Dry-Peelable Temporary Protective Coatings from Waterborne Self-Crosslinkable Sulfourethane–Silanol Dispersions

Kevin Lewandowski, Larry R. Krepski, Daniel E. Mickus

Corporate Materials Research Laboratory, 3M Company, St. Paul, MN 55144-1000

ABSTRACT: Novel temporary protective coatings were prepared by the addition of release additives to waterborne polyurethane dispersions. New types of self-crosslinkable sulfourethane–silanol (SUS) dispersions were utilized as the peelable coatings. These dispersions are stable, low-volatility organic chemical (VOC) waterborne dispersions that spontaneously crosslink upon drying without extra additives or processing steps. Tensile strengths up to 6000 psi with elongations between 300–600% were obtained for the crosslinked films. The adhesion of the films to a variety of substrates can be controlled by the addition of hydrophilic additives, including glycerol, oligomers of glycerol, and poly(ethylene glycol) derivatives.

Alternatively, hydrophobic additives that are water dispersible, such as paraffin waxes and sulfated castor oil, can also be used to control adhesion. In addition, this technique can be utilized for the release of films derived from a wide variety of waterborne urethane dispersions, including carboxylated polyurethane ureas. The removable coatings are useful for the temporary protection of plastic surfaces during thermoforming processes. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1443–1449, 2004

Key words: polyurethanes; dispersions; adhesion; ionomers; coatings

INTRODUCTION

Temporary protective coatings are widely used to protect the surfaces of various products, parts, or components during their manufacture, assembly, and shipping. These coatings are used to prevent surface damage such as scratching, nicking, pitting, staining, or corrosion, and are also used to simplify or enhance cleaning operations, whereby surface contamination is eliminated by the removal of the temporary coating. Temporary coatings are also used to protect the surfaces of automobiles and boats during transportation from a manufacturing site to a retail location.

Removable coatings may also be applied to various surfaces that tend to become contaminated with dirt, oil, or grease through normal use. These products include floors, countertops, shower stalls and appliances. In these applications, the temporary protective coating becomes contaminated or dirty, and the removal of the coating greatly simplifies cleaning of the surface.

A number of approaches that utilize liquid solutions or dispersions as temporary protective coatings have been described. These include solvent-based paints,[1] water-based vinyl-acrylic and acrylic copolymer emulsions,[2,3] poly(vinyl alcohol) films,[4] and water-based polyurethane dispersions.[5–7] Many of these examples are films that are subsequently removed by dissolution in water.

The adhesion of plastics in molding applications can be controlled by the incorporation of the appropriate release agents.[8,9] The release agents, including metal stearates, fatty acids,[10] alkyl phosphates, and silicones, migrate to the surface during molding operations and prevent the polymer from sticking to the mold.

It has recently been found that the addition of release additives to aqueous polyurethane dispersions provides coating compositions that are effective for the temporary protection of the surfaces of various products or components. The coating can be applied in the liquid form as a water dispersion without substantial amounts of organic solvents, and it forms a protective coating when the water evaporates or is removed. The resulting protective coating can be removed by stripping or peeling from the surface without the application of an aqueous or non-aqueous stripping or washing solution. Removable coatings are also useful for the temporary surface protection of plastic sheets during thermoforming operations, after which the coatings may be removed by peeling.

EXPERIMENTAL

Materials

The following reagents were used without further purification: poly(caprolactone diol) (TONE 0201 hy-

droxyl number = 262; Dow Chemical, Midland, MI); 3-aminopropylmethyldiethoxysilane (UCT, Inc., Bristol, PA); Hexapol G-3 and Hexapol G-6 (Hexagon Enterprises, Inc.); Rheolate 278 (Rheox, Inc., Hightstown, NJ); dibutyltin dilaurate, ethylene glycol, isophorone diisocyanate (IPDI) (Aldrich, Milwaukee, WI); Bayhydrol 110, 123, PR 240, and 140 AQ (Bayer Corporation, Pittsburgh, PA); Witcobond W-232, W-505, and W-507 (Crompton Corporation); and Neo-Rez R-972, R-960, R-9367, R-9649, R-9679 (NeoResins, Wilmington, MA).

Preparation of Silanol-Terminated Polyurethane–Urea in Water

A mixture of sulfonated poly(caprolactone diol)[11] (370.6 g, 0.56 mol based on a hydroxyl equivalent weight of 333 for the mixture), poly(caprolactone diol) (TONE 0201, 170.3 g, 0.32 mol), ethylene glycol (44.9 g, 0.72 mol), IPDI (395.6 g, 1.78 mol), dibutyltin dilaurate (0.63 g, 0.93 mmol) and methyl ethyl ketone (528 g) was heated to 80°C with stirring. After 4 h, an aliquot was removed for titration. Determination of the isocyanate equivalent weight of the reaction product was as follows: A sample (6.50 g) of the product mixture was mixed with methyl ethyl ketone (20 mL), and a solution of dibutylamine (4 mL of a 1.71M solution in methyl ethyl ketone) was added. After stirring for 15 min, methanol (20 mL) and 4-5 drops of bromophenol blue indicator were added. The solution was titrated to a yellow endpoint with a 1.0M hydrochloric acid solution in water, and an isocyanate equivalent weight was calculated. A solution of 3-aminopropyltriethoxysilane (78.6 g, 0.36 mol, equimolar to the remaining NCO groups) in methyl ethyl ketone (530 g) was added to the reaction mixture, which was maintained at 80°C for an additional 15 min. Water (1200 g) was added with vigorous stirring over a 15 min period, and methyl ethyl ketone was subsequently distilled from the mixture under reduced pressure to produce a dispersion (44% solids) of a silanol-terminated polyurethane-urea in water. Modulated differential scanning calorimetry (MDSC) and tensile property analyses made of a spun cast film produced from the dispersion indicated that the polymer had a temperature of glass transition (T_g) of 12°C and a tensile strength of 20.3 MPa (2945 psi) at 418% elongation.

Silanol-terminated polyurethane dispersions with varying T_g values were prepared by varying the relative molar amounts of poly(caprolactone diol), ethylene glycol and IPDI.

Preparation of Peelable Coatings

To 100 g of the silyl-terminated sulfo(polyester–urethane) were added 2.4 g (5 wt %) of glycerol. The mixture was agitated briefly by shaking, then allowed to stand at room temperature for 1 h. The dispersion was coated onto a glass plate at a wet thickness of about 0.05 to 0.5 mm (2 to 20 mil) and allowed to dry to form a clear, tough coating, which could be easily removed in a sheet by peeling from the glass plate. Coating formulations with varying urethane dispersions and release additives were prepared in a similar manner.

A rheologically modified (thickened) formulation that was useful for producing thick coatings was prepared as follows. To a silyl terminated sulfo(polyester–urethane) dispersion [121 g, T_g of 30°C and tensile strength of 31.3 MPa (4549 psi) at 345% elongation; 46% solids] was added glycerol (2.75 g), ethanol (12.4 g), and Rheolate 278 (1.62 g). The mixture was agitated for 1 h by tumbling and then allowed to stand overnight at room temperature. The viscosity of the formulated dispersion was determined to be 1812 cP at 25°C, as measured with a Brookfield LV-3 spindle at 50 rpm.

Characterization

Free-standing films were obtained by spin casting in a teflon cup for 17 h at 40°C. The tensile strength and elongation were determined on a Sintech 20 Instron testing machine. The samples were stamped out of cast films using the ASTM 1708 standard (gauge length of 14.29 mm) and were tested at room temperature using a crosshead speed of 2.54 cm/min. The T_g values of the samples were determined by DSC analysis with a TA Instruments 2920 MDSC. A linear heating rate of 5°C/min was applied, with a single heating profile ranging from −125°C to 175°C.

Peel adhesion was measured with an IMASS SP-2000 peel testing instrument, available from Instrumentor's, Inc., Strongsville, OH. In the trials, the force was expressed as Newtons per decimeter of width (N/dm) of film and represents the average of four determinations. The procedure followed was: (1) the polyurethane dispersion was coated onto a clean glass test plate, completely dried, cut into 26 mm wide strips, and one end of each strip was peeled from the substrate; (2) the free end of the specimen was doubled back, nearly touching itself, so that the angle of removal was 180°, and the free end was attached to the adhesion tester scale; (3) the glass test plate was clamped in the jaws of the tensile testing machine, which moved the plate away from the scale at a constant rate of 0.3 m/min; (4) the scale reading in Newtons ("peel value") was recorded as the coating was peeled from the glass surface.

Thermoforming Process

The thermoforming device utilized was a Formech™ 450 vacuum thermoforming machine, available from
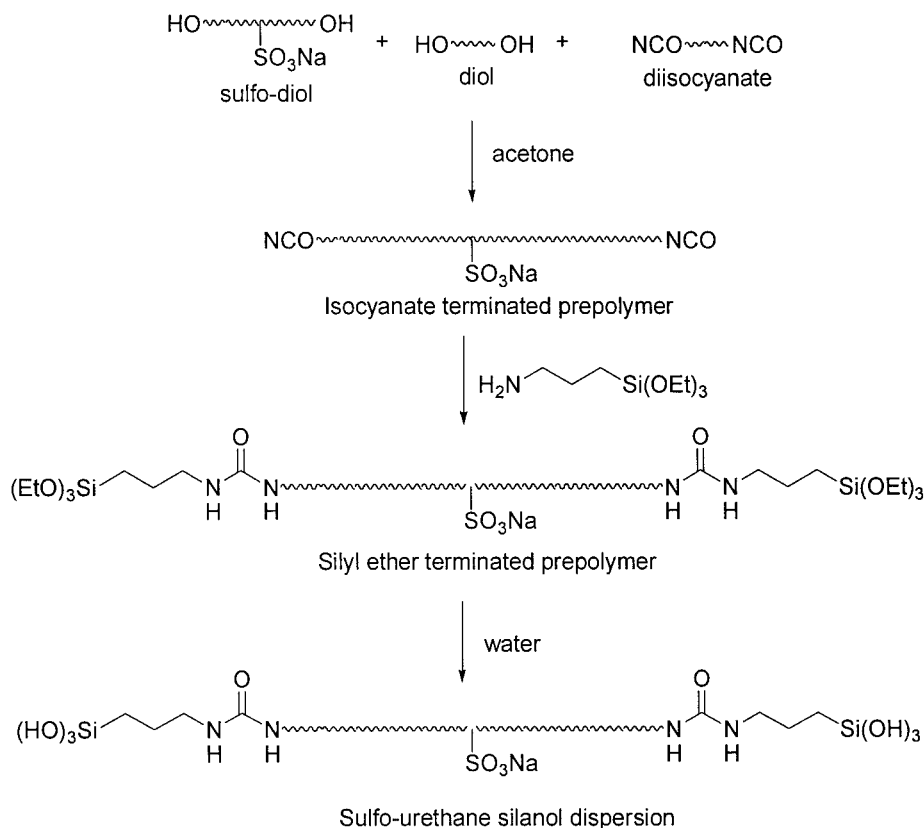
Scheme 1

Formech, Inc., Kings Park, NY. The plastic sheeting (available from McMaster-Carr Supply Co., Elmhurst, IL) used in these experiments was acrylonitrile–butadiene–styrene [ABS, 0.60 mm (23 mil) thickness], high impact polystyrene [HIPS, 0.80 mm (31 mil) thickness], polypropylene [1.6 mm (63 mil) thickness], polyethylene terephthalate copolymer [PETG, 1.6 mm (63 mil) thickness], polycarbonate [1.6 mm (63 mil) thickness], poly(methyl methacrylate) [PMMA 0.80 mm (31 mil) thickness], and poly(vinyl chloride), type 1 [PVC, 1.6 mm (63 mil) thickness]. A square piece of sheeting of approximately 20 × 20 cm was coated with the thickened SUS formulation at a wet thickness of approximately 0.25-0.30 mm (10–12 mil). Temperature controls of the three heating zones of the Formech 450 were set to high. The mold object used was a teflon dome of 7.6 cm diameter by 2.5 cm height. The coated pieces of plastic sheeting were clamped into the forming area of the thermoforming machine, either with the coated side of the sheet up (towards the heating element and away from the mold object), or with the coated side of the sheet down (towards the mold object). The heating element was moved into place, and the plastic sheeting was heated until it visibly started to soften, as observed from the viewing port. The heating element was then removed, the mold object was raised into the plastic sheet, and vacuum

was applied until the plastic sheeting conformed to the mold object. Vacuum was released, and the coated, thermoformed sheet was removed.

RESULTS AND DISCUSSION

SUS Dispersions

Previously, it has been shown that sulfonated polyurethane oligomers terminated with silyl end groups can be utilized for the preparation of stable, crosslinkable, low VOC coatings with excellent physical properties.[11] In this study, the acetone process was used to prepare SUS–polyurethane dispersions (Scheme 1). A sulfonated caprolactone diol was formulated with a poly(caprolactone diol), ethylene glycol, and IPDI and reacted in acetone or methyl ethyl ketone to generate an isocyanate-terminated prepolymer. The isocyanate-terminated prepolymer was then reacted with aminopropyl triethoxysilane to give a silyl ether terminated polyurethane oligomer. The addition of water with rapid agitation, followed by the removal of the solvent, resulted in a stable SUS dispersion in water devoid of volatile organic chemicals. Stable SUS dispersions can be up to 50 wt % solids in water with low viscosity (200–300 cP), and they typically exhibit particle sizes between 100–400 nm. Coatings of the SUS
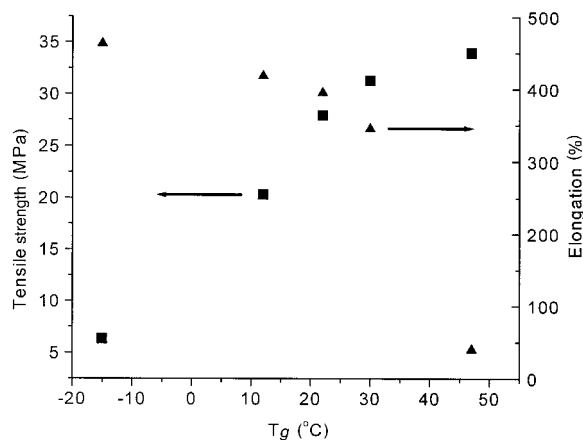
Figure 1 Tensile strength and elongation versus T_g values for SUS dispersions.

Figure 2 Peel average versus glycerol weight percent (SUS, T_g 12°C, 0.2 mm film thickness).

dispersion spontaneously crosslink through the formation of silyl ether linkages upon removal of water. No additional additives or catalysts are needed for crosslinking to occur.

The mechanical and high-temperature properties of polyurethanes are typically modulated by changing the ratio of hard segment components. The excellent physical properties observed for polyurethanes are typically attributed to the formation of hard segment microcrystalline domains within an amorphous polymer matrix.[12] A series of SUS films with different T_g values were prepared by simply varying the amounts of sulfonated diol, poly(caprolactone diol), ethylene glycol, and IPDI. Higher relative amounts of hard segments of ethylene glycol and IPDI result in an increase in T_g. Figure 1 shows that the physical properties of the resulting crosslinked films can be controlled within a broad range.

Typically, SUS films exhibit excellent adhesion to a variety of surfaces, including glass, polyester, and polystyrene. This is most likely due to the reaction of siloxane end groups with reactive surface groups on the substrate. It is desirable to control the level of adhesion for applications such as temporary protective coatings.

Release Additives

Many coatings for temporary protection are either removable with water (water-soluble polymers) or based on polymers that have been designed to exhibit release properties (such as silicones).[1–7] Alternatively, we have identified water-soluble additives that can be added to polyurethane dispersions and will migrate to the coating–substrate interface to control the level of adhesion. Aqueous, sulfonated polyurethane dispersions containing hydrophilic polyol release additives such as glycerol are effective coating compositions for
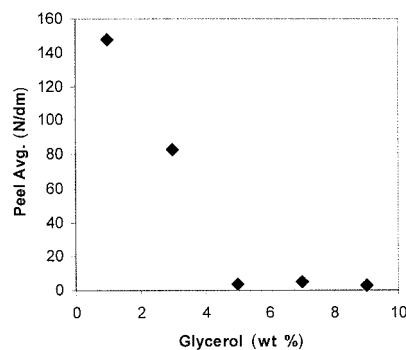
the temporary protection of surfaces of various products or components. The protective coatings can be removed by peeling from the surface without the need for any type of aqueous or non-aqueous stripping or washing solution.

One of the most effective release agents is glycerol. Figure 2 shows the peel strength necessary to remove a SUS film (thickness of 0.2 mm) with a T_g of 12°C from a glass substrate. By controlling the level of glycerol in the coating, the force necessary to peel the film off of the substrate can be controlled within a broad range. There is a large decrease in the peel force at glycerol loadings above 4 wt %. In general, it was found that the T_g of the crosslinked polyurethane film has little effect on peelability. However, if the T_g is below 0°C, the films tear easily, and at T_g values above 40°C the films are too brittle. The advantages of glycerol as a release agent include its high solubility in aqueous polyurethane dispersions and the subsequent formation of clear, defect-free coatings.

The effects of film thickness and substrate were also investigated. Table I shows that SUS films are easily peeled (peel average below 5 N/dm) from a glass substrate at thicknesses between 0.05 and 0.30 mm. The film thickness does not have a large impact on the peel force; however, it is necessary to have a thickness of at least 0.05 mm to prevent tearing of the film as it is peeled. In addition, the films can be removed from a variety of other substrates, including polyester films,

TABLE I
Peel Average for Removable SUS Films

Substrate	Dry Film Thickness[a]	Peel Avg, (N/dm)
Glass	0.05 mm (2 mil)	3.7
Glass	0.10 mm (4 mil)	3.9
Glass	0.20 mm (8 mil)	3.4
Glass	0.30 mm (12 mil)	4.8
Aluminum	0.10 mm (4 mil)	25.6
Polyester	0.10 mm (4 mil)	6.0
Ceramic tile	0.10 mm (4 mil)	2.8

[a] SUS T_g 12°C; 5 wt % glycerol

TABLE II
Peel Average for SUS Films

Release Additive	Wt % Release Additive	Peel Avg, (N/dm)
Triglycerol	5	2.9
Hexaglycerol	5	2.6
SC-PDMS-EO[a]	5	24.1
Block-PDMS-EO[b] (1)	5	33.0
Block-PDMS-EO[c] (2)	5	63.0
Polyethylene glycol 600	5	94.0
Ethylene glycol	5	d
Diethylene glycol	5	d
Triethylene glycol	5	153.3
Polyethylene glycol 2000	5	43.1
PEG 2000 monomethyl ether	5	64.1
PEG 5000 mono methyl ether	5	32.3
Pentaerythritol ethoxylate (1:3)[e]	5	92.3
Pentaerythritol ethoxylate (1:5)[f]	5	62.1
Pentaerythritol ethoxylate (1:15)[g]	5	60.0
Jonwax 26[h]	5[i]	121.2
Jonwax 26[h]	10[i]	108.2
Actrasol C75[j]	5	146.8

[a] poly[dimethylsiloxane-co-methyl(3-hydroxypropyl)siloxane]-graft-poly(ethylene/propylene glycol); [b] poly(dimethylsiloxane) ethoxylated, hydroxypropoxylate end-capped; [c] poly(dimethylsiloxane) ethoxylated, dihydroxy terminated; [d] adhesion was too great for films to be peeled from the substrate; [e] pentaerythritol ethoxylated with 3 moles of ethylene oxide, number average molecular weight 270; [f] pentaerythritol ethoxylated with 5 moles of ethylene oxide, number average molecular weight 355; [g] pentaerythritol ethoxylated with 15 moles of ethylene oxide, number average molecular weight 797; [h] 26% solids polyethylene/paraffin wax emulsion; [i] weight percent relative to urethane dispersion solids; [j] sulfated castor oil available from Actrachem, Bedford Park, IL.

aluminum and ceramic tile. The peel average is highest for SUS film on an aluminum substrate.

In addition to glycerol, other release additives may be added to the aqueous polyurethane dispersions to render the coatings removable. These include higher oligomers of glycerol, such as triglycerol (Hexapol G-3) and hexaglycerol (Hexapol G-6), poly(ethylene glycol), poly(ethylene glycol) ethers of molecular weights about 600 to 8000, pentaerythritol ethoxylate of molecular weights about 250 to 1000, and ethoxylated polydimethylsiloxanes. Table II shows the peel force necessary to remove a SUS coating (T_g of 12°C and film thickness of 0.20 mm) from a glass substrate using a variety of these release additives. In general, the additives containing poly(ethylene glycol) segments are less effective than those containing glycerol at comparable weight loadings in the coating. There is a molecular weight dependency with respect to adhesion for poly(ethylene glycol) additives. For molecular weights below 600, poly(ethylene glycol) is ineffective as a release agent. At higher molecular weights, the additive is more effective; however, over time, linear poly(ethylene glycol) tends to crystallize in the dried films.

In addition to these hydrophilic polyols, other useful release additives include typical mold release additives that are soluble or dispersible in water, such as sulfated castor oil and dispersed waxes. However, hydrophilic release additives are superior with respect to ease of film removal and clarity of coatings.

Aging Studies

A disadvantage of using glycerol in the coatings is the loss of the release additive at elevated temperatures over extended periods of time. The glycerol can slowly evaporate from the coating, resulting in film adhesion variability. This problem can be solved by using higher boiling oligomers of glycerol to provide peelable coatings that remain removable after long periods of heating.

Dispersions with 5 wt % of the specified release additive were prepared from a silyl terminated sulfo(polyester–urethane) dispersion and glycerol, triglycerol, and hexaglycerol. Triglycerol (Hexapol G-3™) has the following approximate composition: 13% glycerol, 17% diglycerol, 51% triglycerol, 11% tetraglycerol, 5% pentaglycerol, and the remainder other glycerols. Hexaglycerol (Hexapol G-6™) has the following approximate composition: 6% diglycerol, 28% triglycerol, 64% hexaglycerol, and the remainder other glycerols. The Hexapol G-3 and Hexapol G-6

Polyurethane Dispersion[a]	Peel Avg (N/dm)
Bayhydrol 110	7.2
Bayhydrol 123	4.3
Bayhydrol PR 240	4.2
Bayhydrol 140 AQ	4.0
Witcobond W-232	1.9
Witcobond W-505	6.0
Witcobond W-507	0.5
NeoRez R-972	2.0
NeoRez R-960	1.4
NeoRez R-9367	1.7
NeoRez R-9649	0.6
NeoRez R-9679	0.9

[a] Film thickness was 0.13 mm (5 mil); 5 wt % glycerol.

materials were dissolved in a small amount of water before mixing with the silyl terminated sulfo(polyester–urethane) dispersion.

The dispersions were coated onto glass plates with a wet thickness of approximately 0.13 mm and allowed to dry at room temperature. The coated plates were then placed in an oven at 60°C. Peelability of the dried films was investigated by periodically removing the coated plates from the oven, allowing them to cool to room temperature, slicing off a 10 cm (0.4 in) wide strip of the film with a razor blade, and peeling the film from the glass. If the films were peelable, the coated plates were then returned to the oven for longer aging. It was found that the films with glycerol as the release agent were still peelable up to about 4 days in the 60°C oven. The films containing Hexapol G-3 were peelable up to about 140 days in the 60°C oven, and the films containing Hexapol G-6 remained peelable after 180 days in the 60°C oven. Therefore, higher oligomers of glycerol are more effective release agents, even after extended periods of time at elevated temperatures.

Additional Polyurethane Dispersions

In addition to SUS dispersions, many other types of aqueous urethane dispersions can be utilized as temporary protective coatings. For example, carboxylate functional polyurethane–ureas prepared from diisocyanates, polyols, and carboxylic acid diols can be utilized. The preparation and description of these aqueous polyurethane dispersions is well known and is described in a number of reviews.[13–16] Glycerol was added at a 5 wt % concentration to a variety of commercial anionic waterborne urethane dispersions. The peel force necessary to remove the films is shown in Table III. In all cases, films were obtained that were easily removed from the glass substrate. Therefore, this method of release is generally effective for many types of waterborne urethane dispersions.

Thermoforming

Thermoforming is the process of manufacturing products from thermoplastic sheets, whereby the plastic sheet is heated to its softening point, formed in a mold by the action of pressure or vacuum into the desired shape, and then be separated from the mold.[17] Durable, high-gloss, plastic sheet goods can be produced by thermoforming, and the plastic surface is subject to damage caused by contact with the mold. Slight imperfections in the mold can result in deformations and scratches or reduction of glossiness of the plastic surface of the thermoformed part. One way to prevent this damage is to protect the surface of the plastic by coating it with a temporary, removable, protective coating that will survive the thermoforming process (Fig. 3). The protective coating is in close contact with the substrate to provide a uniform, defect-free thermoformed surface on the substrate.

A coating formulation containing SUS, glycerol, ethanol, and Rheolate 278 (thickener) was prepared for the thermoforming experiments. This formulation exhibits a higher viscosity that is useful for producing thicker coatings. The SUS coating (wet thickness of approximately 0.25-0.30 mm) was applied to various types of plastic sheeting commonly used for thermoforming processes, including ABS, HIPS, polypropylene, PETG, polycarbonate, PMMA, and PVC. The sheets were then used in a thermoforming process using a teflon block as the mold object. After cooling to room temperature, the temporary protective film could be easily peeled from the plastic sheeting in all cases. When the plastic sheeting was thermoformed with the protective coating facing the mold object, it was seen upon removal of the film that the film had protected the surface of the plastic sheeting from abrasion or de-glossing.

CONCLUSIONS

Temporary protective coatings were prepared by the addition of release additives to waterborne polyurethane dispersions. A new type of self-crosslinkable,
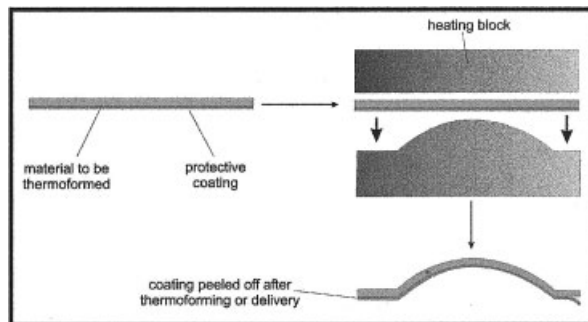

Figure 3 Thermoforming process.

sulfonated urethane dispersion was developed for these coatings. Crosslinked films of these dispersions have high tensile strength (up to 6000 psi) with elongations between 200–500%, and the physical properties are easily adjusted through formulation of the monomers used in the urethane polymerization. The addition of hydrophilic release agents, including glycerol and oligomers of glycerol, reduces adhesion of the films to a variety of substrates, including polyester, glass and aluminum. This concept can also be applied to a variety of commercial waterborne polyurethane dispersions for the simple preparation of temporary protective coatings. The protection of plastic surfaces during thermoforming operations was demonstrated using the temporary peelable coatings.

References

1. Ozeki, K.; Wada, T.; Ito, K.; Tomimori, T.; Takagi, I.; Nekado, M. U.S. Pat. 4,341,687 (1982).
2. Swidler, R. U.S. Pat. 6,124,044 (2000).
3. Salamon, P. A. U.S. Pat. 5,945,462 (1999).
4. Blaine, S. J.; Wilson, K. K. U.S. Pat. 5,494,702 (1996).
5. Muller, H.; Gruttmann, H.; Petzoldt, J.; Muller, H.; Meixner, J.; Kurek, G. Can. Pat. App. CA 2,314,523 (2000).
6. Muller, H.; Gruttmann, H.; Casselmann, H.; Muller, H.; Petzoldt, J.; Bock, M. U.S. Pat. 5,965,195 (1999).
7. Muller, H.; Gruttmann, H.; Casselmann, H.; Muller, H.; Petzoldt, J.; Bock, M. U.S. Pat. 6,172,126 (2001).
8. Owen, M. J. In Encyclopedia of Polymer Science and Engineering; Mark, H., Bikales, N., Overberger, C., Menges, Eds., John Wiley & Sons: New York, 1985; Vol. 14, pp 411–421.
9. Pritchard, G. In Plastic Adhesives: An A-Z Reference; Pritchard, G. Ed.; Chapman & Hall: London, 1998; pp 559-560.
10. Schneberger, G. L.; Nakanishi, T. Polym Eng Sci 1981, 21, 381.
11. Lewandowski, K.; Krepski, L. R.; Mickus, D. E.; Roberts, R. R.; Heilmann, S. M.; Larson, W. K.; Purgett, M. D.; Koecher, S. D.; Johnson, S. A.; McGurran, D. J.; Rueb, C. J.; Pathre, S. V.; Thakur, K. A. M. J Polym Sci Part A: Polym Chem 2002, 40, 3037.
12. Wei, X.; Yu, X. J Polym Sci Part B: Polym Phys 1997, 35, 225.
13. Dieterich, D. Prog Org Coat 1981, 9, 281.
14. Rosthauser, J. W.; Nachtkamp, K. J Coated Fabrics 1986, 16, 39.
15. Dieterich, D.; Uhlig, K. In Ullmann's Encyclopedia of Industrial Chemistry; Elvers, B., Hawkins, S., Schulz, G., Eds.; VCH Publishers Inc.: New York, 1992; Vol. A21, pp 665–716.
16. Ramesh, S.; Tharanikkarasu, K.; Mahesh, G. N.; Radhakrishnan, G. J Macro Sci, Rev Macromol Chem Phys 1998, C38, 481.
17. McDonald, J. In Encyclopedia of Polymer Science and Engineering; Mark, H., Bikales, N., Overberger, C., Menges, G., Eds.; John Wiley & Sons: New York, 1985; Vol. 16, pp 807–832.