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THERMOMECHANICAL CHARACTERISTICS OF RIGID POLY(VINYL CHLORIDE) CROSSLINKED BY A PEROXIDE IN THE PRESENCE OF TRIMETHYLOLPROPANE TRIMETHACRYLATE

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SUMMARY

This paper presents some thermomechanical characteristics of crosslinked poly(vinyl chloride) (PVC) samples such as glass transition temperature (T_g), softening point (T_s), and linear thermal expansion coefficient (α). Probe load of 0.05 N is most suitable to evaluate expansion, softening and contraction of the crosslinked PVC samples. T_g, T_s and α of the crosslinked PVC samples are higher than those of the uncrosslinked samples. The highest T_g is observed in the PVC sample containing 0.4 phr of 1,1-di-(t-amylperoxy) cyclohexane (DAPC) and 10 phr of trimethylolpropane trimethacrylate (TMPTMA). Among the crosslinked PVC samples, the sample with 0.2 phr of DAPC and 15 phr of TMPTMA has the least T_s. The highest α appears in the PVC sample containing 0.4 phr of DAPC and 5 phr of TMPTMA.

I - INTRODUCTION

Thermomechanical analysis (TMA) is an effective method for determination of dimension and thickness changes, thermal characteristics of polymers such as glass transition temperature, softening point, and thermal expansion coefficient, etc. This method shows influence of chemical modification, crosslinking on expansion, softening, and penetration resistance of polymers. For poly(vinyl chloride) (PVC) crosslinked by aminosilanes, Fiaz has shown that crosslinking improved penetration resistance of PVC due to formation of gel part in the material [1, 2]. In a previous paper, crosslinking of rigid PVC by a new peroxide (1,1-di-(t-amylperoxy) cyclohexane) (DAPC) in the presence of trimethylolpropane trimethacrylate (TMPTMA) was reported [3]. Gel content and tensile properties of the peroxide crosslinked PVC samples are higher than those of the uncross-linked PVC samples. The peroxide crosslinking of PVC is expected to enhance penetration resistance and service temperature of PVC. The purpose of this work is to study influence of concentrations of DAPC and TMPTMA on expansion, probe penetration and softening of rigid PVC. Glass transition temperature, softening point, and linear thermal expansion coefficient of the polymer have been determined. From the obtained results, thermal expansion, penetration resistance, service temperature, and softening of the cross-linked PVC samples were evaluated (or determined).

II - EXPERIMENTAL

1. Materials and sample preparation

The PVC used was the K60 PVC suspension resin EVIPOL SH6030 containing 8.6% crystallnity, from EVC (the United Kingdom). The processing aid Paraloid K120N, the lubricants waxes Loxiol G52 and Loxiol G53, the wax PE 190 and the heat stabilizer tribasic lead sulphate (TBLS) were supplied by Rohm Hass (Germany), eChem (the United Kingdom), Hoescht (Germany), and Addis (the United States), respectively. Crosslinking additives were 1,1-di-(t-amylperoxy) cyclohexane (DAPC) from the Institute of Polymer Technology and Material Engineering, Loughborough University (the United Kingdom) and trimethyl-olpropane trimethacrylate $CH_3CH_2C[CH_2\text{-}O\text{-}C(O)\text{-}C(CH_3)=CH_2]_3$ (TMPTMA) from Rohm GmbH (Germany). Proportions of materials used are expressed in parts per hundred of resin (phr). All samples contain 1.2 phr of Loxiol G53, 0.4 phr of Loxiol G52, 0.2 phr of Hoechst PE 190, 1.5 phr of Paraloid K120N, 7 phr of TBLS. Concentrations of TMPTMA and peroxide are varied from 5 to 15 phr and 0.2 to 0.6 phr, respectively.

Dry blends are prepared in a laboratory scale Fielder mixer. All components (except liquid peroxide and TMPTMA) are placed in the mixer when temperature of 50°C is reached. They are mixed at 2000 rpm until the temperature is about 80°C then TMPTMA and peroxide are added, and blending continues until 120°C is reached. Then the dry blend is dumped to a cooled chamber.

Dry blends are milled on two-roll mill for 5 minutes at temperature of 140°C, then pressed for 5 minutes at temperature of 185°C. Finally, the PVC sheet is cooled for 5 minutes.

2. Thermomechanical analysis

A thermomechanical analyzer (Mettler TA4000, Switzerland) with a flat-ended, loaded probe (dia. 3 mm) is used for thermomechanical analysis. PVC samples are heated at 10°C/min from room temperature to 210°C in air. A range of loads (0.01 - 0.1 N) on the probe is investigated. Plots of probe penetration of the above samples are automatically recorded. Thermomechanical characteristics such as glass transition temperature, softening point, and linear thermal expansion coefficient are determined by TMA software connected to the Mettler TA4000. Linear thermal expansion coefficient is calculated by using the point-to-point method (a straight line connecting the chosen temperature limits).

III - RESULTS AND DISCUSSION

Before studying thermomechanical characteristics of the crosslinked PVC samples in detail, it is necessary to investigate loads on the probe to select the most suitable load for the samples. Fig. 1 presents the effect of probe load (from 0.01 to 0.1 N or from 1.02 to 10.2 g) on expansion, softening and contraction of a rigid PVC sample crosslinked by 0.4 phr of DAPC and 10 phr of TMPTMA. When small loads (0.01 and 0.03 N) are used, a significant sample expansion (increase of thickness, positive Δl) occurs. However, it is difficult to estimate contraction of the sample after softening. With a high probe load (0.1 N), it sinks into the sample prematurely (decrease of thickness, negative Δl), and the expansion of the sample is not observed. Using middle probe load (0.05 N), it is able to observe and evaluate both of expansion and contraction of the crosslinked PVC sample easily. The same load was also found to be the optimum in the paper related with silane crosslinking of PVC [1]. Therefore, in the following TMA measurements, 0.05 N probe load is the most suitable for all crosslinked PVC samples.

Fig. 2 performs TMA curvers of PVC samples containing the same concentration of TMPTMA (10 phr) and different concentrations of DAPC. It is clear that the PVC sample without peroxide is easier to be softed and penetrated than the samples crosslinked by the peroxide in the presence of TMPTMA. It also shows the crosslinking of poly-TMPTMA onto PVC to form graft copolymer, crosslinked structures like **PVC-(TMPTMA)$_x$** and **PVC-(TMPTMA)$_x$-PVC** as well as three-dimensional network is able to improve expansion and penetration resistance of the samples.

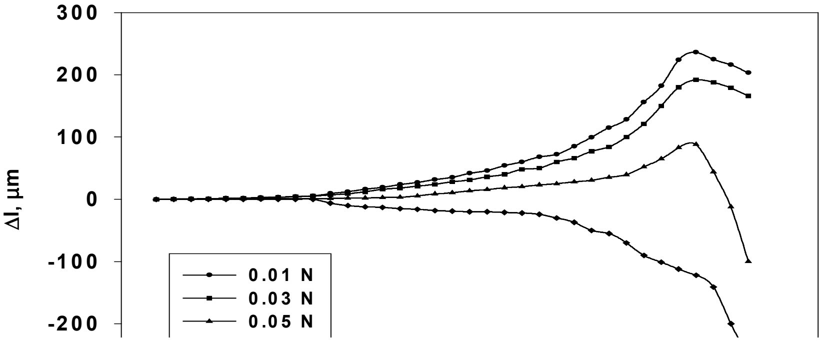

Fig. 1: Effect of probe load on expansion and softening behavious of a rigid PVC sample crosslinked

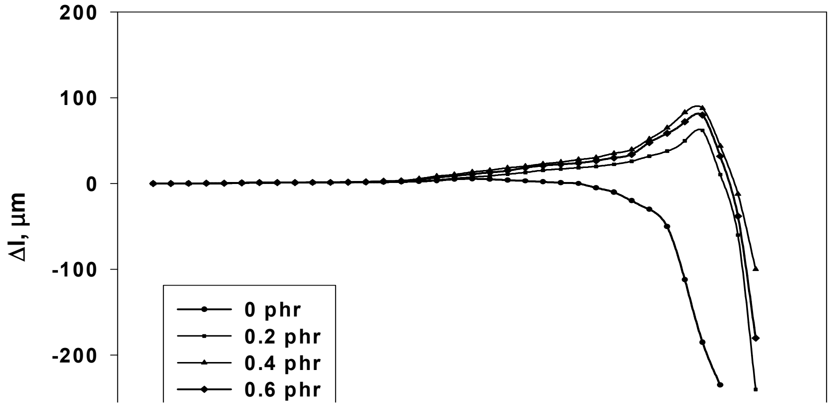

Fig. 2: TMA curvers of PVC samples crosslinked by different concentrations of DAPC and 10 phr of TMPTMA

Glass transition temperatures (T_gs) of the PVC samples containing different concentration of DAPC and TMPTMA are demonstrated in Fig. 3. T_g of all crosslinked PVC samples is higher than that of the uncrosslinked samples. This reflects an useful increase in service temperature of the material. It can be suggested that the increase in T_g also relates to the formation of graft copolymer, with relatively short bulky chains of poly-TMPTMA linking the PVC molecules and three-dimensional network. These structures cause restriction of molecular mobility and orientation of PVC chains and as a result, T_g of the crosslinked PVC samples is higher than that of the uncrosslinked samples [4]. At any concentration of TMPTMA, a maximum T_g of the PVC samples occurs with 0.4 phr of DAPC. The highest T_g at this peroxide concentration is observed in the presence of 10 phr of TMPTMA. T_g of the PVC crosslinked samples decreases with increasing concentration of TMPTMA up to 15 phr. There is possibly still a plasticization effect operating of TMPTMA, reducing T_g of the PVC samples despite the homopolymerisation of TMPTMA like Garcia-Quesada has explained [4]. Therefore, in order to obtain the material with high service temperature, 0.4 phr of DAPC and 10 phr of TMPTMA can be used in PVC compound.

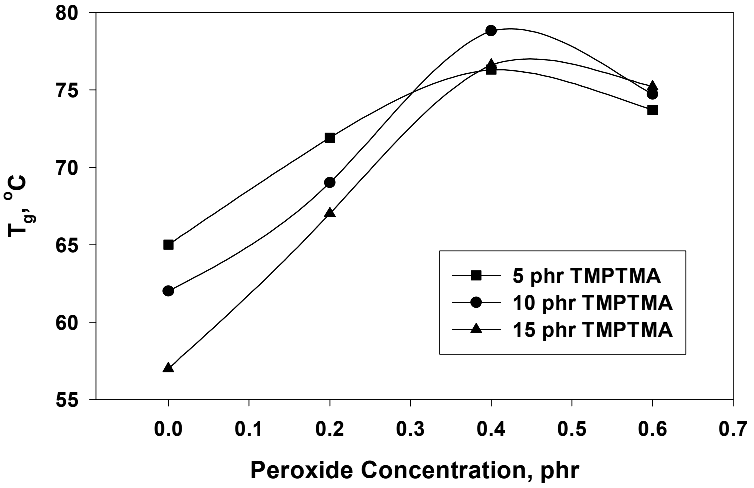

Fig. 3: Glass transition temperature (T_g) of the PVC samples containing different concentrations of DAPC and TMPTMA

Used PVC contains a network of crystallites (8.6%), which act as physical crosslinks, and melt over a wide temperature range starting at about 110 °C. About T_g, softening depends on the melting of these crystallites, but can be changed by a chemical crosslinked network [5]. The crosslinking influences on the softening point (T_s) of the PVC samples in comparing with the uncrosslinked PVC samples (Table 1). For the uncrosslinked PVC samples, T_s decreases with increasing concentration of TMPTMA. This can be also explained by the presence of TMPTMA as a plasticizer. It improves the molecular mobility, melting and softening of PVC and a result, T_s decreases with increasing concentration of TMPTMA [6, 7]. T_s of all crosslinked PVC samples is higher than that of the uncrosslinked samples. Maximum difference of T_s between the uncrosslinked - and crosslinked PVC samples is 16°C. The crosslinking and grafting of poly-TMPTMA chain radical on to PVC molecule to form graft copolymer, crosslinked structures as well as three-dimensional network limit molecular mobility and melting of PVC chains. So, the crosslinked PVC samples are more difficult to be softed and penetrated. Among the samples crosslinked by DAPC and TMPTMA, the sample containing 0.2 phr of DAPC and 15 phr of TMPTMA has the minimum T_s.

Table 1: Softening point of the PVC samples containing different concentrations of DAPC and TMPTMA

Concentrations of TMPTMA	Softening point, °C			
	0 phr of DAPC	0.2 phr of DAPC	0.4 phr of DAPC	0.6 phr of DAPC
0	176	178	181	183
5	175	181	184	186
10	173	184	186	187
15	171	180	185	186

Table 2 presents the influence of concentrations of DAPC and TMPTMA on linear thermal expansion coefficient (α) of the PVC samples. The obtained results show that in the samples without DAPC, α only increases with increasing concentration of TMPTMA up to 10 phr. Thereafter, it decreases with increasing concentration of TMPTMA. α of the crosslinked PVC samples is higher than that of the uncrosslinked PVC samples. This is explained by the crosslinking PVC in the presence of DAPC and TMPTMA as mentioned above. At any concentration of TMPTMA, a maximum α of the PVC samples also appears at 0.4 phr of DAPC. The highest α at this peroxide concentration is observed in the presence of 5 phr of TMPTMA. α of the PVC crosslinked samples decreases with increasing concentration of TMPTMA up to 15 phr. Therefore, in order to obtain PVC having the highest α, 0.4 phr of DAPC and 5 phr of TMPTMA can be used in the material.

Table 2: Linear thermal expansion coefficient of the PVC samples containing different concentrations of DAPC and TMPTMA

Concentrations of TMPTMA	Linear thermal expansion coefficient, μm/m °C			
	0 phr of DAPC	0.2 phr of DAPC	0.4 phr of DAPC	0.6 phr of DAPC
0	4.16	6.58	8.34	8.80
5	49.56	226.92	378.02	298.67
10	58.33	238.89	371.77	301.00
15	42.70	198.64	212.69	204.85

IV - CONCLUSION

1. For thermomechanical analysis of crosslinked rigid PVC, probe load of 0.05 N is the most suitable to observe and evaluate expansion, softening and contraction of the sample.

2. Glass transition temperature of the PVC samples crosslinked by DAPC and TMPTMA is higher than that of the uncrosslinked samples. It reflects an useful increase in service temperature of the material. At any concentration of TMPTMA, a maximum glass transition temperature of the PVC samples occurs with 0.4 phr of DAPC.

3. The crosslinked PVC samples are more difficult to be softed and penetrated than the uncrosslinked ones. Maximum difference of softening point between the uncrosslinked - and crosslinked PVC samples is 16°C. Among the samples crosslinked by DAPC and TMPTMA, the sample containing 0.2 phr of DAPC and 15 phr of TMPTMA has the minimum softening point.

4. The PVC sample crosslinked by 0.4 phr of DAPC and 5 phr of TMPTMA has the highest linear thermal expansion coefficient.

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