

Effects of Internal Plasticization on the Physical and Mechanical Properties of Castor Oil - Based Polyurethane Foams

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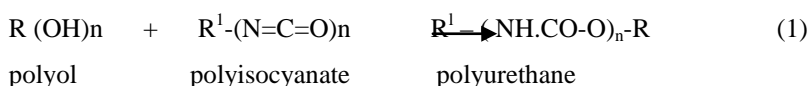
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Abstract - Flexible castor oil-based polyurethane foams were produced by the one-shot method of foam synthesis. Foam formulation involved pure castor oil/castor oil modified with heptachloroheptadecane (HCHD), a novel C-17 chlorinated hydrocarbon internal plasticizer, 80:20 mixture of 2,4 - and 2,6 - toluene diisocyanate (TDI) at room temperature (30 - 35°C). Foam reaction took place in presence of stannous octoate and dimethylaminoethanol (DMAE) catalysts, methylene chloride (physical blowing agent) and silicone oil (surfactant). Isocyanate/polyol (NCO/OH) ratio was 1/1. Concentration of plasticizer used varied from 0.4 - 2.4 wt%. Foams obtained were tested for their physical and mechanical properties. Suggested mode of action and the influence of the incorporated internal plasticizer (HCHD) on these properties are discussed. Results indicate reduction in the density and compressive strength of the foams, but enhancement of their % creep recovery and water absorption as plasticizer concentration increased. These property changes suggest greater flexibility, extensibility and workability of foam. The most flexible foams were obtained at 2.4wt% concentration of the incorporated plasticizer. Areas of potential applicability or end-use of the new products are highlighted.

Index Terms - castor oil; plasticizer; flexible foam; properties.

INTRODUCTION

Polyurethanes (PUs) are polymers containing the urethane linkage (-NH-CO-O-) in the main chain. Polyurethane foams (PUFs) can be produced by reacting a polyol with an excess of organic polyisocyanate (in presence of catalysts and other additives) according to the generalized PU reaction.



(where $n \geq 2$)

The replacement of petroleum-based polyols or petropolyols such as polyether and polyester polyols with polyols derived from renewable materials of plant origin in the synthesis of PUFs has resulted in cheaper, safer, more environment friendly products with excellent thermal stability and oxidation resistance. Superior thermal stability and oxidation resistance of plant oil polyols over petropolyols are believed to be due to higher hydrocarbon content in the former (Javni *et al.*, 2000, Petrovic *et al.*, 2005; Badri; 2012). In the adhesive industry, for instance, this innovation has yielded degradable castor oil-based PU adhesives (Somani *et al.*, 2003; Gayki *et al.*, 2015).

However, most PU products obtained from unmodified triacylglycerol (TAG)-based oil polyols (chiefly soybean, castor, palm and canola oil polyols) are reported to be crosslinked materials or thermosets (Guo *et al.*, 2000; Zlatanovic *et al.*; 2002; Petrovic *et*

al.; 2005); except in plant oils containing secondary hydroxyl groups, where so-called ‘dangling’ chains in the oil’s TAG molecules are believed to exert steric hindrance to crosslinking (Xu, 2008; Fan, 2012). These crosslinked materials are characterized by high mechanical strength, high hardness index, but low resilience (Randall, 2002; Bleys, 2012). The materials are therefore hard to melt and reprocess, making them non-recyclable. Thus in the PUF industry where flexible PUFs used in cushioning, bedding and packaging applications are the chief products, use of unmodified plant oil polyols is definitely not a viable option.

In recent years, researchers have resorted to the chemical modification of plant oils to obtain PUs of desired physical and chemical characteristics. In castor oil-based PUF synthesis, a major attempt at remedying the situation involved the use of ‘mixed’ polyol formulations in which the conventional, commercial (polyether/polyester) polyol is mixed with low or moderate proportions of castor oil to obtain flexible PUFs (Xu *et al.*, 2008; Zhang, 2008; Xing, 2014; Sharma *et al.*, 2014). However, despite cost-benefit analysis of blending the conventional base polyol with castor oil indicating some level of cost effectiveness (Ogunfeyitimi *et al.*, 2012; Thorat and Patil, 2015), these mixed polyol recipes were not quite successful on grounds of low local content input (often no more than 15-25% castor oil) that cannot support sustainability. Another drawback is the compatibility question arising from mixing the two components.

The advent of inter-penetrating polymer networks (IPNs) presents another dimension to the modification of plant oils to obtain PUs. These materials are obtained as a result of permanent entanglement between two or more distinctly crosslinked polymers and the excellent properties they exhibit are believed to be as a result of the interlocking of polymer chains in their structure (Sperling, 1981; Islam *et al.*, 2014).

Mention should also be made of the many other chemical modification recipes involving castor oil polyols (transesterification, epoxidation, acrylation etc) that often result in improved and varied polymer characteristics and end-uses. These have been adequately reported in literature (Ogunniyi, 2006; Del Rio, 2011; Mubofu, 2016). But one area in which very little has been investigated and reported is the introduction of an internal plasticizer into the castor oil component prior to foam synthesis (Murkherjea *et al.*, 1978; Pandey and Vatsa, 2010). A plasticizer is an additive used to increase the flexibility and extensibility of a material by lowering its glass transition temperature (T_g) and softening the final product, with attendant loss of material strength and hardness, among others.

The present investigation reports on the application of heptachloroheptadecane (HCHD), a C-17 straight chain chlorinated hydrocarbon, as an internal liquid plasticizer introduced into castor oil polyol component of foam formulation prior to foam synthesis. The effects of this novel, oil-compatible plasticizer on the physical and mechanical properties of the castor oil-based PUFs synthesized are also reported.

MATERIALS AND METHODS

Materials

Mechanically extracted castor oil from wild *Ricinus communis* Linn seeds (Yusuf, 2016) was used as polyol. TDI (80:20), silicone oil (surfactant), stannous octoate (gelation catalyst), DMAE (amine catalyst) and methylene chloride were the other foam-making chemicals used. They were kindly supplied by Vitafoam Nig. Plc, Jos. Distilled water was used as chemical blowing agent. 2,5,6,7,8,11,15-heptachloroheptadecane (HCHD) (Fig. 1) was purchased from a local supplier in Nigeria and used as internal plasticizer.

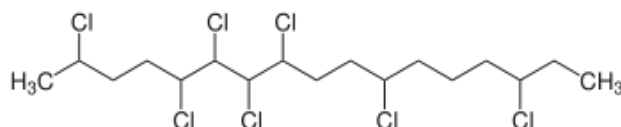


Fig. 1: Structure of HCHD (C₁₇H₂₉Cl₇)

Methods

Foam Preparation

Foams were prepared by the one-shot method (ASTM D 7487) of foam synthesis. Foams were prepared in locally fabricated open moulds of dimension 18x15x9 cm³ at room temperature, by the free rise method. Castor oil and all other foam-making chemicals (less TDI) were accurately measured as per formulation (Table 1) into a plastic mug, with constant vigorous stirring using a high speed (1000 rev/min) mechanical stirrer. This is the polyol component. 0.4, 0.8, 1.2, 1.6, 2.0 and 2.4 parts per hundred (pph) polyol portions of the internal plasticizer (HCHD) were separately added as part of polyol component, with continuous stirring. TDI, measured out separately in another container, was then rapidly added to this uniform mixture with continuous stirring, to ensure the formation of homogeneous foam. Solidifying foam product was kept in a fume cupboard for 24 hrs to cure completely, before demoulding.

Table 1: Foam formulation – NCO/OH (1/1)

Component	Actual weight (g)	Pph polyol
Neat/modified CO polyol	50.00	100.00
TDI	49.10	98.20
Methylene chloride	1.50	3.00
Stannous octoate	0.25	0.50
DMAE	0.225	0.45
Silicone oil	0.25	2.50
Water	1.00	2.00

Pph = Parts per hundred (polyol)

Determination of Physical Properties

Density determination

ASTM D 1622-08 procedure was used to evaluate the apparent density (kg/m³) of foam samples based on mass/volume measurements.

Water absorption

Water absorption test was performed in accordance with ASTM D590-98 and ASTM D2842-12. Water absorption of foam was evaluated as.

$$\% \text{ water absorption} = \frac{\text{Weight of wet foam} - \text{Weight of initial foam}}{\text{Weight of initial foam}} \times 100 \quad (2)$$

Determination of Mechanical Properties

Compressive Strength

Compressive strength of plasticized and unplasticized castor oil-based PUFs was measured in accordance with ASTM D1621-10 procedure using Instron universal tester. Compressive strength was taken as the force (N/M²) required at 10% deformation based on the original specimen thickness.

Creep recovery

Creep recovery test for the plasticized and unplasticized foams was performed on a Creep Machine - TecQuipment (TQ) SM 1006 (Cell load 250N) - as per ASTM D2990-09 procedure. Creep recovery was evaluated as the difference between the total extension (mm) on application of load and the relaxation (mm) on removal of load after 5 seconds. Percentage creep recovery was then calculated as:

$$\% \text{ creep recovery} = \frac{\text{Creep recovery or resilience}}{\text{Extension on application of load}} \times 100 \quad (3)$$

RESULTS AND DISCUSSION

Physical Properties of the Castor Oil-Based PUFs

General physical features

Synthesized foams were observed for colour, texture and shrinkage post-cure. No foam showed signs of shrinkage post-cure, suggesting that the foams were of good dimensional stability. The colour of the (neat) foam was pale yellow while colour range for the plasticized foams was pale yellow to colourless. Texture varied from semi-rigid (neat foam) to soft and flexible (plasticized foam).

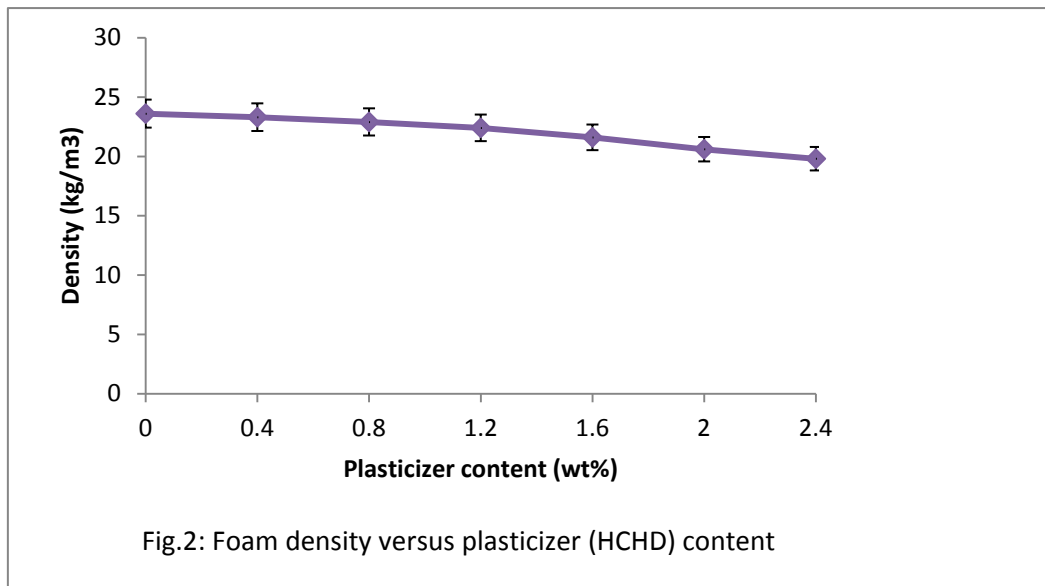
Table 2: Observed general physical features of the PUFs

PU foam	Colour	Texture	Post-cure state
Unplasticized (neat)	Pale yellow	Semi-rigid	No shrinkage
Plasticized (wt% modifier)			
0.4	Pale yellow	Semi-rigid	No shrinkage
0.8	Pale yellow	Semi-rigid	No shrinkage
1.2	Pale yellow	Soft to semi-rigid	No shrinkage
1.6	Pale yellow	Soft to semi-rigid	No shrinkage
2.0	Colourless	Flexible	No shrinkage
2.4	Colourless	Soft and flexible	No shrinkage

Colour assumed by foam seemed to depend either on the natural colour of the base polyol - castor oil (yellow) or that of the modifier (colourless) or both. On the other hand, changes in foam texture and feel are consistent with structural changes undergone by the PUF as a result of increased plasticization.

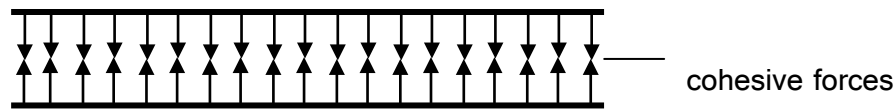
Effect of plasticization on foam density

It is observed that foam density decreased gradually with increased plasticizer concentration (0.4 - 2.4 wt%) (Fig. 2). According to Fox (2008), the effect of plasticization is to reduce the cohesive intermolecular forces between polymer chains and create greater free volume between them. The incorporated internal plasticizer in this study (HCHD) is an oil-compatible chlorinated hydrocarbon known for enhancing material flexibility and extensibility, in addition to its fire retardancy characteristics (Klorfin, 2012). It is thought that during the polymerization and foaming stages which occur simultaneously, reacted HCHD moieties are chemically grafted onto PU main chains (with the double bonds and ester linkages in castor oil TAGs likely serving as grafting centres) and the unreacted dispersed in between them. However, migration of plasticizer out of the PU matrix would be unlikely because of the fairly big size of the HCHD chain molecules.



This development creates greater free volume between PU chains and weakens cohesive intermolecular forces of attraction between them, resulting in greater segmental mobility within the PU matrix (Fig. 3). The C-17 HCHD chain molecules aligned between the PU main chains tended to mask or block interaction sites for the formation of cohesive intermolecular forces of attraction. Longer plasticizer chain means ability to block greater number of such interaction sites along the PU main chains. These are consistent with the observed density decline and relatively more flexible and softer structural features of foam with increase in HCHD content from 0.4 - 2.4 wt%.

(a) Unplasticized



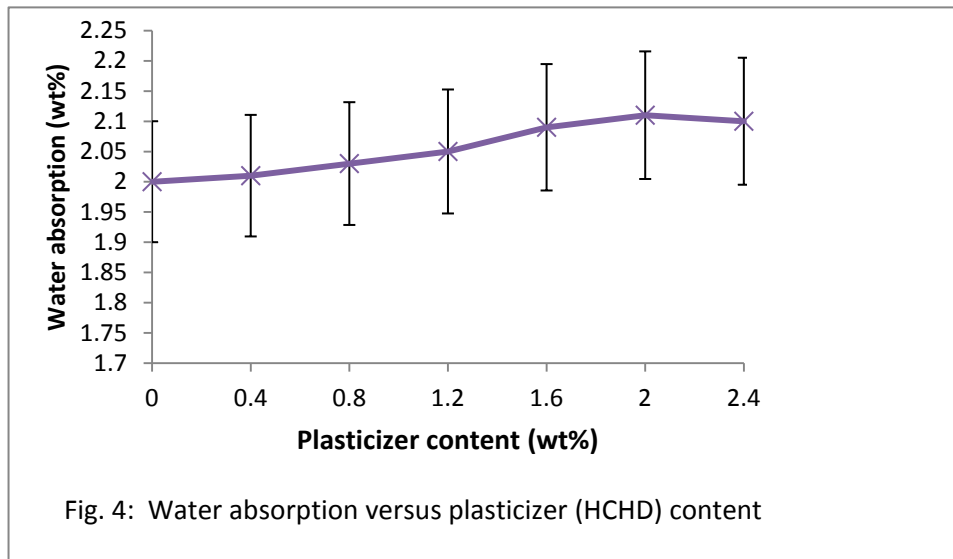
(b) Plasticized



Fig. 3: Schematic arrangement of reactive plasticizer molecules in PU matrix.

Effect of plasticization on water absorption

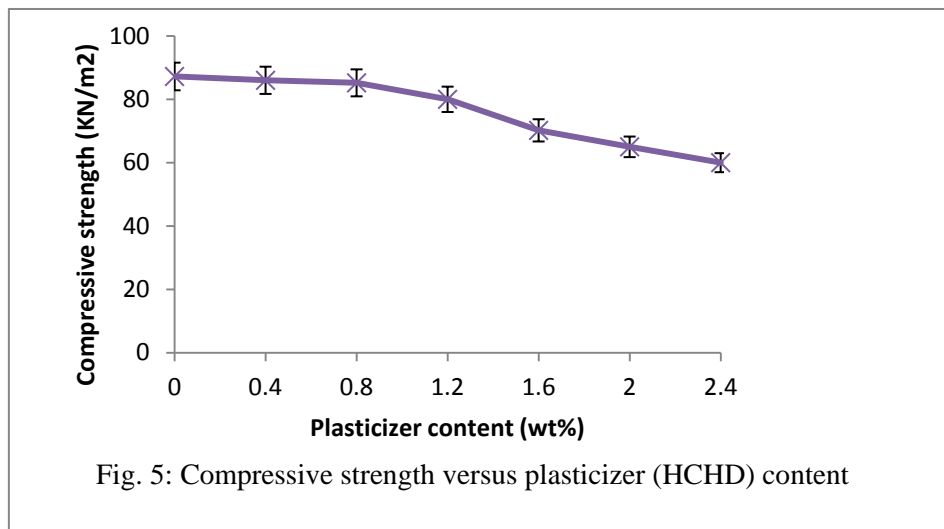
Greater free volume in PU foam matrix with increased HCHD content resulted in increased water absorption (Fig. 4). This explains the observed greater water sorption in the plasticized foams which are structurally more porous compared to the control (neat) foam, where the PU main chains are strongly held by cohesive forces of attraction, typically involving mono- and bidentate hydrogen bond formation (Yilgor, 2000). Water absorption is an important parameter for consideration, especially with regard to materials with outdoor application.



Mechanical Properties of the Castor Oil - Based PUFs

Effect of plasticization on compressive strength and percentage creep recovery

In Fig. 5, foam compressive strength declined steadily with increase in HCHD content. This is consistent with foam density decline as HCHD content increased (Fig. 2). Mechanical properties of PUFs such as tensile strength, compressive strength, compressive modulus, creep recovery etc are known to depend strongly on density (Saint-Michel *et al.*, 2006; Song *et al.*, 2009) as well as on the material composition. Foam density therefore is a very important physical property which has great influence on the mechanical properties of PUFs (Thirumal *et al.*, 2008). For a foamed polymer generally, compressive properties are important because they describe the behaviour of the foam when it is subjected to compressive load. HCHD plasticized PUFs exhibited lower compressive strengths than the control (neat) PUF.



This is explained in terms of the C-17 HCHD chain molecules constituting a great impediment to inter-chain polymer interactions that could produce rigid or semi-rigid foams, and at the same time offering substantial free volume in the PUF matrix for segmented mobility.

Conversely, %creep recovery of foam was substantially enhanced with increase in plasticizer content (Fig. 6). Creep recovery describes the extent to which a polymer under plastic deformation recovers its original shape over time. In other words, creep recovery is a function of foam resilience.

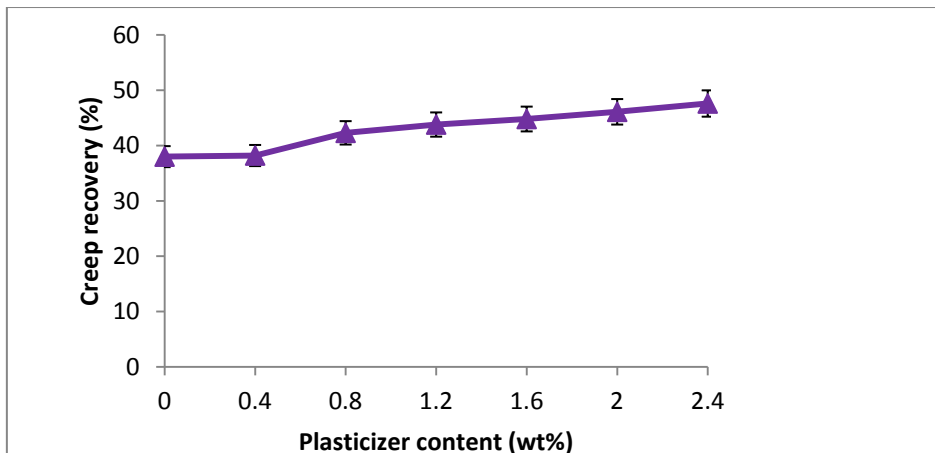


Fig. 6: Creep recovery versus plasticizer (HCHD) content

Compressive strength is a support-factor that is related to foam load-bearing capacity or ‘firmness’, while creep recovery is an indicator of foam resilience. These parameters are very important especially in PUF application that requires high energy impact absorption such as packaging, furniture and beddings, foot wears etc.

Conventional (Standard) Flexible PUF Versus Plasticized Castor Oil-Based PUF

The ability of HCHD plasticization to produce fairly soft and flexible castor oil - based PUFs has prompted a comparison between their physical and mechanical properties, and those of conventional (standard) flexible PUFs (Table 3).

Table 3: Values of physical and mechanical properties of flexible castor oil-based PUFs *versus* international standards for the conventional flexible foam.

Property	Observed	Standard
Density (Kg/m ³)	19.50 – 21.45	12.81 – 40.05 ASTM D 3574-11
Water absorption (wt.%)	2.24 – 2.26	<3 (ASTM D570-98)
Compressive Strength (KN/m ²)	48.80 – 51	>172 (ASTM D1621-10)
Creep recovery (%)	44.20 – 47.60	-

Divergent compressive strength and to a lesser extent density values between the two foam types might be as a result of the application of reinforcing fillers in some formulations to enhance foam firmness in the commercial flexible PUF.

Scanning electron microscopic (SEM) analysis of the castor oil - based PUFs has shown that soft, flexible foams can be produced at relatively higher plasticizer content in the formulation (Fig. 7).

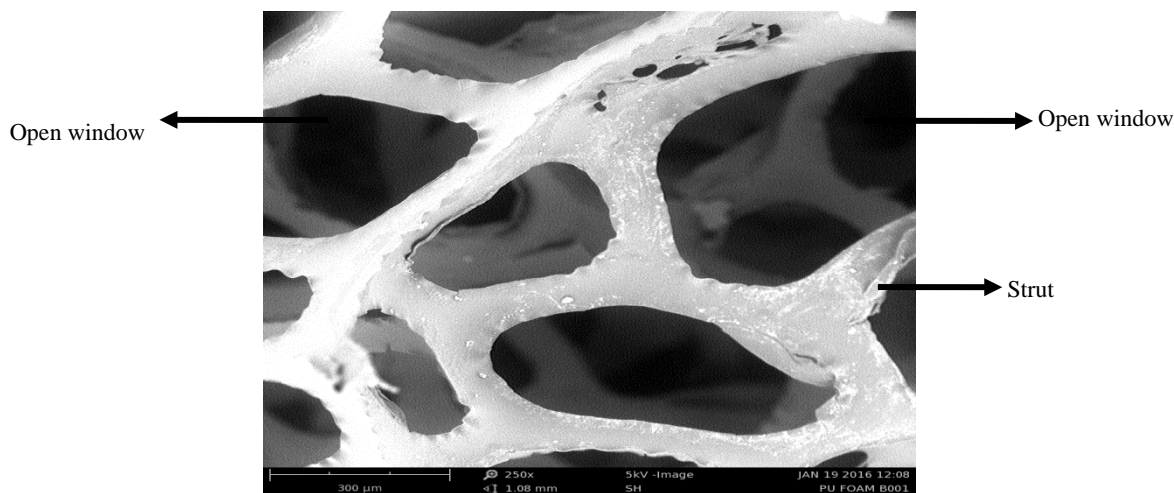


Fig.7: SEM image of HCHD plasticized castor oil-based PUF at 2.4 wt% plasticizer concentration, showing open-cell cellular structure.

CONCLUSION

The *in-situ* chemical modification of castor oil with a novel, oil-compatible C-17 chlorinated hydrocarbon internal plasticizer (HCHD) prior to foam reaction with TDI has yielded soft, flexible castor oil-based PUFs with physical and mechanical properties comparable to those of the conventional, standard flexible PUF. The new products should provide a number of advantages including processability, mouldability, high impact absorption and provision of comfort if applied in furniture, beddings, foot wears etc. But more importantly, having been obtained from almost 100% castor oil polyol, their availability could assist in reducing the importation of commercial polyol by the foam industry in Nigeria, thereby conserving foreign exchange for the country. The control (neat) foam showed typical characteristics of semi-rigid foam and therefore can be used in thermal insulation, refrigeration, packaging and transportation.

Another major advantage of the new products is their fire retardancy (Yusuf *et al.*, 2016). However, the use of low concentrations (0.4 - 2.4 wt%) of HCHD in the foam formulations was in order not to drastically alter the polymerization and foaming stages of the foam reaction that occur simultaneously, and to reduce the potential toxicity of the chlorinated hydrocarbon plasticizer.

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