Storing plastics in the cold: more harm than good?

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Abstract

Storage of plastics at low temperatures has been proposed as a low-cost, low-maintenance technique. The research described here concerned the results of cooling thin- and thick-walled (greater than 10 mm) plastics materials. Tinytalk® loggers were used to record temperature profiles during cooling from ambient. Methylene blue powder was used to indicate the formation of condensation. Dimensional changes were determined on cooling. Thin-walled plastics may be safely placed in freezers protected only by a closed polyethylene bag. The same approach cannot be applied to thick-walled plastics, particularly those containing plasticized PVC because of large dimensional changes and formation of condensation.

Keywords

plastics, preventive conservation, cold freezer, shrinkage, condensation, PVC

Introduction

Storage of plastics at low temperatures (between 10 and –20 °C) has been proposed as a relatively low-cost, low-maintenance technique for slowing the rate of the most common chemical degradation reactions, such as hydrolysis and oxidation (Michalski 2002). The basis for this assertion is that a ten degree reduction in temperature halves the rate of chemical reactions and many plastics have a short lifetime of between 1 and 50 years (European Union Commission 2000) Some physical degradation processes are also inhibited by cold storage; reducing the storage temperature from ambient to that of a domestic freezer reduces the rate of migration of plasticizer from polyvinyl chloride (PVC) by 15 (Shashoua 2004). Because long-term, low-temperature storage is only routinely applied to film archives and not to three-dimensional objects, we have limited practical experience of its effects. However, based on their physical and chemical structures, both reversible changes (including dimensional and tensile) and irreversible changes (including extent of crystallization and mechanical failure) may occur when plastics are cooled.

On cooling, plastic materials tend to contract or shrink considerably more than other materials found in museum collections such as metals, ceramics and glass. The linear coefficient of expansion for thermoplastics ($4.0–20.0 \times 10^{-5}$/°C) is five to ten times greater than those of most metals ($1.0–2.5 \times 10^{-5}$/°C). For example, a copper pipe will shrink by 0.01 per cent if the temperature is reduced by 10 °C. Under the same conditions, a high density polyethylene pipe would shrink by 0.07 per cent, and polypropylene and hard polyvinyl chloride (PVC) pipes by 0.04 per cent (Nason et al. 1951). Although shrinkage of plastics is an unavoidable process on cooling, it is reversible. In the absence of degradation, the plastics object will assume its original dimensions on its return to ambient conditions.

Recent research into cold storage of rolls of cellulose acetate-based movie film with an equilibrium relative humidity (RH) of 50 per cent concluded that a maximum of six to ten degrees temperature variation between film and its storage container or anywhere in the mass of materials, should be maintained to avoid formation of condensation (Padfield 2002). Air close to warmer areas of film can hold more water vapour than air close to colder areas, resulting in movement of moisture between the object undergoing cooling and its container, condensation and possible physical damage to the film. Many plastics can absorb moisture, for example in the form of condensation, swell and possibly physically fail. Water acts as a plasticizer for many of the early plastics, notably casein, and can displace plasticizer from PVC (Shashoua 2001). Polyamides, such as nylon, are the most hygroscopic polymers in common use, containing up to 3 per cent moisture by weight under ambient conditions. In the same environment, cellulose acetate and poly (methyl methacrylate) contain 0.8 per cent, PVC contains 0.4 per cent and polystyrene (PS) 0.1 per cent moisture by mass.

The opportunity for the development of condensation or for structural damage due to dimensional changes on cooling to freezer temperature has only been studied in detail for film, which comprises layers of thin plastics materials adhered together, and not for solid plastics. The research described here investigated the influence of the rate of cooling plastics materials typically found in museum collections from ambient to freezer temperature, on dimensional changes and the risk of formation of condensation at surfaces.

Selection and characterization of sample plastics

All the sample plastics selected were amorphous thermoplastics; such materials represent those frequently found in collections concerned with everyday life after World War 2. Amorphous plastics are those in which the polymer chains have no well-defined order. Thermoplastics are easily melted and reformed because few cross-links are established during processing. Furniture and flooring are usually constructed from thermoplastic vinyls or polyesters. Telephones, computers, television housings and electronic devices are commonly made of acrylonitrile-butadiene-styrene (ABS). Most flexible toys contain thermoplastic PVC.

The plastics materials under investigation were divided into thin-walled (a polyester cassette tape in a polystyrene case and a ship form made out six ABS Lego® bricks, neither of which were visibly degraded) and thick-walled which contained a bulk of material at least 10 mm thick. Thick-walled materials selected were a PVC photograph album and a pile of ten long-playing (LP) vinyl records in paper folders within card sleeves protected by PVC pockets, both in good condition with the exception of the plasticized PVC components which had slightly shrunk and cockled due to loss of plasticizer. The polymer types present in the sample objects were identified non-destructively using attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy and comparing the resulting spectra with references.

The glass transition temperatures of the sample plastics ranged from –20 °C (plasticized PVC in record sleeve) to 30–80 °C (vinyl acetate/vinyl chloride copolymer in record) 80–100°C (ABS Lego bricks and PS cassette cases) (Brydson 1999). Glass transition temperature (T_g) is a property of amorphous polymers. Above the T_g, there is sufficient energy for molecular movement, resulting in polymers that are soft and flexible. When polymers are cooled below this temperature, they become hard and brittle due to a lack of molecular mobility, so achieve a glassy state. In their new state, their response to stress as a result of handling and moving changes, allowing the possibility to 'freeze in' molecular orientations, not present under ambient conditions. If the orientations vary from place to place in the structure, sufficient stresses may be established to cause the plastics material to distort.

The incorporation of plasticizers into some polymers reduces T_g. The small plasticizer molecules migrate between the polymer chains, creating space. The presence of increasing amounts of plasticizer improves the resistance of plastics to stress and flexing, two phenomena frequently experienced by objects during handling at low temperatures. A boot constructed from PVC with around 50 per cent plasticizer by mass remains flexible when cooled to –50 °C whereas a vinyl floor containing 23 per cent plasticizer is likely to crack if flexed below 0 °C (Wilson 1995). The plastics components of the sample cassette tapes and Lego® bricks remain below their T_g (in their glassy state) both at ambient and at freezer temperature while the outer sleeve (plasticized PVC) of the vinyl records and the photograph album remain above their T_g (rubbery state).

The equilibrium RH around each object was measured by placing it in a polyethylene zip-lock bag together with a Tinyview® RH sensor, pressing as much air out as possible and storing the whole at 20 ± 2 °C away from sources of light which were likely to produce localized warming (Figure 1). After 2 h, stable equilibrium relative humidities between 50 and 60 per cent for all sample plastics were recorded (Table 1).

Figure 1. Equilibrium relative humidity of sample plastics was measured by placing them in a closed polyethylene bag with a Tinyview® RH sensor

Table 1. Equilibrium relative humidity of sample plastics at 25 °C

Plastics materials	Equilibrium relative humidity at 25 ± 0.2 °C (%)
Cassette tape	59.5
Lego® ship	50.0
Photograph album	52.0
Pile of LP records	50.5

Cooling regime

When museum objects in the National Museum of Denmark are treated with cold to eradicate pests, they are first enclosed in polyethylene bags to prevent contact with condensation on warming after treatment, before transferring them directly from ambient conditions to a freezer. The same procedure was applied to the selected sample plastics. Plastics were conditioned at ambient temperature and RH (20 ± 2 °C and 40 ± 2 per cent respectively) for 48 h before cooling. Cooling was done by enclosing each plastic in close-fitting zip-lock low density polyethylene (LDPE) bags with as much air as possible removed. Thereafter, samples were

Figure 2. Sample plastics were insulated by loosely packing them with expanded polystyrene chips to slow the rate of cooling

placed in acid-free cardboard boxes with fitted lids. Boxes had volumes approximately double those of the sample plastics they contained. In an attempt to further slow the rate of cooling, the air space between plastics and box was filled either with closely packed polyethylene foam or with loosely packed expanded polystyrene insulating chips (Figure 2). Boxes were then placed in a frost-free, domestic chest freezer, set to deliver temperatures between –25 and –30 °C.

Examination of sample plastics

Temperature profiles during cooling regime

Tinytalk® temperature loggers, fitted with 10 k NTC Thermistors (encapsulated) sensors and sensitive within the range +50 to –30 °C were used to record temperature profiles at the surfaces (temperature sensor 1) and central locations (temperature sensor 2) of sample plastics during cooling from ambient to freezer temperature (Table 2). Sensor accuracy was ±0.2 °C and resolution 0.25 °C across the loggers' temperature range. The thermistors of the sensors were held in position with adhesive tape so that they made close contact with sample plastics (Figure 3**)**. In addition, a Tinytalk® temperature logger was placed in the freezer beside the boxed sample plastics to monitor the air temperature external to the experiment (temperature sensor 3). Temperature was recorded once per minute; values were downloaded through an interface cable and plotted against time using Gemini Data Logger's software. Measurement of temperature profiles on cooling was repeated three times for each sample plastic with and without insulation.

RH around the enclosed sample plastics was not measured; past experience has shown it difficult to accurately measure RH under steadily falling temperatures and over a large temperature range.

Table 2. Positioning of Tinytalk® temperature loggers to measure temperature profile on cooling

Sample plastic	Temperature sensor 1	Temperature sensor 2	Temperature sensor 3
Cassette tape	External surface of case	Between two winds at midpoint of tape	Air in freezer
Lego® ship	External surface of bricks	Internal surface of bricks	Air in freezer
Photograph album	External cover	Between centre photo pockets	Air in freezer
Pile of LP records	External surface of PVC sleeve	Surface of middle record	Air in freezer

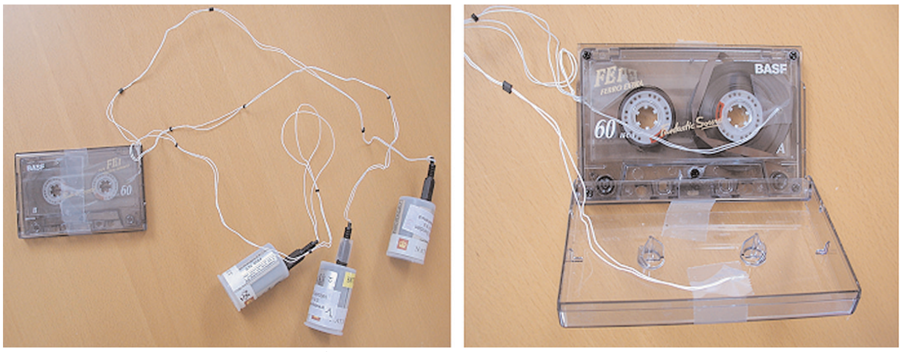

Figure 3. Thermistors of Tinytalk ® data loggers were held in close contact with surfaces of sample plastics using tape

Thin-walled plastics objects (cassette tape and Lego® ship) cooled from ambient to freezer temperature in 45 min or less without insulation, compared with a period of 90 min for thick-walled objects (photograph album and a pile of ten LP records**)**. Insulating sample plastics objects prolonged the period taken by them to attain freezer temperature regardless of type or packing arrangement of insulating material.

The mean maximum temperature difference between surfaces and central areas of thin-walled materials was never greater than 10 °C, whereas it was as high as 31 °C for 5–10 min for thick-walled materials. The greatest temperature difference always occurred at the start of the cooling process (Figures 4 and 5).

Insulating sample plastics usually increased the maximum temperature difference between surfaces and central areas by slowing the initial rate of cooling of peripheries adjacent to insulating foam.

Dimensional changes due to cooling regime

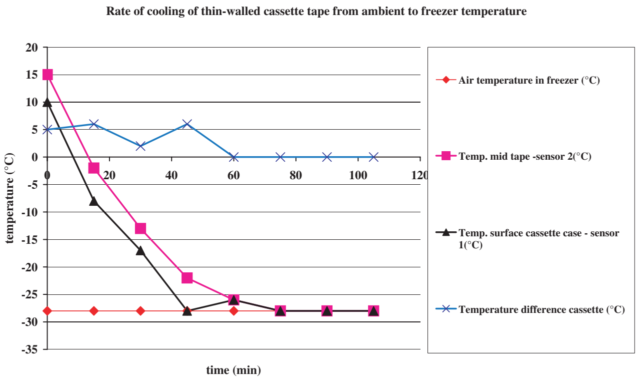

Figure 4. Rate of cooling of thin-walled cassette tape from ambient to freezer temperature

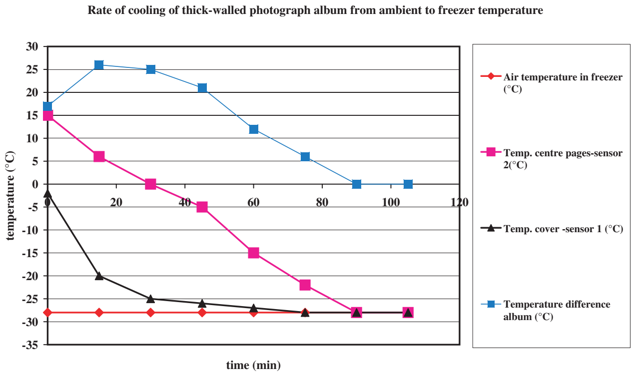

Figure 5. Rate of cooling of thick-walled photograph album from ambient to freezer temperature

The heights at three positions of each sample plastic were measured using callipers under ambient conditions (20 ± 2 °C and 40 ± 2 per cent RH), immediately after removal from the freezer and again after 48 h in ambient conditions. Determination of change in dimensions on cooling and on achieving ambient temperature again was repeated three times for each sample plastic and the mean value calculated.

Percentage linear shrinkage on cooling at each of the three positions was calculated from the following formula and the mean shrinkage for the sample plastic was obtained:

$$\text{percentage linear shrinkage on cooling (per cent)} = (H_{\mathrm{RT}} - H_{\mathrm{F}})/H_{\mathrm{RT}} \times 100$$

where H_{RT} = original height under ambient conditions (millimetres), and
H_{F} = height at freezer temperature (millimetres).

A similar formula was used to calculate the percentage linear shrinkage on return to ambient. All changes in dimensions on cooling were fully reversed within experimental error (±0.02 mm) when sample plastics attained ambient

Table 3. Results from cooling profile measurements and detection of condensation formed during cooling regime

Sample plastic/insulation	Mean time for all areas of sample plastics to attain freezer temperature (min)	Mean maximum temperature difference between temperature sensors 1 and 2 (°C)	Formation of condensation?
Cassette tape			
no insulation	45	5	No
close PE foam	90	6	No
loose PS chips	90	10	No
Lego® ship			
no insulation	30	6	No
close PE foam	45	2	No
loose PS chips	45	6.5	No
Photograph album			
no insulation	90	26	Yes
close PE foam	105	30	Yes
loose PS chips	105	31	Yes
Pile LP records			
no insulation	90	6	No
close PE foam	105	14	No
loose PS chips	105	15	No

temperature again (Table 4). A percentage shrinkage of less than 1 per cent was measured for thin-walled plastics. Mean linear shrinkage of the cassette tape on cooling was greater than that of the Lego® ship as expected from their respective linear thermal coefficients of expansion (12.4×10^{-5} cm/cm/°C for polyester and 7.2×10^{-5} cm/cm/°C for ABS).

By contrast, the results from measurement of shrinkage of thick-walled plastics were more complex to interpret. There was clear evidence of deformation by the plasticized PVC components of thick-walled plastics on cooling, which caused an apparent increase in dimensions or swelling. However, the linear thermal coefficient of expansion for plasticized PVC (25×10^{-5} cm/cm/°C) suggested that the thick-walled plastics should exhibit greater shrinkage than that shown by the cassette tape and Lego® ship.

Table 4. Dimensional changes of sample plastics on cooling and return to ambient

Plastics materials	Mean percentage shrinkage on cooling in freezer from ambient (%)	Mean percentage shrinkage on warming to ambient (%)	Comments
Cassette tape	0.40	0.00	
Lego® ship	0.32	0.01	
Photograph album	200.00	0.01	Deformation and stiffening of PVC pages on cooling caused album to occupy more space than at ambient
Pile of LP records	–8.30	0.02	Deformation and stiffening of PVC covers on cooling caused records to occupy more space than at ambient

Figure 6. PVC photograph album at 20°C (upper) and at –25°C (middle). Pages of the album were cockled and stiffened on cooling (lower)

The pages of the photograph album, already slightly shrunken due to loss of plasticizer, became increasingly cockled and stiffened on cooling, reducing the ability of pages to pack together as closely as they did at ambient (Figure 6). The Glass Transition temperature of plasticized PVC is approximately –20 °C, suggesting that the plastic components of the photograph album underwent a change in phase from rubbery at ambient temperature to glassy on cooling in the freezer; this accounted for the increased stiffness. The combination of cockling and stiffening of the pages on cooling resulted in an apparent expansion of the album. If the album had contained photographs or negatives, the contents would have been folded or distorted during cooling, probably resulting in irreversible damage. PVC outer sleeves of LP records exhibited identical behaviour to the pages of the photograph album, becoming distorted and stiff on cooling. Such changes were fully reversed 24 h after removal from the freezer.

Formation of condensation due to cooling regime

Methylene blue powder is highly sensitive to the presence of liquid water, changing colour from grey when dry to an intense blue colour when dissolved. It has been used to indicate the presence of condensation in similar investigations (Padfield 2002). Sheets of Whatman's filter paper were dusted lightly with methylene blue and the grey powder was distributed evenly using a soft brush to produce indicator sheets for condensation.

Indicator sheets, cut to thin strips of 10 mm × 2 mm, were placed in the middle of the centre wind, between the two outer winds of the cassette tape and in the air space between tape and case. A sheet of indicator paper was placed in contact with the external and internal surfaces of the Lego® ship. To investigate the possibility of formation of condensation in the photograph album, indicator sheets were placed in contact with front and back covers and their respective adjacent pages and between the centre pages. Indicator sheets were also placed between the outer PVC sleeve and card cover of the pile of LP records and so that they made contact with the middle record (Figure 7).

Figure 7. Methylene blue indicator sheets were used to detect the formation of condensation on cooling

Condensation was not detected in any thin-walled sample plastics during cooling, a finding similar to Padfield's experience that a temperature difference lower than six to ten degrees did not support the formation of condensation in materials at equilibrium with 50 per cent RH (Table 3). The only sample plastic in which condensation was detected was the thick-walled PVC photograph album. Condensation was only detected between the front cover (that uppermost in the cardboard box and first, cockled page of the photograph album, regardless of the material's rate of cooling. The mean maximum temperature differences between the cover and centre photo pockets (pages) were 26–31 °C, notably higher than for the other sample plastics. Cooling the photograph album surrounded by foam rather than without insulation, slowed cooling of the front cover while having no influence on the temperature between the centre pages. The result was an increase in the already high initial temperature gradient throughout the object and the opportunity for condensation to form.

Because the pile of LP records showed mean maximum temperature differences between external surfaces and the middle record higher than the six to ten degree 'limit' during cooling, condensation was expected. The fact that it was not detected may be attributed to the presence of layers of moisture-absorbing card and paper sleeves and covers which may have interrupted the free flow of water vapour between various areas of the record pile.

Conclusion

The risk of either physical damage or the formation of condensation at surfaces due to cooling from ambient to freezer temperature at an uncontrolled rate, was insignificant for thin-walled plastics such as cassette tapes and Lego® bricks. Such materials attained freezer temperatures rapidly, that is within 30–45 min, and did not experience a temperature gradient greater than ten degrees between surfaces and central areas, thereby not supporting the formation of condensation. Insulating plastics prior to placing in a freezer raised the temperature gradient through the material and thereby prolonged the period required to achieve –25 °C. Dimensional changes on cooling thin-walled plastics were minimal (less than 0.4 per cent) and fully reversible on realizing ambient temperature again regardless of plastic type.

Thick-walled plastics which contained a bulk of material at least 1cm thick required a longer period to attain the same temperature as the freezer in which they were stored than thin-walled materials. Such slow cooling from ambient to around –25 °C resulted in temperature differences between peripheral and central areas of plastics higher than the ten degree 'limit' for the formation of condensation. Condensation was detected between the front cover and first page of the PVC photograph album. If allowed to remain in contact, water can displace plasticizer from PVC imparting an opaque appearance. Insulating with foam prior to cooling extended the period required to attain freezer temperature, thus further increasing the temperature gradient throughout the plastic object at the start of the cooling process.

Plasticized PVC components in thick-walled objects caused apparent linear swelling by up to 200 per cent of the original height. A change in phase from rubbery at ambient temperature to glassy on cooling to approximately –20°C caused stiffening of the photograph album's already crinkled pages. The resulting distortion would have caused any enclosed photographs or negatives to fold irreversibly.

In conclusion thin-walled objects, regardless of plastic type, may be safely placed in freezers protected only by a closed polyethylene bag to prevent contact with any condensation formed on removal from the freezer. The same approach cannot be applied to thick-walled plastics objects, particularly those containing plasticized PVC, because the dimensional changes and risk of formation of condensation resulting from cooling to freezer temperature are likely to damage other nearby materials. Use of insulation to slow the rate of cooling offers no advantages over cooling in the absence of insulation. Further investigations are necessary to identify either the minimum temperature that thick-walled plastics can tolerate without exhibiting physical damage or a technique based on storage in a freezer which could minimize the negative changes identified in the present research.

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