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SHORT COMMUNICATION

Sticky Glues for Rat Control

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ABSTRACT

A number of polymeric glues based on linseed oil, animal hide and hydroxy-terminated polybutadiene (HTPB)-derived polyurethanes have been synthesised. These glues are sticky in nature and characterised by viscosity, FTIR spectra and adhesive strength. These glues were evaluated for rat control. The HTPB-derived polyurethane, poly [HTPB-hexamethylene-diisocyanate (HMDI)] and linseed oil-based glues were found to be effective in controlling the rats. Storage ageing studies of these glues were also carried out. It was found that the exposed layer of linseed oil-based glue dried up after 9 months but still remained effective after removing top layer and the HTPB-HMDI-derived polyurethane is effective for 18 months.

Keywords: Rat control, sticky glues, trap, linseed oil, animal hide, polyurethanes

1. INTRODUCTION

The commensal rats are cosmopolitan in nature and are found in human dwellings. They are generally omnivorous with a great sense of discretion. Their fastidious nature of feeding and gnawing causes enormous damage to human beings. It has been estimated that at an average 10 per cent of food materials in storage (approx. 33 million tons) is contaminated by the rats in tropical and subtropical countries every year[1,2]. Rats have an inherent behavioural habit of gnawing and contaminating food materials with their faeces and urine. They also act as a reservoir of a large number of infectious organisms, which on transmission cause various diseases to human beings and domestic animals.

Various methods have been employed for the control of commensal rats, such as rodenticide, chemosterilant, and ultrasound with different results. Since every method has its own limitation, an integrated rat-control management has been advocated. Keeping in view of bait shyness, resistance to rodenticide, and adaptation to ultrasonics, etc., there is a necessity to develop nontoxic, eco-friendly method for the control of commensal rats. Therefore, an effort has been made to develop and evaluate various types of glues against rats (*Rattus rattus*) in the laboratory.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Linseed oil, animal hide, hydroxy-terminated polybutadiene (HTPB) (Nocil, India), toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), hexamethylene-diisocyanate (HMDI), dibutyltin dilaurate (DBTL) (Fluka, Switzerland) and zinc chloride (Sd Fine Chemical, Mumbai) were procured from trade and used as received.

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2.2 Rats for Experiments

Male and female rats weighing approximately in the range 200-300 g, 300-400 g, and more than 400 g were drawn from colony of commensal rats-*Rattus rattus* maintained at the Defence Research & Development Establishment (DRDE), Gwalior. The food and water were provided *ad libitum*. The food was obtained from Amrut Laboratory, Animal feed, Nava Maharastra, and Chakan Oils Mills, Sangli, Pune. Eco-traps supplied by Ecosafe Traps (India) Ltd, Yusuf Building, M.G. Road, Mumbai, were taken for comparison[3].

2.3 Synthesis of Glue

2.3.1 *Glue based on Linseed Oil*

Linseed oil was heated in a steel container on a heating mantle. When the temperature reached more than 397 °C, ignition took place in linseed oil. After ignition was over, some grey colour viscous and sticky mass was left out at the bottom[4]. Using this procedure, glue was prepared in bulk.

2.3.2 *Glue from Animal Hide*

Aanimal hide (100 g) was soaked in cold water (400 ml). After 8-10 h, it was heated at 140-150 °C in the presence of (10-20 per cent) zinc chloride which resulted in viscous and sticky glue[4].

2.3.3 *Glue based on HTPB-derived Polyurethanes*

HTPB (Mn = 2600 and hydroxyl value of 37) reacts with diisocynates (keeping the OH:NCO ratio 1:1) and produces linear polyurethanes[5]. However to get sticky polyurethanes, amount of diisocyanate (MDI, TDI, and HMDI) should be less than the stoichiometric amount. Thus, amount of diisocyanate was varied and it was reacted with HTPB (10 g) using DBTL as catalyst (Table 1).

3. CHARACTERISATION OF GLUES

Synthesised glues were characterised for their solubility (in organic solvents and water), relative viscosity, infrared spectrometry, adhesive strength, and storage ageing.

Relative and intrinsic viscosities of polymeric glues were measured in toluene and water at 30 °C using ubbelhode viscometer. FTIR spectra were recorded in the range 400-4000 cm^{-1} using Perkin Elmer FTIR-1720X spectrometer. Adhesive strength of these glues were also measured by applying 0.3 g of each type of glue over perspex sheet (based on polymethylmethacrylate) having dimensions 2.5 cm × 6.0 cm × 0.5 cm. The glue-coated strip was covered by another strip leaving part of strip uncovered (10 mm). Thus, 50 mm of strip was used for the measurement of adhesive strength using universal tensile testing machine (Micro-350 Good Brand Jaeffrey, UK). Storage ageing of glues was also studied by keeping 100 g of each type at ambient temperature and changes in liquid state were observed.

4. RAT CONTROL EFFICIENCY TEST

The three types of glues and the eco-trap were evaluated against lab-bred wild-type rats. Evaluation experiments were carried out with the application of 95 g, 105 g, 115 g and 125 g of glues on cardboard or aluminium tray (46.0 cm × 30.5 cm × 0.1 cm) and kept on both sides of the entry point in a rectangular chamber (1m 88 cm × 1m 9 cm × 79 cm) partitioned in the middle by sliding plywood. A hole (91.5 cm× 91.5 cm) at the entry point was made to facilitate movements of the rats for food and water kept in either chambers to make their movements. The chambers were covered by a wire-mesh to prevent escape of the animals. Six lab-bred wild-type rats (weight range 100-400 g were used for measured quantity of glue for testing the efficacy of the glues[6].

5. RESULTS & DISCUSSION

Three types of glues were synthesised for the present study. Polyurethanes prepared by the reaction of HTPB with diisocyanates (eg, TDI, MDI, and HMDI) using DBTL as catalyst at the ambient temperature are flowing-to-highly viscous liquids, and non-flowing liquids (Table 1). The amount of MDI was varied from 0.2-0.5 g/10 g of HTPB in each case, resulting into polyurethanes which were flowing liquids and nonsticky in nature. These polyurethanes have intrinsic viscosity of 0.10-0.33 dl/g at 30 °C in toluene and adhesive strength of 0.04-0.11 kg force/50 mm. Similarly, reaction of 0.14 g of TDI/10 g of HTPB gave polyurethane of 0.09 dl/g at 30 °C in toluene and adhesive strength of 0.28 kg force/50 mm. This is a flowing liquid, nonstiky in nature. Their viscosities were in the range 0.16 dl/g to 0.24 dl/g and their respective adhesive strength were 0.28 kg force/50 mm to 0.57 kg force/50 mm. At higher concentration of TDI(0.4 g), HTPB-TDI polyurethanes were flexible as well as solid. To get sticky polyurethanes, HMDI (0.1-0.4 g) was also reacted with HTPB at room temperature. At 0.1 g of HMDI, HTPB-derived polyurethanes were flowing liquids having viscosity of 0.11 dl/g and adhesive strength of 0.31 kg force/50 mm. Similarly, at higher concentration of HMDI (0.4 g), polyurethanes were solids, non-flowing liquids, and non-sticky in nature. At intermediate concentration of HMDI (0.2-0.3 g), the resultant polyurethanes were viscous-to-highly viscous liquids, and their viscosities and adhesive strength were in the range 0.18-0.22 dl/g at 30 °C in toluene and 0.52-0.61 kg force/50 mm, respectively. These polyurethanes were also sticky in nature (Table 1).

Polyurethane-based glues [HTPB-diisocyanate (DI)-based polyurethanes] were light yellow. FTIR spectra of these urethanes indicate bands at 3443 cm^{-1} due to *–OH* group of HTPB. Bands at 2845 cm^{-1} and 1728 cm^{-1} might be due to *CH* stretching and carbonyl group, respectively. Further, peak at 1645 cm^{-1} might be due to *–CH=CH–* unsaturated double bond present in HTPB, and therefore, in corresponding polyurethane[7]. However, band at 2000-2200 cm^{-1} due to *–NCO* is absent, confirming its consumption/conversion to urethane group *–NH–C–O–* during reaction[8] of HTPB and DI. The synthesis of polyurethanes from reaction[8] of HTPB and diisocyanates has already been reported[5].

Table 1. Formulation of polyurethanes

Diisocyanate (g)		HTPB (10 g) Properties of resulting polyurethane: Nature	Viscosity [n] dl/g	Adhesive strength kg force / 50 mm
TDI	0.14	FL	0.09	0.31
	0.22	VL(S)	0.16	0.52
	0.30	HVL(S)	0.24	0.61
	0.40	NFL (NS)	0.32	0.59
MDI	0.20	FL	0.10	0.04
	0.30	FL	0.20	0.09
	0.40	FL(NS)	0.25	0.09
	0.50	NFL(NS)	0.33	0.11
HMDI	0.10	FL	0.11	0.31
	0.20	VL(S)	0.18	0.52
	0.30	HVL(S)	0.22	0.61
	0.40	NFL(NS)	0.32	0.58

FL = Flowing liquid, NFL = Non-flowing liquid, VL = Viscous liquid, HVL = Highly viscous liquid, S = Sticky, NS = Non-sticky solution for viscosity 1 %, TDI : Toluene diisocyanate, MDI : Diphenylmethane diisocyanate, HMDI : Hexamethylene-diisocyanate,

Table 2. Characterisation of polymeric glues

Properties	Glues				
	Linseed oil	HTPB-based polyurethanes			Animal hide
		TDI	HMDI	MDI	
Colour	Dark olive green	Dark yellow	Light yellow	Yellow	Dark brown
Soluble in	Toluene	Toluene	Toluene	Toluene	Water
Smell	Pungent	Pleasant	Pleasant	Pleasant	Unpleasant
Specific viscosity	0.40*	***	***	***	0.28**
Adhesive strength (kg force/ 50 mm)	0.48	0.52	0.61	0.11	0.34

*Viscosity in toluene at 30 °C 1 % solution
**Viscosity in water at 30 °C 1 % solution
***Given in Table 1

Linseed oil-based glues are dark olive green and have pungent smell (Table 2). This glue is soluble in toluene and has a relative viscosity of 0.40 dl/g in toluene at 30 °C. Linseed oil contains linoleic, linolenic, oleic acids which are long chain unsaturated acids along with some saturated acids[7] (palmitic/stearic acid). During the ignition process, polymerisation takes place at the double bond, resulting into glue of higher viscosity. Further, the unsaturated double bond ($CH_3(CH_2)_4CH{=}CH{-}CH_2{-}CH{=}CH\,(CH_2)_2$ $-COOH$) was missing in the IR spectra of resulting glue produced from ignition of linseed oil[7,9]. Other groups like aliphatic CH-stretching at 2911 cm^{-1} and 2853 cm^{-1} and due to carbonyl group at 1740 cm^{-1} were observed in the IR spectra of linseed oil-based glue. The adhesive strength of this glue was 0.48 kg force/mm. Also, the glue remained liquid and no change in viscosity was observed when kept for storage ageing at ambient temperature up to 9 months. After this period, the glue started solidifying at the top surface while rest of the glue remained liquid.

Third type of glues are those based on animal hides. Animal hide glues are essentially natural high polymer proteins. These organic colloids are derived from collagen, which is the protein constituent of animal hides, connective tissues and bones. There are two main types of animal glues: Hide and bone, differing in the type of raw materials used. In both the cases, animal glue was obtained by the hydrolysis of the collagen in the raw material. Further, collagen and animal glues obtained from the collagen are closely related as to chemical composition and properties.

$$\underset{\text{Collagen}}{C_{103}H_{149}O_{38}N_{31}} + H_2O \rightarrow \underset{\text{Animal glue protein}}{C_{103}H_{151}O_{39}N_{31}}$$

Glue molecule consists of amino acids connected through polypeptide linkages to form long-chain polymers of varying molecular weights[10]. These glues are dark brown and soluble in water only. Therefore, viscosity of these was found to be 0.28 dl/g in water at 30 °C. Adhesive strength of these glues was 0.34 kg force/mm (Table 2). Further, their structure is supported by IR spectra. The band at 1650 cm^{-1} is due to carbonyl group of amino acid. Broad peak between 3200-3500 cm^{-1} is due to overlapping of peaks due to $-NH$ and $-OH$, resulting into a broad peak. Peak at 2930 cm^{-1} aliphatic $-CH-$ stretching, and thus, confirming the structure of these glues[7].

6. COMPARATIVE STUDIES

Linseed oil-based glues, polyurethanes, and animal hides have been compared for their properties. Among the three types of glues, polyurethanes were superior due to their higher viscosity and corresponding adhesive properties. Further, these urethanes can be easily prepared in comparison to that of linseed oil-based glues where high temperature ignition is required. These are also colourless-to-light yellow with pleasant (ester-type) smell. However, linseed oil-based glues are dark olive with pungent smell. Similarly, animal hide-based glues are dark brown with untolerable smell.

Hence, considering the above-mentioned properties, polyurethene-based glues were preferred in comparison to glues based on linseed oil and animal hide. This is further proved by the animal studies carried out using these glues against the rats.

Among the three types of polyurethanes produced, ie, P(HTPB-MDI), P(HTPB-TDI) and P(HTPB-HMDI), rat-trapping efficiency of each type of polyurethene (PU) was determined using 6 lab-bred wild-type rats. It was found that HTPB-HMDI-based polyurethene (viscosity 0.22 dl/g and adhesive strength 0.61 kg force/50 mm) was able to capture/trap 5 out of 6 rats used. HTPB-TDI-based polyurethene (0.24 dl/g and adhesive strength 0.57 kg force/50 mm was able to capture/trap 3 rats, whereas HTPB-MDI polyurethane failed to capture any rat. Therefore, HTPB-HMDI polyurethane was found to be the best and selected for further comparison and detailed animal studies.

Table 3 presents the comparative evaluation of glue applied as 95 g, 105 g, 115 g, and 125 g per cardboard or aluminium dish. Application of glue (95 g) has moderate effect in the weight range 200-300 g for all the three types of glues. As the quantity of application was increased in an ascending order, the rat trapping was also increased. The traps containing 115 g application was found quite appropriate for trapping in all the three glues types of glues. While 125 g application of glue was the most effective for all the weight ranges of rats taken. Maximum number of rats were trapped when 125 g P(HTPB-HMDI)-based glue was applied and was the most suitable for trapping. Adhesive properties of P(HTPB-HMDI) and linseed oil-based glues were excellent and able to trap the rats. Due to exhaustion trapped rats died within 12-24 h an effort to get themselves free from the adhesion. This rat control method is eco-friendly as the glues used were inaquious.

Commercially available eco-trap was able to trap only 2 rats in the weight range 200-300 g and 300-400 g. However, the ingredients used for making the eco-traps are not known.

Table 3. Comparative evaluation of glues, viz., synthetic glues (HTPB), animal hide-based glues, and linseed oil-based glues

Glue applied (g)	Weight range of rats (g)	No of rats trapped in 24 h		
		P(HTPB-HMDI)	Animal hide	Linseed oil
95	200 - 300	2	One	2
	301 - 400	1	Nil	1
	> 400	1	Nil	Nil
105	200 - 300	4	3	3
	301 - 400	3	2	2
	> 400	2	1	2
115	200 - 300	5	4	5
	301 - 400	5	4	4
	> 400	4	1	4
125	200 - 300	6	4	5
	301 - 400	4	3	5
	> 400	5	3	4

No. of replicate-6 wild-type rats-*Rattus rattus*

Table 4. Storage stability of HTPB, animal hide-based and linseed oil-based glues

Time (months)	No of rats trapped*		
	P(HTPB-HMDI) glue	Animal hide-based glue	Linseed oil-based glue
1	5	3	4
3	5		5
6	5		5
9	4	Since the upper layer dries up after coming into contact with air, forbidding trapping	5
12	5		5
15	6		4
18	5		5

*Rats weighing > 400 g were taken
125 g glue applied on cardboard or aluminium dish
No. of replicates - 6

Tests for the storage stability of these glues were also carried out by keeping glues at normal atmospheric conditions (Table 4). Results of these tests show that HTPB-HMDI-based and linseed oil-based glues were found to be the most effective in trapping. However, linseed oil-based glue dried up at the top surface after 9 months. This can be further used after removing top layer. HTPB-HMDI-derived polyurethanes, however remains liquid after 18-24 months.

Tests were carried out only up to 18 months of storage and these glues were able to trap 5 rats of 125 g size and found to be the most effective glue for rats control. Their adhesiveness is the same as freshly prepared glue even after 18 months of storage at ambient temperature. Animal hide glues started drying after two months and its stickness were also reduced. This glue completely failed to trap the rats.

6. CONCLUSION

P(HTPB-HMDI) polyurethane-based glues were found the most effective for rat control . These polyurethanes are eco-friendly and may be used as a ready-to-use formulation on different matrices. These glues may be used to control the rats in the hotels, shops, houses, godown, and other such places.

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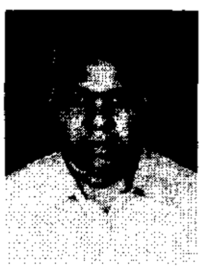

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