it will revert to its relaxed state. This is readily accomplished by heating above the material's softening temperature, and constitutes a useful and practical way of gauging a part's level of orientation [37]. The greater the shrinkage and distortion on heating, the greater the frozen-in stress. Comparison with acceptable product gives a basis for ranking parts. Generally, the smaller the change on heating, the less likely the part is to fail.

In practice, most plastics are not annealed to relieve internal stress, and so may have considerable residual stress. This can contribute to failure in various ways, including warpage and environmental stress-cracking. Just as is possible with externally applied stress, internal stress can combine with environmental agents to cause failure. Piano keys of SAN failed by stress-cracking at a point where they picked up a ketone solvent used in cleaning a nearby part of the piano. The solvent evaporated and condensed on the SAN parts, where it caused environmental stress-cracking. Failure occurred mainly because of high internal stress from molding, which can be reduced by appropriate molding conditions of melt temperature, mold residence time, and mold temperature.

In fracture, stress is additive: internal stress of molding, external mechanical stress of a spring, and the environmental stress condition. All together, the parts could not resist the total stress. The solvent stress-cracking agent may be thought of as "the straw that broke the camel's back." The high frozen-in stress is indicated in

Figure 2.38 [4] by the shrinkage and distortion of a piano key on heating above the glass transition temperature (T_g), compared with an unheated key. Fracture occurred at a protruding hook at the gate end from the tension of an attached spring. The frozen-in stress was particularly high at that point, as indicated by heat shrinkage (Fig. 2.39). Redesign and molding to reduce orientation improved the product. Cracking of PE paint cans was also attributed to frozen-in stress (Fig. 7.9).

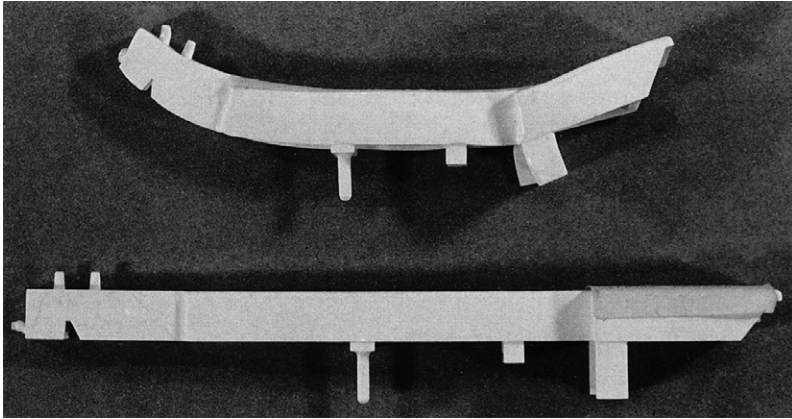


FIGURE 2.38 Piano key before and after heating to release frozen-in stress ([4], Fig. 2, reproduced with permission)

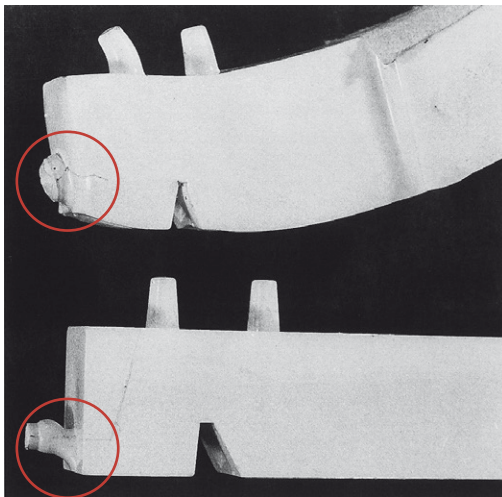


FIGURE 2.39 Closeup of hook end (left) on SAN piano key before (bottom), and after heat shrinkage (top) ([4], reproduced with permission)

■ 5.5 Fusion

While all plastics must be well fused to have good strength and avoid early failure, certain polymers are particularly sensitive in this regard (Section 5.8.3, PVC). The easy cracking of PE garden hose on bending is another case (Section 2.6.4).

■ 5.6 Processing Methods

5.6.1 Injection Molding

This processing method involves all the points made above, including factors and variables common to processing methods in general high shear rate and high orientation (frozen-in stress), dispersion of formulation ingredients, and others. Injection molded parts have gates and weld lines that can provide inherent weak points in the parts (Section 3.2.20). Shear rate, for example, is higher in injection molding than in extrusion and rotomolding, by about an order of magnitude—a substantial difference, giving high frozen-in stress and other potential sources of failure. The main variables in injection molding processing are temperature, pressure, residence time, and cooling conditions. One of the most common mistakes in injection molding is to reduce cycle time too much, possibly requiring a colder mold. While this may appear to increase productivity, it often results in high frozen-in stress, causing stress-cracking or warpage. Use of too low mold temperature in molding speakers of impact polystyrene led to distortion in service [12]. It is possible to calculate the proper cooling time as a function of temperature condition [13].

A method for optimizing production parameters for injection molding uses stress-cracking tests [14]. Stress-cracking solvents are given for many plastics (Table 5.2) [14]. In Table 5.3 is the point rating system for type and extent of damage [14]. After exposing samples molded under various conditions to precise solvent test conditions, the damage is rated. The advantages of the method are simplicity and the minimal equipment required. Use of the point rating system makes the process more objective than in previous tests. The influence of melt temperature, injection speed or injection time, and holding pressure were studied. The procedure helps to achieve the minimum in internal stresses in the finished article.

The weld line and gate area are particularly vulnerable to failure, especially when mold conditions are set for maximum production rate. While molding conditions are important for all areas of the molded part, the real test of the optimum balance between speed and pressure, melt temperature, and mold temperature is if the part is failure-free at the weld line and gate, especially the weld line or lines.

TABLE 5.2 Test Media for Establishing Internal Stresses in Injection Moldings of Various Plastics Materials^a

Material	Test medium
ABS	Acetic acid (conc.); methyl alcohol
PS, SB	Mineral spirits; n-heptane
SAN	Toluene + 2-propanol (1:5)
PE, PP	Strong surfactants (10 to 15% watery solutions)
	Chromic acid (50 °C)
PA 6, 66	Zinc chloride (watery solution, saturated, 50 °C)
POM	Sulphuric acid (50 °C)
PC	Toluene + 2-propanol (1:3)
PPE	Methyl alcohol + trichloroethylene (2:1); tributyl phosphate
PSU	Ethylene glycol monoethylether
PVC	Methyl alcohol
PMMA	Ethyl alcohol; toluol + n-heptane (1:2)

^a [14] reproduced with permission

TABLE 5.3 Points Rating for Type and Extent of Damage Caused by Solvents (Table 5.2)^a

Type of damage	Point rating of damage to surface or edge up to		
	1/3	2/3	3/3
Surface damage			
Silver haze	2	4	6
Short surface cracks	3	6	12
Long surface cracks	5	10	15
Cross-over surface cracks	10	15	20
Up to three started	10	15	20
or complete cracks	15	20	25 w.b.
More than three started	20	30	45
or complete cracks	30	44	55 w.b.
Crosswise running cracks	40	50	70
Edge damage			
Surface cracks	2	4	6
Crosswise running surface cracks	4	8	12
Cracks	5	10	15
Crosswise running cracks	15	20	25
Other visual damage	4 to 10		

^a [14] reproduced with permission

w.b. = with break

Every weld is a potential failure site, so the fewer weld lines, the better. Some designs utilize a “meld” line, which is generally stronger than a weld line (Section 3.2.20). Hall [15] reported on control of the position of weld line relative to product performance. Malguarnera [16] reported on how to strengthen the weld line by means of melt temperature, mold temperature, injection speed, and mold cooling time.

An injection molding coupling split open at the weld line after several years of use (Fig. 3.32). The thread component experienced a great amount of hoop stress from insertion of the male component. Teflon tape was used to seal the joint between the male and female (Fig. 3.35). The use of Teflon tape can take up space at the root of the thread. This can significantly raise the stress level in the part and result in creep failure. The weld line is typically one of the weakest regions in the part, and can be the first place for a crack to form.

Flow and orientation were described as “pathways to part perfection” with ABS [17]. Failures have been reported due to failure to apply sufficient time and pressure to freeze the gates, leading to shrinkage voids (Fig. 5.6) [18]. The effect of mold temperature on orientation and on the weld line is shown by tensile specimens molded at three temperatures [19]. At the lowest temperature, orientation and frozen-in stress are the highest, as readily seen by shrinkage after heating (Fig. 5.7) [19]. The relationship between melt flow and shrinkage, warpage, and structural performance is important for strong and stable mechanical properties [20]. Frozen-in stress and related features of injection molding are treated with respect to the distribution of physical properties in molded parts [21].

Figure 5.8 illustrates the sequence that polymer molecules go through before, during, and after injection molding. Initially, the polymer is not oriented during the melt stage of the process before molding. Orientation comes about as the polymer speeds through the gate into the mold. In order to pass through the gate, the molecules have to get out of each other’s way. They do this by stretching into elongated

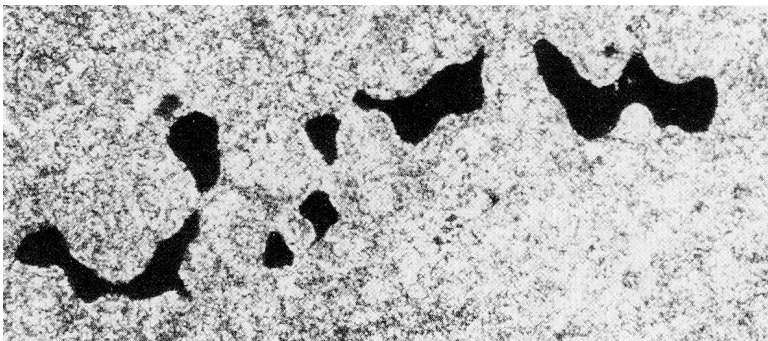


FIGURE 5.6 Shrinkage voids created by insufficient time and pressure to freeze the gates during injection molding process ([18], Fig. 15.4, courtesy of Engineering Design, published by E. I. Du Pont de Nemours and Co., Inc.)

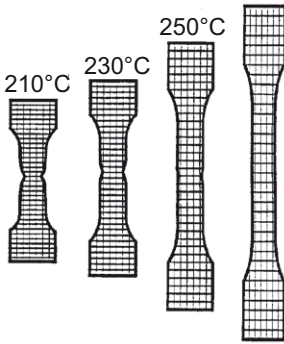


FIGURE 5.7 Thermally shrunken double-gated standard tensile bars of polystyrene molded at melt temperatures: 210, 230, and 250 °C (from left to right); mold temperature, 40 °C. As molded bar, not thermally shrunken, far right (Section 1.14 [29], (Fig. 6) and [19], reproduced with permission)

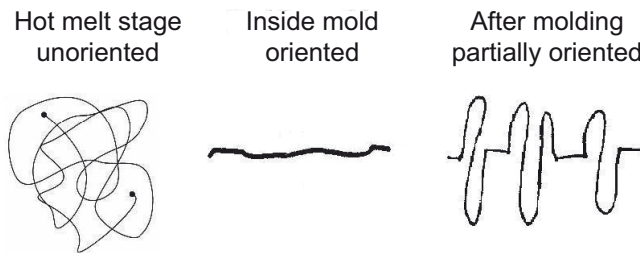


FIGURE 5.8 A conceptual portrayal of polymer molecular orientation at various stages of injection molding (Section 1.14 [29], (Fig. 5) and [19], reproduced with permission)

molecules (Fig. 5.8). The high directional force associated with molding enhances the alignment of molecules. On cooling in the mold, some orientation is retained, which can cause problems associated with internal stress, such as environmental stress-cracking. In the figure, partial orientation after molding is not intended as an accurate depiction of that state. The purpose is to suggest a partially oriented configuration, not necessarily as depicted.

At best, injection molding involves compromises to make a part that won't fail and can be processed economically and profitably. Three of the main processing variables are melt temperature, mold temperature, and cycle time (time in the mold). A material variable is MW (melt index). A mold design variable is gate size. Clearly, material, design, and processing all are involved and related to each other in making a successful injection molded part.

Section 2.6.3 in Chapter 2 reports the case of SAN (styrene acrylonitrile) injection molded piano keys that failed due to environmental stress-cracking when MEK (methyl ethyl ketone) solvent was used to clean the back of the piano. MEK condensed on the piano keys, causing stress-cracking. Section 2.6.3 assigns responsibility for the failure mainly to processing, which gave a high level of frozen-in stress, particularly at the hook end (Fig. 2.39) where failure occurred. Note the very high shrinkage at the hook end after heating the part to relieve frozen-in stress.

PC molded parts are sensitive to brittle failure and high rate impact. The effect is very sensitive to processing conditions [22]. In addition to moisture causing hydrolysis to lower MW and thus more brittle behavior, bubbles at the surface of molded parts due to moisture also increase brittleness. Bubbles are seen as silver streaking or splay radiating outward from the gate location of injection moldings. When the surfaces containing bubbles were removed with a fly cutter, the PC fractured ductilely when impacted at a high rate, instead of in a brittle manner as in the presence of splay bubbles [22]. Processing conditions that affected the amount of bubbles or splay in a molding also affected high-rate brittle impact behavior. The effect of bubbles is due to the increased number of stress concentration points, which lower strength properties.

High melt temperature may contribute to polymer degradation during processing [23]. The result may be weak parts because of low MW. Sufficient antioxidant or stabilizer is needed to minimize this problem. The total heat history for high temperature processing and reprocessing of regrind may be too great for a low level of stabilizers. When PVC degrades, it may also corrode metal due to HCl evolved [24].

An example is given of oxidative degradation of a polymer, which is very readily degraded in processing and service if there is inadequate antioxidant, by small PP rotors used in hot water service (Section 1.14 [32]). Pellets, as-molded rotors, and degraded rotors were available to track OIT values from “cradle to grave.” See Table 4.1 and Section 5.8.3 (Test Methods) regarding OIT. Rotors in service for about a year experienced substantial degradation under service conditions of hot water, steam, and air. Figure 5.9 (Section 1.14 [32] Fig. 2) shows a complete unused rotor, which measures 2 inches in diameter. The photo includes a close-up of the degraded end of a fin of a used rotor. Figure 5.10 (Section 1.14 [32] Fig. 3) is the DSC-OIT thermogram of pellets, unused rotor as molded, and a rotor degraded in service.

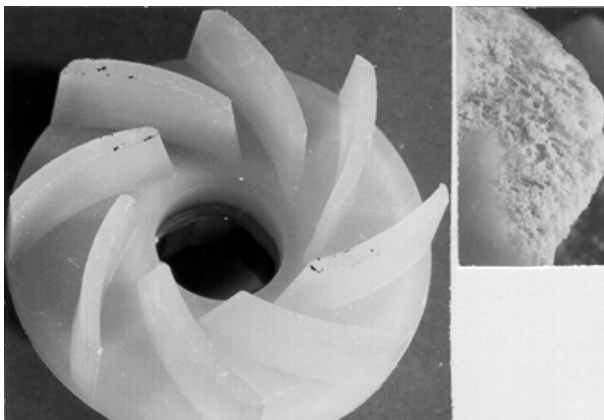


FIGURE 5.9 Unused PP rotor and close-up of a degraded fin of a used rotor (Section 1.14 [32], Fig. 2, reproduced with permission)

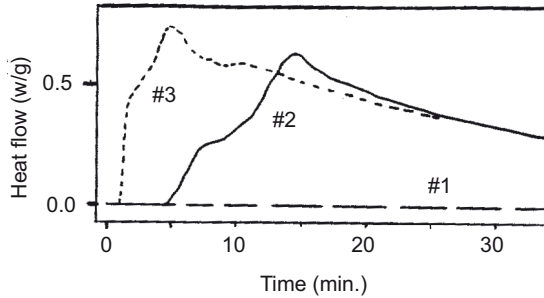


FIGURE 5.10 DSC-OI time at 200 °C of #1 unmolded PP pellets (> 50 min.); #2 unused molded rotor (4 min.); #3 rotor degraded in service (1 min.) (Sec. 1.14 [32], Fig. 3, reproduced with permission)

Isothermal DSC temperature was 200 °C. The OI time for pellets was > 50 minutes; for as-molded rotors, time was 4 minutes; and degraded rotor was 1 minute. Time to purge the DSC cell with oxygen following equilibration in nitrogen was about 1 minute, so that the OI time of degraded rotor was practically zero.

The pellets were well stabilized (OIT > 50 min.), so that an OIT value of 4 minutes for molded rotor indicates that most of the antioxidant was consumed in processing. The type of service (hot water, air) readily consumed the remaining antioxidant, leaving the rotors very susceptible to degradation in service. It is possible another antioxidant system might have provided better protection in processing and service.

Jetting [25] is a problem peculiar to injection molding (Fig. 5.11[b]). It is associated with the swelling melt emerging from the gate and not striking the walls as it enters the mold. Thus, jetting is accentuated by melts exhibiting low extrudate swell, and by gate design that causes emerging melts not to strike the mold walls. Molded parts formed by jetting are not desirable from the point of view of both appearance and strength.

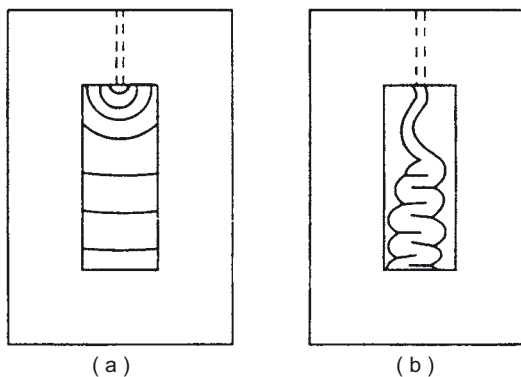


FIGURE 5.11 Diagram of (a) simple mold filling and (b) jetting ([25] p. 2328, reproduced with permission)

14.4.4.1 Further Cases of Identification of Contaminants

The first case is of controlled low adhesion for electrical cable. A cellulosic contaminant contained in zinc stearate was at fault when the stearate was used to reduce bond strength between the outer jacket and the carbon black-containing insulation shield over insulation in an electrical cable. The stearate is applied as a fine powder before the jacket is extruded over the cable [8]. Without it, the polymers in the jacket and in the insulation shield would fuse together when the jacket is extruded over the insulation shield. The purpose of the stearate, and of another coating applied to the insulation shield, is to permit easy removal of the jacket (strippability) when connections are made in service. At some locations the bond was too strong, so the jacket could not be stripped off readily. Microphotography (Fig. 14.16) and micro IR (Fig. 14.17) revealed the presence of a cellulosic film contaminant in the stearate. The spectrum is for the area in the circle on the contaminant in Figure 14.16.



FIGURE 14.16 100X microphotograph of a contaminant in zinc stearate ([8], Fig. 3, courtesy of the Society of Plastics Engineers, Newtown, CT, www.4spe.org)

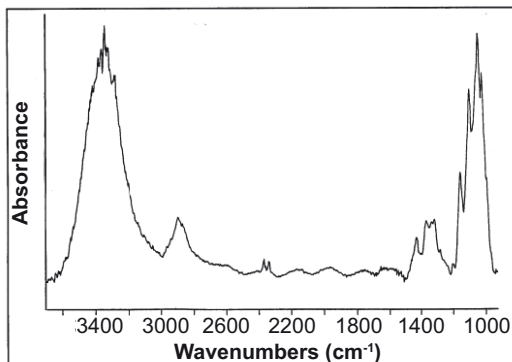


FIGURE 14.17 Micro IR spectrum of contaminant in Fig. 14.16 ([8], Fig. 4, courtesy of the Society of Plastics Engineers, Newtown, CT, www.4spe.org)

Where the contaminant was at the surface between the jacket and the rest of the cable, the stearate was absent and so could not control adhesion as intended. Note that the magnification in Figure 14.16 is 100X, indicating the micro capability of the micro IR.

14.4.4.2 An Unusual Case of Failure Due to Plasticizer

Cellulosic lint fibers on epoxy-phenolic coating over aluminum for bottle caps led to localized delamination of plasticized vinyl latex applied to the lower coating. Both coatings contain liquid additives such as plasticizers that migrated freely between the two coatings. Where the interface consisted of an uninterrupted tight bond between the coatings, the exchange of plasticizers did not affect adhesion. At lint contaminant sites, however, plasticizer could not transfer freely across the interface, causing some to be deposited at the interface, lowering the bond strength at the contaminant sites. Micro IR, microphotography, and GC/MS showed that plasticizer was present as a tiny pool at delaminated sites [17, 25].

14.4.4.3 Failure Due to Polymeric Contaminant as Processed

Figure 2.26, Section 2.4.2.1, is a photograph of 1/8 inch thick HDPE formed into desired shapes by punch cutting. There is a raised area formed by punching. Small pieces of a thin film were found in these. These are not intentional, being a foreign contaminant. Where present, the foreign film prevented PE on either side from fusing normally. With the application of the punch die to cut out shapes, the low adhesion caused by the contaminant film led to raising of unbonded areas. In most cases of poor adhesion, the problem is at the surfaces, and it is there that adhesion is affected. In this unusual case, it is a matter of internal fusion and adhesion.

■ 14.5 Processing Aspects of Adhesion Failure

14.5.1 Surface Condition

Adhesion is a process that takes place at surfaces. The adhesive has to “wet” the surface to ensure bonding. Generally the surface needs to be free of all substances that would reduce bond strength. That may mean surface cleaning or preparation, such as by sanding, before application of adhesive. Even a trace of oil on metal, needed for example for moving metal wires through their processing, can adversely affect adhesion. Analysis (Section 14.3) may identify the material causing the problem.

until better data are available on that question. Frankly, we consider 153 ppm a startlingly high level of a packaging migrant in any food, let alone one like cheese that is consumed in large quantities by children.” The positions of the FDA and consumer groups on safety of plastics packaging appear to be far apart.

16.8.5 British Studies of Styrene, Benzene, and Other Materials in Plastics Packaging and Foods

Extensive studies have been reported by the Food Standards Agency of the British Ministry of Agriculture Fisheries and Food [49]. The levels of compounds in foods were too low to be of concern as to health effects. Aromatics such as benzene were included because of their absorption by packaging materials from airborne gasoline vapors [50, 51, 52]. To put the intake of hydrocarbons from food and plastic packaging in perspective, the estimated number of micrograms per person per day for benzene is 1 to 2. Estimates of daily exposure to benzene from air are up to about 1000 [53].

16.8.6 Teflon—Polytetrafluoroethylene

Teflon (PTFE) has a melting point of 326 °C. For many years metal cooking utensils, especially frying pans, have been coated with Teflon as a nonstick surface. Because of its high melting point and lack of reactivity with most compounds, it has been considered “safe.” That is being questioned, citing evidence of hazardous breakdown products formed on heating at high temperature. A typical paper is “Avoid Teflon Pans;” the original title was “Your Teflon Frying Pan May Be Causing Problems” [54]. Such claims are very likely being refuted by the Teflon industry.

■ 16.9 Pollution of Oceans and Waterways by Discarded Plastic Waste

“Trashed: Across the Pacific Ocean, Plastics, Plastics Everywhere” is the title of a 2003 paper [55] on observations in the North Pacific subtropical gyre (A gyre is a giant circular oceanic current [Merriam-Webster on-line dictionary, <http://www.merriam-webster.com/dictionary/gyre>]) about halfway between Hawaii and the mainland. The author reported, “As I gazed from the deck (of a sailing ship) at the surface of what ought to have been a pristine ocean, I was confronted, as far as the eye could see, with the sight of plastic.” Further, “In the week it took to cross the subtropical high, no matter what time of day I looked, plastic debris was floating

everywhere: bottles, bottle caps, wrappers, fragments.” Also, it has been “estimated that the area, nearly covered with floating plastic debris, is roughly the size of Texas.”

This problem may have escaped attention because the North Pacific Gyre is not heavily traveled or fished. The flow of natural currents in the oceans tends to push debris into this region of the Pacific Ocean. The source of plastic debris in large part is very likely from waste dumped by cruise and other ships into the oceans over the last approximately 50 years. That has been a common practice in the past for centuries, but before plastics most things dumped in the ocean would be degraded by ocean microorganisms and disappear or would be heavy enough to sink to the bottom. Not so for plastics. California is starting to have regulations about dumping plastics debris in the ocean [57]. Unfortunately very little can be done to remove the enormous weight of plastic debris floating in the oceans that the paper reports [55]. A New York Times editorial [56] says that much of the plastic refuse comes from land, not ships, which seems unlikely.

As tragic as that is, even more so is the impact on birds and marine life that depend on the ocean for their food and life. This is not entirely a new phenomenon. Rubber balloons released into the air as part of a celebration or popular cause may fall into an ocean or waterway. Birds and marine life that mistake rubber for food may die because they cannot digest rubber. PE six-pack rings for beer cans have been known to strangle birds and marine life if their necks become entangled in the rings. All this is tragic. What is happening in the North Pacific is especially disturbing, not only because of the very large area covered with plastic debris but also because birds such as the Laysan albatross feed in these waters. Figure 16.5 shows plastic objects inside the decomposed carcass of an albatross on Kure Atoll. The bird probably mistook the plastics for food and ingested them while foraging for prey [55]. The living bird is in Figure 16.6. It is estimated that plastic debris traps as many as a million seabirds every year and 100,000 marine animals [56].

An American Chemical Society meeting suggests that plastics in seawater break down faster than expected, releasing contaminants including harmful styrene compounds not normally found in nature [56]. What has happened is another large-scale, potentially tragic, uncontrolled experiment that humans have conducted on their environment without intending to [56].

Surely the dumping of large quantities of plastic debris in the ocean from cruise ships and the like was done on the assumption that the ocean would decompose it and disperse it in the ocean, as has been the case for other materials dumped overboard for centuries. But many plastics have lower density than water, so they do not sink to the bottom but float instead. And, being petroleum based, they cannot be degraded by microorganisms in the ocean. It is not likely that someone dumping plastics in the ocean wants to kill birds and marine life or realizes that it is an unintended consequence of the practice.



FIGURE 16.5 Plastic objects inside the decomposed carcass of a Laysan albatross on Kure atoll in the North Pacific Ocean ([55], photo by Cynthia Vanderlip for Algalita Marine Research Foundation, reproduced with permission)



FIGURE 16.6 Laysan albatross that feeds in the North Pacific Ocean where there are large areas of floating plastic debris (photo source unknown)