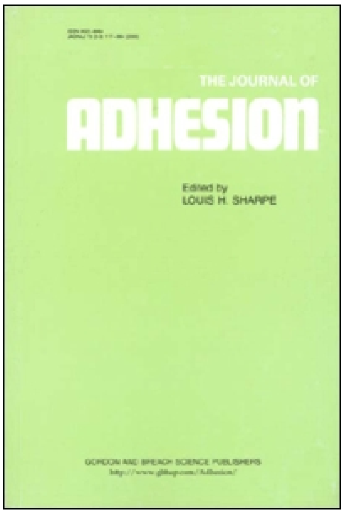

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Polyurethane Solvent-Based Adhesives for Footwear Applications

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NOTE

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Polyurethane solvent-based adhesives with and without tackifier having different solid contents were prepared. Viscosity of adhesives was found to increase with increasing resin content. Peel strengths of adhesives before and after aging were measured on PVC-Leather substrates and TPR-Leather substrates. It is found that the tackifier improves the adhesive strength of the polyurethane. In the case of TPR-Leather substrates all adhesives give good performance immediately on application of adhesive whereas in the case of PVC-Leather substrates good results are achieved only after 24 hrs of application. Shelf-life of the adhesives is found to be 6 to 12 months.

Keywords: Polyurethane; tackifier; adhesive; PVC sole; TPR sole; leather; footwear application

INTRODUCTION

Polyurethane (PU) adhesives are chosen for bonding footwear materials when polychloroprene adhesives are not satisfactory. This is the case with soles based on PU elastomers, thermoplastic rubber (TPR) and lightly-filled and highly-plasticized PVC. They are also

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often used to bond synthetic shoe uppers based on textiles coated with plasticized PVC [1].

Among the variety of PU adhesives, solvent-based adhesives are advantageous over one- and two-component reactive adhesives and hot-melt adhesives since they can conveniently be handled and used. Single-component reactive adhesives always suffer from poor shelf-life. Two-component reactive adhesive systems require accurate metering facilities for use. Hot-melt adhesives require specially-designed machinery. Considering all these facts, development of solvent-based PU adhesives with properties comparable with reactive and hot-melt adhesive systems would be commercially attractive. To achieve this, the objective of the present investigation, solvent-based PU adhesives along with a tackifier were studied. Because the tackifier facilitates bond formation and, therefore, improves the strength by increasing the cohesive strength of the adhesive, it was included in the formulations. With a view to improving the adhesive strength on plasticized PVC, it is advantageous to use a tackifier since it is an appropriate compromise substance that increases the elastic modulus of the adhesive and, therefore, increases strength during detachment. The selected tackifier was a hydrocarbon-based, low-molecular-weight polymeric resin designated Picotac®. Since there are no reactive functional groups in the Picotac, it can be blended with the PU resin without affecting the viscosity or shelf-life of the finished product.

The polyurethane selected for this study was Uthane-5731, which is a polyester-based thermoplastic PU. Uthane-5731 is an ideal adhesive for bonding shoe soles to shoe uppers for the following reasons [2].

1. It bonds to a wide range of substrate materials such as leather, PVC, PU, TPR, etc.
2. It provides excellent green strength for subsequent handling of the adherends.
3. It is soluble in many commonly-available solvents.
4. It has an ideal open tack time (not too long or too short).

EXPERIMENTAL

Materials

A thermoplastic and highly-crystallizable polyurethane resin, Uthane-5731 ($Mn = 3.9 \times 10^4$, $Mw = 5.0 \times 10^4$ and polydispersity = 1.280), was obtained from Urethanes India Limited. Picotac® (Mw = 1500) was obtained from Hercules Co, USA. Commercial grade acetone and methyl ethyl ketone were used without further purification. The halogenating reagent was prepared by dissolving 2.2 gm of Halopowder (Mydrin Shoe Components) in 100 ml of methyl ethyl ketone.

Preparation of Polyurethane Adhesives

A 250 ml capacity reaction kettle fitted with a mechanical stirrer was charged with the calculated amount of solvents. Controlled agitation was started. To the reaction kettle, the required quantity of polyurethane resin granules was added slowly for 4 to 6 hours. The agitation was continued until the highly-viscous solution became clear. The srirrer speed was maintained at 175 – 200 rpm throughout the experiment. In the case of the formulations involving tackifier, the calculated amount of Picotac was added to the solvent prior to the addition of polyurethane granules.

TESTING PROCEDURE FOR PU ADHESIVES

Viscosity

The viscosities of the adhesives were measured at 30°C, using a LVT model Brookfield viscometer. The spindle number was 2 and rpm was 6 and 3.

Specimen Preparation [3]

PVC and TPR (Chemcrown India Ltd.) soles were obtained from the local market. Buff upper leather was obtained from CLRI. Both the PVC and TPR were sized to the specification covering 70 mm width, 60 mm length and 3 – 3.5 mm thickness using a roughing machine (Bombelli, Italy). The leather substrate was sized similarly to the synthetics except for the thickness.

Before applying adhesives to the sole materials, the TPR and PVC substrates were subjected to halogenation and solvent wiping (MEK) respectively. The adhesives were applied (using a brush) on the leather substrate and PVC immediately after solvent wiping and the substrates were allowed to dry for 15 min. After solvent evaporation, the substrates were subjected to heat reactivation in an activator capable of giving 80°C within 10 seconds. Subsequently, the substrates were fixed together and were subjected to 50 kgf/cm^2 of pressure for 10 sec. The experimental conditions for preparing TPR – Leather substrates were identical to the procedures for PVC – Leather substrates except that a 1-hour time was allowed to elapse between halogenation and adhesive application. After 1 hour the adhesive specimens were cut into 4 pieces having identical dimensions and tested for peel strength.

Peel Strength [4]

The peel strength of the adhesives after one hour, 24 hours and 168 hours from the time of application and of the adhesives subjected to the ageing test were measured on an Instron series IX automated materials testing system 1.04, with a cross-head speed 100 mm/min. The values are reported in kg/cm.

Ageing

The specimens were kept in an oven in such a way as to avoid direct contact with the metal surface of the oven and maintained at 50°C for 14 days. At the end of the experiment the specimens were removed from the oven and subjected to the peel strength analysis.

Shelf-life

25 gms of the adhesives were placed in a 50 ml reagent bottle and stoppered in an inert atmosphere. The flow behaviour of the adhesive was observed monthly for six months and the observations are described in the discussion.

RESULTS AND DISCUSSION

Uthane-5731 is a thermoplastic, polyester-based polyurethane resin soluble in acetone and methyl ethyl ketone. Bulk addition of resin to the solvent was avoided since it forms lumps and takes a longer time to give a clear solution. The formulation details and properties (viscosity and solids content) of the adhesives are given in Table I. The solid content is varied from 17.5% to 27.5%.

Viscosity and peel strength are the important limiting factors for adhesives used for shoe assembling. Viscosity, of course, increases with increasing polyurethane content. The solution viscosity of a polymer is sensitive to both the concentration and the solvents used. The effect of concentration, solvent and solvent mixtures on the viscosity of Uthane-5731 has been reported [2]. It was found that the tackifier did not improve the viscosity. This is due to the low molecular weight ($M_w = 1.5 \times 10^2$) of the tackifier compared with high molecular weight polyurethane resin ($M_w = 5.0 \times 10^4$).

All of the adhesives show good green strength for TPR-Leather substrates (Tab. III) whereas they fail for PVC-Leather substrates

TABLE I Formulation and properties of PU adhesives

S.No	*Formulation*		*Properties*	
1	Acetone	37.50 pbw	Brookfield viscosity (cps)	2950
	MEK	37.50 pbw	Solids content (%)	25
	Uthane-5731	25.00 pbw		
		100.00 pbw		
2	Acetone	38.75 pbw	Brookfield viscosity (cps)	2050
	MEK	38.75 pbw	Solids content (%)	22.5
	Uthane-5731	22.50 pbw		
		100.00 pbw		
3	Acetone	40.00 pbw	Brookfield viscosity (cps)	813
	MEK	40.00 pbw	Solids content (%)	20
	Uthane-5731	20.00 pbw		
		100.00 pbw		
4	Acetone	41.25 pbw	Brookfield viscosity (cps)	500
	MEK	41.25 pbw	Solids content (%)	17.5
	Uthane-5731	17.50 pbw		
		100.00 pbw		
5	Acetone	36.25 pbw	Brookfield viscosity (cps)	3325
	MEK	36.25 pbw	Solids content (%)	27.5
	Picotac	2.50 pbw		
	Uthane-5731	25.00 pbw		
		100.00 pbw		
6	Acetone	37.00 pbw	Brookfield viscosity (cps)	3363
	MEK	37.00 pbw	Solids content (%)	26
	Picotac	1.00 pbw		
	Uthane-5731	25.00 pbw		
		100.00 pbw		

(Tab. II). The TPR sole materials are usually produced without plasticizers and, thus, do not affect the cohesion properties of the adhesive film. In the latter case, failure of the adhesives is due to the

TABLE II Peel strength of the PU adhesives. Substrate: Leather and PVC

Adhesive	*Peel strength in Kg/cm (Fail type)* within 1 hr	*after 24 hrs*	*after 168 hrs*	*after aging*
PU-adhesive 1	2.1 (100% ACF)	4.6 (100% ACF)	5.4 (50% ACF 50% SULF)	5.5 (100% ACF)
PU-adhesive 2	2.7 (50% ACF 50% SULF)	4.4 (100% ACF)	5.7 (80% ACF 20% SULF)	3.7 (100% ACF)
PU-adhesive 3	1.1 (100% ACF)	4.1 (100% ACF)	4.7 (50% ACF 50% SULF)	2.5 (100% ACF)
PU-adhesive 4	1.5 (100% ACF)	4.3 (100% ACF)	5.0 (80% ACF 20% SULF)	3.0 (100% ACF)
PU-adhesive 5	1.0 (100% ACF)	6.2 (100% SULF)	5.8 (80% ACF 20% SULF)	3.6 (100% ACF)
PU-adhesive 6	1.4 (100% ACF)	5.3 (100% SULF)	6.6 (80% ACF 20% SULF)	4.7 (100% ACF)

ACF - Adhesive cohesive failure.
SULF - Surface upper leather failure.

TABLE III Peel strength of the PU adhesives. Substrate: Leather and TPR

Adhesive	*Peel strength in Kg/cm (Fail type)* within 1 hr	*after 24 hrs*	*after 168 hrs*	*after aging*
PU-adhesive 1	3.5 (100% ACF)	7.2 (100% SULF)	6.8 (100% ACF)	6.1 (100% ACF)
PU-adhesive 2	7.1 (100% SPF)	7.4 (100% SSF)	8.3 (100% SSF)	7.1 (100% SPF)
PU-adhesive 3	2.9 (100% ACF)	4.4 (100% SULF)	5.1 (100% ACF)	4.2 (100% SULF)
PU-adhesive 4	7.2 (100% ST)	9.7 (100% ST)	9.0 (100% SSF)	8.5 (100% SPF)
PU-adhesive 5	6.1 (100% SPF)	7.9 (100% SSF)	8.4 (100% SSF)	6.9 (100% SPF)
PU-adhesive 6	6.9 (100% SPF)	10.2 (100% ST)	8.4 (100% SSF)	8.2 (100% SPF)

ACF - Adhesive cohesive failure. SPF - Surface plastic failure. SULF - Surface upper leather failure. ST - Sole tear. SSF - Surface sole failure.

plasticizer present in the sole material which prevents the formation of a bond between the surfaces.

Peel strengths, of the adhesives tested after 24 hrs. on PVC-Leather substrates and TPR-Leather substrates are listed in Tables II and III, respectively. Typical force-extension peeling graphs are given in Figure 1 and the pattern of load *versus* displacement is comparable with the ideal curve. The strength is much improved and exceeds minimum requirement of 4 kg/cm. Considering adhesives 1 to 4, there is a trend observed in the PVC-Leather substrates that the peel strength decreases with decreasing polyurethane content. Such a systematic variation in the peel strength is not observed in the case of TPR-Leather substrates. This is not surprising because, as already mentioned, the PVC sole materials are highly plasticized and their poor adhesion property results in adhesive cohesive failure in the adhesive, in the case of TPR, the adhesion property with the thermoplastic polyurethane is excellent and results in failure of the sole material.

Even though the polyurethane resin content of adhesives 1, 5 and 6 are identical, adhesives 5 and 6 show higher peel strength than adhesive 1 for both the PVC-Leather and TPR-Leather substrates. This is due to the presence of tackifier. Also, the surface upper leather failure for adhesives 5 and 6 in the case of PVC-Leather substrates supports the pronounced effect of tackifier in improving the peel strength. Galan and co-workers [5] studied the effects of Picotac® in pressure sensitive hot-melt adhesives based on styrene-butadine-styrene rubber and they found that the tackifier increases the peel strength by increasing the cohesion of the adhesive.

Peel strengths of the adhesives tested after 168 hours on PVC-Leather substrates and TPR-Leather substrates are also included in Tables II and III. Compared with the 24-hour test, here the peel strength is increased due to improved physical curing. Another important observation is that 50% adhesive/cohesive failure and 50% surface upper leather failure was found for PVC-Leather substrates. Such good adhesion of PVC to leather is only possible by using polyurethane adhesives [1]. Since no detailed report is found in the literature dealing with the effect of PU adhesives on leather and different synthetic substrates, it is very difficult to compare the results. Xueyue [6] prepared a PU adhesive using 4-4′-Diphenylmethane

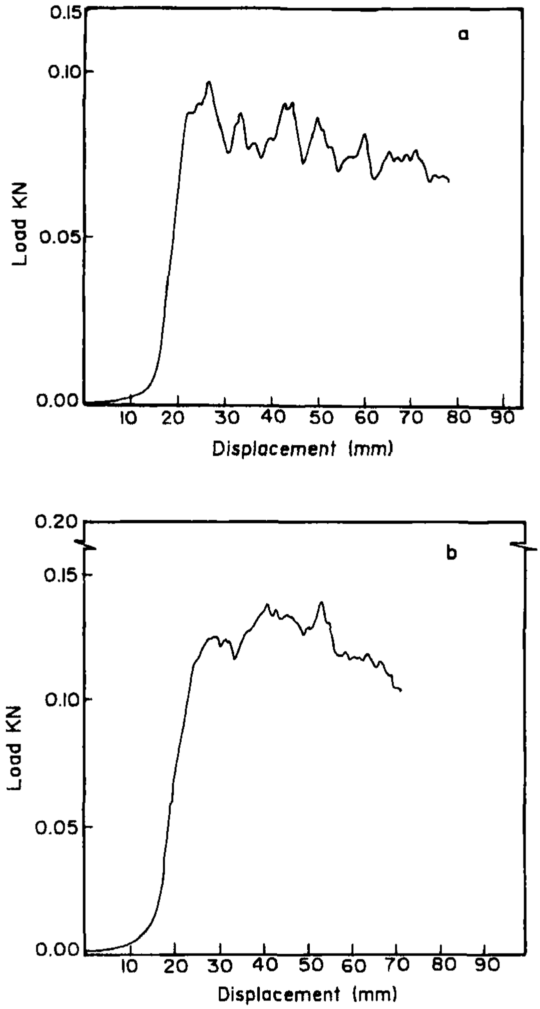

FIGURE 1 Force-extension peeling graph of: a) PU-adhesive 1 tested after 24 hrs on leather-PVC substrates and b) PU-adhesive 1 tested after 24 hrs on leather-TPR substrates.

diisocyanate-1,4-butanediol-adipic acid-TDI copolymer and found that the peel strength was 9.2 kg/cm (normal temp.) or 5.6 kg/cm (50°C, 15 min.) with PVC-Leather substrates. Bondarev and co-workers [7] prepared a powder adhesive based on thermoplastic polyurethane and found that the peel strength was 4.2 kg/cm with PU-Leather substrates.

After ageing, adhesives 3 and 4 show poor performance on PVC-Leather substrates but there is no appreciable change in the peel strength on TPR-Leather substrates (Tabs. II and III). It can be concluded that there may be a limitation on the resin content of adhesives employed for PVC-Leather substrates.

All of the adhesives show good shelf-life properties, as no increase in the viscosity was observed during six months in ideal storage conditions.

CONCLUSIONS

1. Picotac® tackifier was found to be compatible with Uthane-5731 (a polyester-based thermoplastic PU) and increased its peel strength on the studied substrates.
2. The Picotac was also found to be an appropriate compromise substance for the plasticizer present in the PVC sole materials.
3. The studied adhesives were found to be most suitable for TPR-Leather substrates but were also suitable for PVC-Leather substrates.

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