PROBLEMATIC HEELS: THE IDENTIFICATION, CHARACTERIZATION, AND TREATMENT OF TPU TOP PIECES IN THE MUSEUM AT FIT'S COLLECTION

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ABSTRACT

During the second half of the 20th century, low-cost petroleum-based plastics infiltrated the footwear industry leading to a rapid decline in labor-intensive and expensive leather products. New thermoplastic techniques allowed soles, heels, and heel tips (top pieces) to be molded and attached to shoes with direct injection molding as one operation, or with top pieces, as separate injection-molded pieces. Thermoplastics, chiefly thermoplastic rubber, thermoplastic polyurethane (TPU), and poly vinyl chloride, now make up approximately 50% of shoe sole production alongside molded polyurethane, ethylene vinyl acetate, and styrene-butadiene rubber.

In museum collections TPU top pieces increasingly exhibit characteristic and advanced degradation, posing conservation challenges when caring for and exhibiting modern and contemporary shoes in otherwise excellent condition. In collaboration with The Museum at FIT (MFIT) and the 2022 *Shoes: Anatomy, Identity, Magic* exhibition, this paper briefly outlines the production of injection molded TPU top pieces, identifies common shoe brands known to use TPU, and provides characterization of the degradation patterns with photographic examples of shoes in MFIT's collection to aid in visual material identification. The paper then presents interventive treatments and preventive conservation solutions employed by MFIT's conservation staff when working with this specific material.

Tacones problemáticos: la identificación, caracterización y tratamiento de capelladas de poliuretano termoplástico en el museo de la colección del *Fashion Institute of Technology*

RESUMEN

Durante la segunda mitad del siglo 20, los plásticos de bajo costo en base de petróleo se infiltraron en la industria del calzado, lo que provocó una rápida disminución en el uso de la mano de obra y productos de cuero costosos. Las nuevas técnicas de fabricación permitieron que las suelas, los tacones y las puntas de los tacones (piezas superiores) se moldearan y adhirieran a los zapatos con moldeo por inyección directa como una operación, o con piezas superiores específicamente, como piezas separadas moldeadas por inyección que luego se unen en el proceso de fabricación. Los principales materiales utilizados en el moldeo por inyección fueron el cloruro de polivinilo, el caucho termoplástico, el poliuretano y el poliuretano termoplástico (TPU).

En las colecciones de moda actuales, las piezas superiores de TPU exhiben una degradación característica y avanzada, lo que plantea desafíos de conservación específicos para el cuidado y la exhibición de zapatos modernos y contemporáneos, en otros tiempos en excelentes condiciones. En colaboración con el Museo del FIT (MFIT) y la preparación de la exposición 2022 *Zapatos: Anatomía, Identidad, Magia*, este documento describe brevemente la producción de puntas de tacones de TPU moldeadas por inyección, identifica marcas de calzado comunes que se sabe que usan TPU y proporciona caracterización de los patrones de degradación con ejemplos fotográficos de zapatos en la colección de MFIT para ayudar en la identificación visual del material. Luego, el documento propone varios tratamientos de intervención y soluciones de conservación preventiva empleadas por el personal de conservación de MFIT cuando trabajaron con este material específico.

01.
INTRODUCTION

Shoes in collections are increasingly exhibiting failing polyurethane elements with visible degradation appearing in as little as five years. Their fast rate of deterioration relative to development of conservation methodologies and the wide range of urethane-based materials is why polyurethane is so difficult to conserve. Thus far studies have been focused primarily on foams leaving insufficient understanding of elastomers, coatings, adhesives, and fibers. This publication compiles research conducted to aid material identification of thermoplastic polyurethane top pieces in MFIT’s collection and presents treatments developed to stabilize, consolidate, and replace them.

02.
TOP PIECES

Heels are made with a durable wearing layer or ‘top piece’: vulcanized rubber in men’s shoes and rubber, thermoplastic rubber (TPR), or thermoplastic polyurethane (TPU) in women's shoes (Abbott 1996). TPU was first used in footwear in the 1970s for top pieces and it remains the best polymer for them. TPU has excellent strength, abrasion resistance, flex properties, shock absorption, low-temperature performance, a higher load bearing capacity than rubbers, and greater impact resistance than most plastics. TPUs can be clear, colored, matte or shiny, and can be molded in complicated shapes maintaining high definition (Ames 2004). While TPR has also been used, it is unsuitable for stiletto heels because of spreading in wear (Abbott 1996). Even so, top pieces are not meant to last the shoe’s lifetime and are replaceable. They are generally molded with a hard thermoplastic material around a metal pin for strength, and a softer thermoplastic grade molded around or on the bottom surface providing traction and shock absorption (figure 1).

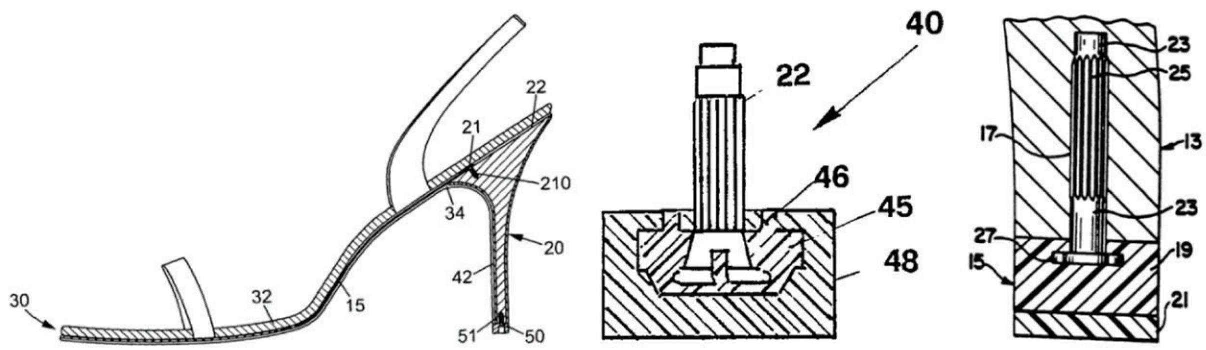


Figure 1. Several varieties of top pieces from patent diagrams. Far left: 50 and 51 point to the pin and two-part molded top piece (Rio 2010). Center: Top piece construction where 45 locates the hard material grade and 48 locates the soft material grade (Bramucci, 1990). Far right: Top piece construction where 19 locates the hard material grade and 21 locates the soft material grade (Lock and Scholl 1994).

03.
THERMOPLASTIC POLYURETHANE (TPU)

TPU is a thermoplastic urethane-based elastomer. Polyurethanes are segmented structures composed of strong, hard segments and elastic, soft segments. The ratio between segments produces materials ranging from flexible elastomerics to brittle high modulus plastics (Drobny 2014). TPU differs from polyurethane in the hydrogen bonds between polymers, reversible in heat resulting in thermoplasticity, as opposed to the irreversible covalent bonds in polyurethane (França de Sá 2017).

TPUs are created by reacting:

- a diisocyanate,
- a polyol or long-chain diol,
- and chain extenders or short-chain diols.

The chain extender and diisocyanate determine the hard segment characteristics (physical properties) (De and White 2001). There are two types of diisocyanates: aromatic and aliphatic. Aromatics are stronger and more common in soles than aliphatics (Ames 2004). The soft segments, made by the polyol, controls TPUs low temperature properties and chemical resistance. Two types are used: polyesters and polyethers. Ester-TPUs give higher physical performance and ether-TPUs are more resistant to hydrolysis. Both can be used for top pieces and ether-ester-TPUs are possible (De and White 2001).

3.1
DEGRADATION PATHWAYS OF TPU

Like all polymers, oxidation is a significant degradation pathway in TPU: ozone is a powerful oxidizing agent, breaking double bonds in elastomers (Shashoua 2009). In general, ester-TPUs are most susceptible to hydrolysis and ether-TPUs are most susceptible to photo-oxidation (França de Sá 2017).

Hydrolysis in both results in chain scission and decreasing molecular weight manifesting as short-term catastrophic cracking and gradual softening (Prakash 1982). Ether-TPUs are subject to acid hydrolysis of the urethane linkages (Drobny 2014). Alkali conditions and microbial attack hydrolyze the ester groups in ester-TPUs resulting in acidic products (adipic acid) appearing on the material surface as a white bloom, becoming more crystalline over time (Verkens 2021). Microbial attack initially becomes visible as discoloration (concealed by coloring) and surface cracks prior to complete failure (BASF n.d.).

Chemical resistance also depends on hardness. Chain scission in water or solvents is preceded by swelling (decreasing hydrogen bonds) (BASF n.d.). Harder grades have more hydrogen bonds and higher chemical stability. Type of diisocyanate determines UV resistance: ether-TPUs formed with aromatic diisocyanates are highly vulnerable to photo-oxidation resulting in chain scission, short-term yellowing (concealed by coloring), and gradual loss of mechanical properties (De and White 2001). Aliphatic diisocyanates and ester-TPUs are more resistant to ultraviolet radiation (Huntsman 2013).

04.
TOP PIECES IN THE MUSEUM AT FIT'S COLLECTION

MFIT has approximately 5,000 pairs of shoes dating from the 17th century to present day. In preparation for the *Shoes: Anatomy, Identity, Magic* exhibition and accompanying publication, 450 pairs representative of the breadth of the collection were photographed, 324 of which were exhibited. Of those exhibited, seven stilettos featured top piece degradation: three Manolo Blahnik, two Charles Jourdan, one Roger Vivier, and one Tokio Kumagaï. Anecdotally, other Charles Jourdan and Manolo Blahnik heels exhibit this characteristic degradation.

Without access to instrumental analytical testing, the Manolo top pieces were identified as polyether-type TPU molded around a metal pin covered in acrylonitrile butadiene styrene by Manolo Blahnik's production team (Collins 2022). Technical literature and degradation suggest the other top pieces are also TPU.

4.1
CHARACTERIZATION OF DEGRADATION

Four major forms of degradation were noted in the seven heels: catastrophic cracking, softening, blooming surface deposits, and crystalline surface deposits (figure 2). Degradation discrepancies between brands suggest material differences, either in the polyol, diisocyanate, or additives, or different agents of deterioration and degradation pathways. Without corroborating instrumental analysis of the polymers, additives, and surface deposits, no clear deductions can be made.

05.
INTERVENTIVE TREATMENT

Treatment was undertaken to stabilize the top pieces and designed to mask the visually detracting material.

5.1
MECHANICAL AND AQUEOUS CLEANING

Most of the top pieces were too fragile to withstand mechanical cleaning: the crystalline deposits were securely adhered. However, the bloom on a Jourdan (87.109.3) was carefully removed with soft mechanical action of a dry cotton swab. While the bloom did return, the material remained hard. No aqueous or solvent cleaning of TPU is advisable: polar solvents and water lead to softening and loss of mechanical properties.

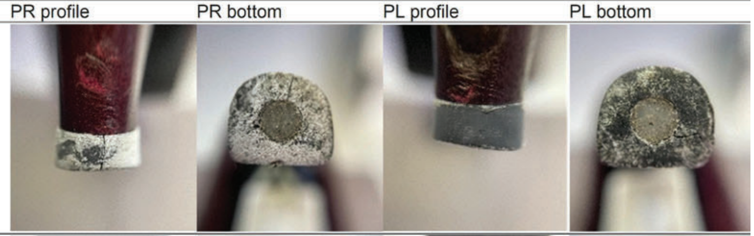
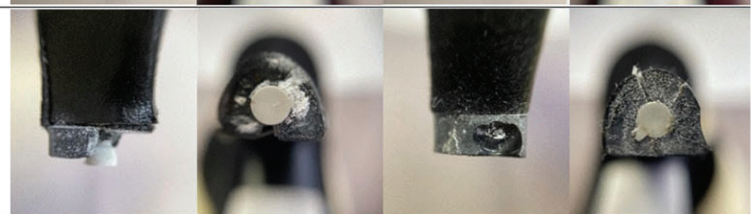
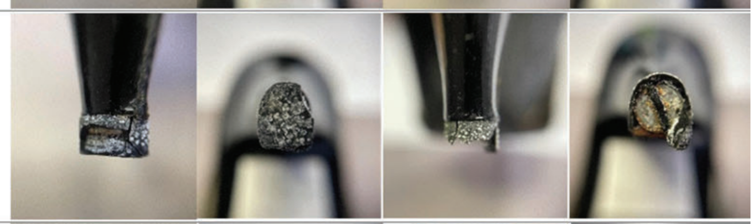
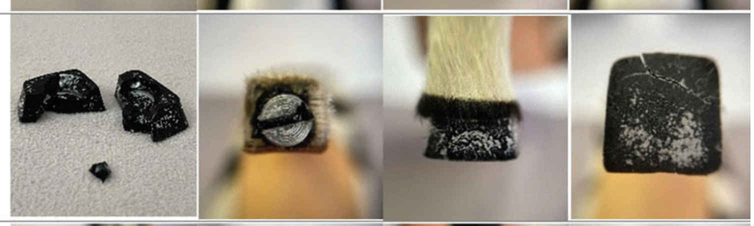
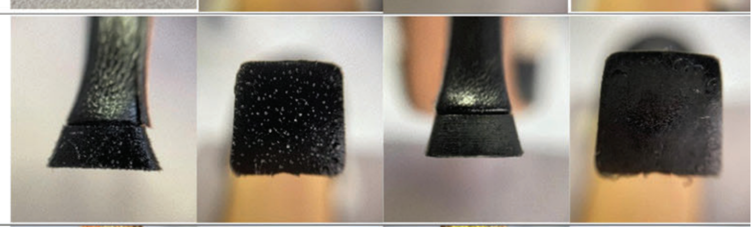
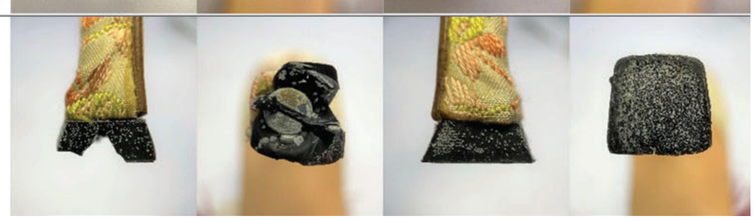
Object	PR profile	PR bottom	PL profile	PL bottom
Accession #: 87.109.3 Maker: Charles Jourdan Date: c. 1975 Material: Likely TPU Degradation: Cracking and blooming *PL top piece previously surface cleaned with mechanical action				
Accession #: 86.171.8 Maker: Charles Jourdan Date: c. 1979 Material: Likely TPU Degradation: Catastrophic cracking and blooming				
Accession #: 91.45.9 Maker: Roger Vivier Date: 1985-1988 Material: Likely TPU Degradation: Cracking, crumbling, mild softening, and crystalline deposits				
Accession #: 87.150.5 Maker: Tokio Kumagaï Date: 1985-1986 Material: Likely TPU Degradation: Cracking, crumbling, mild softening, and crystalline deposits				
Accession #: 98.77.1 Maker: Manolo Blahnik Date: 1998 *never worn Material: Polyether-type TPU formed around a metal pin covered in ABS Degradation: Catastrophic cracking, significant softening, and crystalline deposits				
Accession #: 98.77.2 Maker: Manolo Blahnik Date: 1998 *never worn Material: Polyether-type TPU formed around a metal pin covered in ABS Degradation: Crystalline deposits, mild softening				
Accession #: 98.77.3 Maker: Manolo Blahnik Date: 1998 *never worn Material: Polyether-type TPU formed around a metal pin covered in ABS Degradation: Catastrophic cracking, significant softening, and crystalline deposits				

Figure 2. Characterization of degradation present in the top pieces of the seven stiletto heels included in the exhibition before exhibition.

5.2
CONSOLIDATION

A previously successful treatment by MFIT associate conservator Alison Castaneda was used as a model for consolidation: a wrap of black Japanese paper was adhered around a top piece with 100% Elvace adhesive. The treatment aged well with no visible changes in four years. The wrap effectively holds fractured pieces together and provides future fracture an outlet at the bottom.

In the present treatments, to better conceal the surface deposits, very thin 100% abaca tissue was painted on one side with 100% black Jacquard acrylic paint, left to dry, and heat-set. A pillow and tie secured the shoes upside down and the pieces were carefully reassembled before wrapping. Strips of the painted tissue were cut to the correct height and 100% Lascaux Acrylic Adhesive 498 HV was brushed onto the unpainted face before wrapping around the exterior, overlapping at the front, and leaving to dry. Several combinations of Lascaux (498 HV and 303 HV) were tested on commercially available replacement top pieces before determining that the 498 HV had superior strength.

The treatment successfully consolidated the pieces, supported the shoes, significantly improved their appearance, and held up through the four-month exhibition with no visible changes (figure 3).

Figure 3. Top row: Process images of aligning broken fragments and applying consolidating wrap during treatment of ca. 1979 Charles Jourdan heels (86.171.8). Bottom three rows: Before and after treatment images of the top pieces in profile (left and center columns) and after treatment images of top piece bottoms (right column). Objects from top down: 86.171.8, 91.45.9, 87.150.5.

The angled Manolo top pieces were not conducive to wrapped consolidation. Custom-molded replacement pieces were designed but required mechanical removal of material still attached to the pin. Adhesive reassembly was the least invasive option. 100% Lascaux 498 HV was painted onto the pieces before adhering together. While the adhesive kept the material in one piece on the heel for the length of the exhibition, the TPU's fragility prevented close adhesion creating larger gaps between pieces as no significant pressure could be applied.

5.3
COMPENSATION FOR LOSS

Once no material remains, a replacement fill can be molded to support the heel. 3M 3748 black hot melt adhesive was identified as a fill for failing elastomerics by a study at the Brooklyn Museum (Wight Tyler 2019). The hot melt can be injected into any silicone mold, performs well imitating black elastomerics, and passes the Brooklyn Museum's Oddy Test Procedure (ibid.). Inexpensive replacement top pieces in a range of shapes and sizes can be purchased, matched to the degraded top piece, and used to make silicone molds into which the hot melt is injected to form the replacement. After hardening, a hole or divot can be carved or drilled to accommodate what remains of the pin. This divot holds the heel onto the piece for exhibition but allows it to be removed for storage.

06.
PREVENTIVE CONSERVATION

Polyurethanes degrade even when exposed to controlled conditions. Dark, anoxic, low temperatures at an RH of 45–55% are promising preventive measures, with open storage being the most harmful (França de Sá 2017). In composite objects like shoes, cold storage isn't always appropriate due to the other materials in the object. At MFIT, shoes are stored at general conditions for textiles (18–21°C and 45–55% RH) in closed, but not sealed, shoe boxes.

6.1
ARCH SUPPORT

Heels are supported in shoeboxes with custom arch supports like those detailed in MFA Boston's Costume Accessory Conservation Project (Gausch and Thompson n.d.). Ethafoam is custom carved to the shape of the arch, padded, and covered with Tyvek. The arch holds the shoe above the bottom surface, and a thin sheet of Ethafoam is inserted under the toe box allowing the top piece to float (figure 4).

Figure 4. Custom arch support for Manolo Blahnik heels (98.77.1).

07.
CONCLUSION

This research provides a starting point in identifying, treating, and caring for TPU components in composite objects. Further instrumental analysis of polymers, additives, and degradation products is needed, but this study does provide a foundation to monitor TPU degradation overtime and evaluate the long-term success of the presented treatments.

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MATERIALS AND SUPPLIERS

L-2 Spider tissue, 9 gm2
University Products
517 Main St
Holyoke, MA 01040
USA
+1 800 628 1912
www.universityproducts.com

Jacquard light body opaque acrylic paint
BLICK Art Materials
1849 Green Bay Rd Suite 310
Highland Park, IL 60035
USA
www.dickblick.com

Lascaux 498 HV
TALAS
330 Morgan Ave
Brooklyn, NY 11211
USA
+1 212 219 0770
www.talasonline.com

3M 3748 Black hot melt adhesive
3M Center
St. Paul, MN 55144-1000
USA
+1 888 364 3577
www.3m.com

33700 EasyMold silicone putty
Joann Fabric and Crafts
5555 Darrow Rd
Hudson, OH 44236
USA
www.joann.com

Replacement heel tips
Amazon
410 Terry Ave N
Seattle, WA 98109-5210
USA
www.amazon.com

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