

Additives Effects on the Shrinkage Behavior of PVC Sheets

P. Hadi, A. A. Babaluo

Research Center for Polymeric Materials, Sahand University of Technology (SUT), Tabriz, Iran

Received 3 January 2007; accepted 26 June 2007

DOI 10.1002/app.27045

Published online 4 September 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Despite the unique applications of heat shrinkable PVC sheets in food packaging industry, a few works have been carried out on the shrinkage behavior of this kind of sheets. So, in our work, investigation of the shrinkability of PVC sheets and influence of different parameters on the above-mentioned property has been focused, intensively. This paper presents the results of research aimed at characterizing the shrinkage behavior of PVC sheets, accompanied by the effect of different additives and their weight fractions on the shrinkability of the prepared sheets using experimental design Taguchi method. Also, shrinkage behavior of PVC sheets at opti-

mum conditions has been studied and the stretching and shrinking temperature effects have been investigated. It was found that, among seven investigated variables, plasticizer has the most significant effect on the shrinkability of PVC sheets. Also, at optimum conditions, an increase in the stretching temperature can extensively influence the crystalline structure of the polymer and subsequently, shrinking temperature. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3967–3974, 2007

Key words: PVC sheet; shrinkage; additive; experimental design

INTRODUCTION

Shrinkage occurs when heat is applied to a stretched polymer. This driving force gives mobility to the oriented molecular chains that tend to return to their initial state, according to the principle of the increase of entropy.¹ The stretching or deformation of the polymer, accompanied by heating, results in the orientation of the macromolecular chains and elastic stress is developed in the material. If the polymer is cooled in this stretched condition, reformation of the plastic crystalline domains freezes the elastic stress in the material. The material retains the expanded shape, even on the removal of the deforming force, which is called the shape memory phenomenon. This material is now heat shrinkable, and the stored stress can be recovered at any time by heating it to a high temperature. Heat shrinkable polymers have a wide application in the packaging industry, electrical power and electronic equipment, cable industry, and in the preparation of heat shrinkable tubes and connections.²

It is shown that the crystalline domain of a polymer can be more oriented than the amorphous domain. On the other hand, results have shown that

drawing results in the alignment of crystallites within the plain of the film, together with the formation of mesomorphous structure. Despite the low value of crystallinity in some polymers such as PVC (approximately 10%), it has a significant effect on these materials processing, properties, plasticization, orientation, and thus shrinkage behavior.¹ Also, some additives, such as plasticizers and internal lubricants, play an important role on the properties of these low crystalline polymers. Because these additives are incorporated in the amorphous part of polymers while the structure and size of any crystalline part remains unaffected.^{3,4}

Plasticizers are one of the most important additives used in the plastics industry.⁵ The primary role of these materials is to improve the flexibility and processibility of polymers by lowering the second order transition temperature. The most frequently used plasticizer in food packaging industry is di(2-ethylhexyl)phthalate (DEHP), which is added to heat shrinkable PVC films in order both to impart the required deformability and to reduce the rate of dehydrochlorination of PVC by inhibiting the growth of polyene sequences.^{3,6–10}

Nevertheless, thermal degradation of PVC is one of the inherent problems associated with the manufacture and use of some polymers.¹¹ These problems can be minimized by introducing stabilizing additives, which generally contain heavy metals such as cadmium and lead, organotin compounds,¹² phosphites,¹³ and calcium and zinc salts.^{14,15} But it is shown that

Correspondence to: A. A. Babaluo (a.babaluo@sut.ac.ir).

Contract grant sponsor: Sahand University of Technology (SUT).

TABLE I
Characteristics of Materials

Materials	Function	Molecular formula	Characteristics	Supplier
Polyvinylchloride	Matrix phase	PVC	Fine white powder K -value = 5765	Abadan Petrochemical Co. ^a
Dioctylphthalate	Plasticizer	DOP	Transparent liquid	Farabi Petrochemical Co. ^b
Calcium carbonate	Filler	CaCO ₃	Fine white powder	Poodrkar Co. ^c
Calcium stearate	Stabilizer	Ca(OCOC ₁₇ H ₃₅) ₂	Fine white powder	Poodrkar Co. ^c
Zinc stearate	Stabilizer	Zn(OCOC ₁₇ H ₃₅) ₂	Fine white powder	Poodrkar Co. ^c
Stearic acid	Lubricant	C ₁₈ H ₃₆ O ₂	Crystalline particles	EPS IMPEX Co. ^d
Paraffin wax	Lubricant		Transparent liquid	Poodrkar Co. ^c

^a Abadan Petrochemical Company, Abadan, Khuzestan, I.R. Iran.

^b Farabi Petrochemical Company, Tehran, I.R. Iran.

^c Poodrkar Company, Tehran, I.R. Iran.

^d EPS IMPEX Company, Sabah, Malaysia).

the latter ones have less toxicity and so they can be used as heat stabilizers in most applications, especially food packaging and medical devices.^{16–18}

Another class of additives is lubricant which reduces the friction either between the polymer chains, leading to a noticeable reduction in viscosity, or between the polymer and hot metal of the processing equipment.^{19,20} Also, to lower the compound cost, solid fillers such as CaCO₃ are used which strongly influence the mechanical and dimensional properties (shrinkage) of polymers.^{21,22}

An enormous amount of work has already been carried out on the effect of additives on various properties of polymers. But there is little systematic information available concerning the effect of additives on the shrinkage behavior of polymers. Mishra et al.²³ have investigated the behavior of heat shrinkable polymer blends. Khonakdar et al.²⁴ have studied shrinkage behavior of PE. But no work has been carried out on the parameters affecting PVC shrinkage behavior. Therefore, investigating the effects of key variables on the shrinkage behavior of PVC as a commonly-used polymer in food packaging industry is necessary.

The aim of the present study was to investigate the effect of different additives such as plasticizer, filler, stabilizer and lubricant and their weight fractions on the shrinkability of PVC sheets by using experimental design Taguchi method. Also, the influence of the stretching temperature and shrinking temperature on the shrinkage behavior of PVC sheets was studied at optimum conditions determined by experimental design.

EXPERIMENTAL

Materials

The characteristics of materials used in this work are given in Table I.

Sample preparation

Commercial PVC was compounded with plasticizer, stabilizer, lubricant, and filler with different weight

fractions according to the experimental design array, as shown in Table II. Then, it was dry blended to reach the uniform state at high temperatures about 120°C. The film preparation took place during uniaxial compression molding of sheet samples using a laboratory hot press at elevated temperature of 175°C and pressure of 70 bar for 1 min. Then, after removal of heating, the sheet samples were naturally cooled to ambient temperature.

Stretching

PVC sheet samples, based on the experimental design array, were stretched at the ambient temperature with stretching rate of 100 mm/min and stretching level of 100% strain in a tensile machine (Adamel, Lhomargy, Model DY 26, French). After 24 h, the stress was released and the film was allowed to relax. The final stretching level after relaxation was about 50%. The optimum samples, according to the experimental design results, were stretched isothermally in a heating chamber at two different stretching temperatures, 100 and 120°C, with a rate of 100 mm/min up to 200% in a tensile machine (Autograph, Shimadzu, Japan) according to ASTM D 882. The stretched samples were immediately cooled

TABLE II
Experimental Design Array

No.	Factors	Level 1	Level 2	Level 3
1	PVC ^a	1	2	
2	Plasticizer	35	40	45
3	Filler	5	10	15
4	Stabilizer ratio ^b	0.5	1	2
5	Stabilizer	1	2	3
6	Lubricant ratio ^c	0	1	Infinite
7	Lubricant	0.2	1	2

^a "PVC_1" and "PVC_2" indicate K -values 57 and 65, respectively.

^b "Stabilizer ratio" denotes calcium stearate to zinc stearate weight ratio.

^c "Lubricant ratio" denotes stearic acid to paraffin wax weight ratio.

TABLE III
L₁₈ Orthogonal Taguchi Array and the Experimental Results

Trial no.	PVC M.W.	Plasticizer	Filler	Stabilizer	Stabilizer ratio	Lubricant	Lubricant ratio	Results	
								Rep. 1	Rep. 2
1	1	35	5	1	0.5	0.2	0	14.4	14.1
2	1	35	10	2	1	1	1	12.8	13.5
3	1	35	15	3	2	2	Inf.	12.8	12.8
4	1	40	5	2	0.5	2	1	11.24	11.5
5	1	40	10	3	1	0.2	Inf.	11.3	10.3
6	1	40	15	1	2	1	0	11.24	10.3
7	1	45	5	1	1	1	Inf.	11.24	10.9
8	1	45	10	2	2	2	0	9.6	9.6
9	1	45	15	3	0.5	0.2	1	8.34	8.3
10	2	35	5	3	2	1	1	14.65	14.1
11	2	35	10	1	0.5	2	Inf.	13.5	12.8
12	2	35	15	2	1	0.2	0	12.76	11.5
13	2	40	5	3	1	2	0	11.24	10.9
14	2	40	10	1	2	0.2	1	10.5	10.9
15	2	40	15	2	0.5	1	Inf.	11	10.3
16	2	45	5	2	2	0.2	Inf.	11	10.3
17	2	45	10	3	0.5	1	0	8.84	9.0
18	2	45	15	1	1	2	1	8.0	8.3

in the stretched condition to room temperature and then was removed from the apparatus and conditioned at ambient temperature.

Shrinkage studies

The specimens were put in a bath (Julabo, Model 20B, Germany) with circulating water at a temperature range of 20–100°C for 10 s. Then, the final lengths of the specimens were measured according to ASTM D 2732. As the definition says: shrinkage presents the percentage change of dimensions of the specimens before and after heating. Therefore, the shrinkage formula will be²:

$$\text{Sh}\% = \frac{L_0 - L_1}{L_0} \times 100$$

where Sh is the percentage shrinkage, L_0 is the initial length of the sheet before heating, and L_1 is the final length after shrinkage.

Thermal analysis

Mass loss during heating of the PVC films was measured by a Perkin–Elmer, Pyris Diamond (Japan) thermogravimetric analyzer (TGA) with heating at a rate of 20°C min⁻¹ from 30 to 500°C under 40 cm³ min⁻¹ nitrogen gas flow.

Statistical survey of the heat shrinkable PVC sheets

Experimental design is generally applied to determine the dependence of a target variable such as shrinkability, Sh%, on the rest variables.

The effects of one variable at two levels and six variables at three levels (Table III) on the shrinkage behavior of the heat shrinkable PVC films were investigated. To reduce the total number of experiments, a fractional factorial design was employed. The Taguchi statistical method is well suited to the study of a process that has many factors that need to be evaluated at several levels.

An L_{18} ($3^6 \times 2^1$) orthogonal array of experiments was chosen for the initial set of experiments. This L_{18} array can be used, in principle, to examine the effects of six variables at three levels and one variable at two levels on a target variable (Sh%) in only 18 experiments.²⁵

RESULTS AND DISCUSSION

Shrinkage behavior and statistical analysis

L_{18} orthogonal array of shrinkage experiments for PVC sheets is shown in Table III. Also, individual experimental results with two repetitions are included in this table.

A statistical analysis of the results has been carried out to identify the effect of individual variables and their interactions. The statistical technique popularly known as analysis of variance (ANOVA) was used to determine the significance of each variable and their interaction effects. The signal-to-noise ratio (S/N) was used in the statistical analysis of the results. In fact, it is a way of isolating the sensitivity to noise factors.^{25–27} The results are set out as shown in Table IV. Equations for conducting the analysis of variance are presented in Appendix.

TABLE IV
Analysis of Variance (ANOVA)

No.	Factors	DOF	Sums of squares	Variance	F-ratio	Pure sum	Percent
1	PVC	1	0.231	0.231	14.743	0.215	0.610
2	Plasticizer	2	27.366	13.683	871.769	27.334	77.414
3	Filler	2	5.517	2.758	175.755	5.485	15.536
4	Stabilizer ratio	2	0.481	0.240	15.328	0.449	1.273
5	Stabilizer	2	0.251	0.125	8.023	0.220	0.624
6	Lubricant ratio	2	0.970	0.485	30.929	0.939	2.660
7	Lubricant	2	0.428	0.214	13.636	0.396	1.123
	Other/error	4	0.061	0.015			0.760
	Total	17	35.309				100.000%

The statistical analysis of the results shows that, within the selected range of variables, DOP, as plasticizer, has the greatest effect on the shrinkage behavior of heat shrinkable PVC films. Also, CaCO_3 has a considerable effect on the mentioned property of the films. But the influence of the rest variables is small in comparison with the former mentioned variables (plasticizer and filler).

Evaluation of the effect of additives on shrinkage behavior

Plasticizer

The shrinkability of PVC films decrease by increasing the plasticizer content, as shown in Figure 1(a). Plasticizers are actually low molecular weight resins

or liquids, which form secondary bonds to polymer chains and spread them apart. Thus, plasticizers reduce polymer-polymer chain secondary bonding and provide more mobility for macromolecules, resulting in softer mass and reduced-modulus materials.² Therefore, these materials reduce the polymeric chain entanglements, leading to less shrinkage. Another factor can be presumed to be the reduction in resin content by increasing additives content, which causes to change the final product properties (e.g., shrinkability).

Filler

Figure 1(b) shows that filler has a reverse effect on shrinkability, i.e., shrinkability decreases by increas-

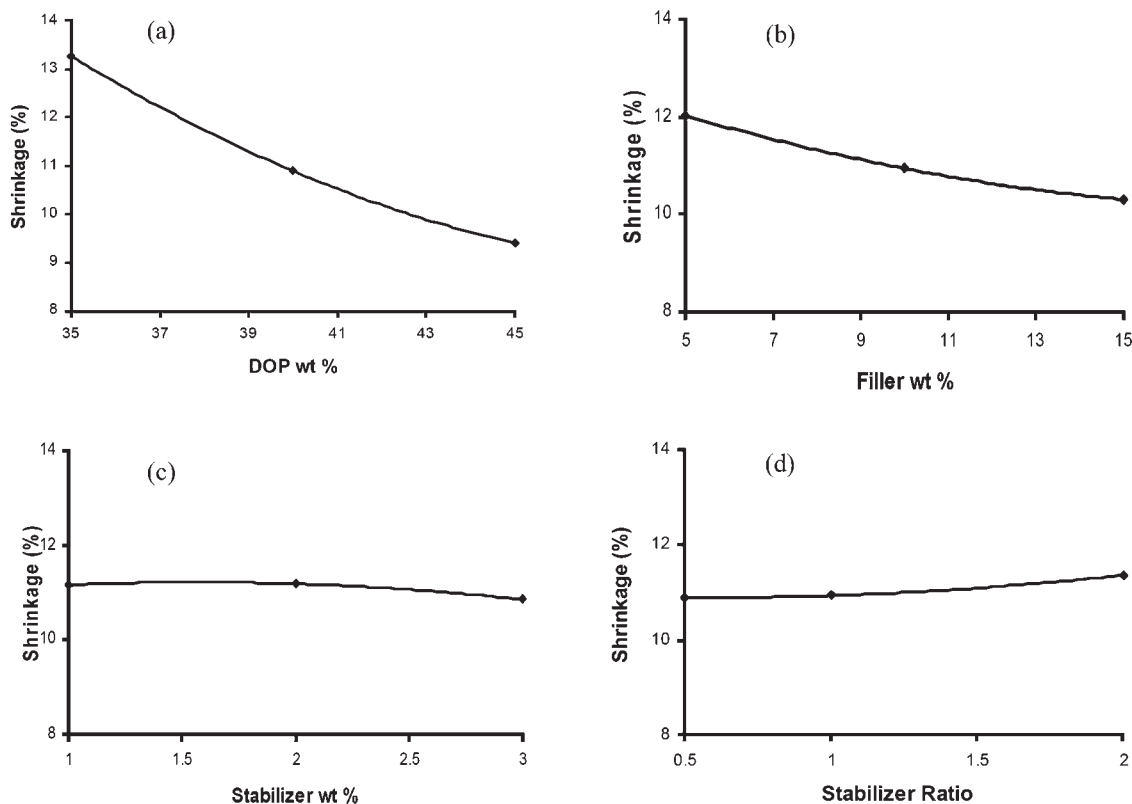


Figure 1 Effect of (a) plasticizer, (b) filler, (c) stabilizer, (d) stabilizer ratio on shrinkability of PVC sheets.

ing the filler content. These results are in good agreement with the literature.²² This behavior can be attributed to the stiffening effect of extender filler on the polymeric chains and segments. Also, the disruption of the crystallite structure of PVC by adding filler,²¹ might be another factor which results in a decrease in the shrinkability.

Stabilizer

As shown in Figure 1(c), the stabilizer influence on the shrinkability is negligible and can be pooled. This behavior can be related to the fact that the contents of both zinc and calcium stearate with two different roles in the stabilizer system, increase by increasing the stabilizer content. Zinc stearate is a primary heat stabilizer, which participates in blocking polyene formation, whereas calcium stearate is a secondary stabilizer, which does not directly influence the dehydrochlorination rate, nor do they displace labile chlorine. The main function of the calcium salt is believed to be reaction with HCl and ZnCl₂ to prevent them from accelerating further degradation.¹⁷ Hence, two mechanisms for stabilizer system exist: zinc stearate functions by substituting chlorine atom with the stearate group and thus, the steric effect in the stabilized polymeric chains results in less mobility of the chains and less shrinkage. On the other hand, calcium stearate probably causes more HCl evolution and polyene formation, which leads to more shrinkage. Consequently, these two counteracting mechanisms cause to weaken the effect of stabilizer content.

Stabilizer ratio

Despite the nonsignificant effect of the stabilizer content, as shown in Figure 1(d) and Table IV, the effect of stabilizer ratio on the shrinkage behavior is considerable. By increasing stabilizer ratio, zinc stearate content decreases and thus, the amount of stearate group replacing chlorine decreases, leading to less steric effect in the chains and consequently more shrinkage, whereas calcium stearate content increases, which results in more shrinkage due to more polyene formation. Thus, in contrary to stabilizer effect, these two mechanisms support each other and the influence of stabilizer ratio is more pronounced.

Lubricant

As discussed before, lubricant has a plasticizer-like behavior and is expected to lower the shrinkability by increasing its weight fraction. But the lubricant weight fraction is very low in comparison with plas-

TABLE V
Effect of Lubricant Ratio on Shrinkability

	Lubricant ratio level		
	Level 1	Level 2	Level 3
Stearic acid	0	1	1
Paraffin	1	1	0
Lubricant ratio	0	1	Inf.
Shrinkage percent	10.98	10.76	11.47

ticizer. Therefore, its effect on shrinkage behavior of PVC sheet is not comparable with plasticizer (see Table IV).

Lubricant ratio

The shrinkage results have been presented in Table V in three levels which are derived from experimental design results. As illustrated in this table, simultaneous presence of the two lubricants causes a reduction in the shrinkability, i.e., the two lubricants support each others negative effects.

PVC molecular weight

Commercial PVC polymers with two different *K*-values (molecular weights) have a very low influence on shrinkability, so that the shrinkage results of PVC polymers were obtained 11.21 and 10.92% for *K*-values of 57 and 65, respectively. However, polymer molecular weight has a reverse effect on shrinkability. This can be related to decrease in the crystallinity of PVC by an increase in molecular weight, which is in good agreement with the literature.²⁸

Interaction effects

The synergistic effect of two or more factors in a factorial experiment where effect of one factor depends on the variation of another is called interaction and the same are shown in Table VI. The severity index is the measure of the extent of the interaction between two chosen parameters. It can be inferred from the values indicated in the table, that the factors lubricant and stabilizer have the maximum interactions with lubricant ratio, respectively. As the

TABLE VI
Interacting Severity Index of Variables

No.	Interacting factor pairs	Columns interaction	Severity index (SI, %)
1	Lubricant ratio × lubricant	6 × 7	88.97
2	Stabilizer × lubricant ratio	5 × 6	72.43

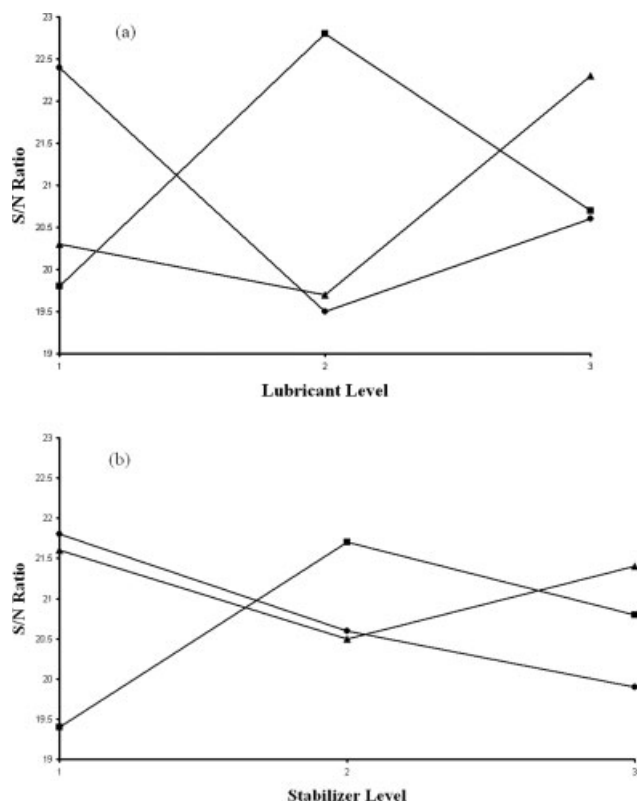


Figure 2 Graph showing the interaction of (a) lubricant and lubricant ratio, (b) stabilizer and lubricant ratio (●—Level 1, ■—Level 2, ▲—Level 3).

severity index increases, the lines in the graphs showing the interactions of the parameters tend to intersect each other at right angles and as it decreases the lines tend to be parallel to each other (see Fig. 2). In other words, the severity index is expressed in percent, ranging between 0 and 100, which corresponds to angle between the lines in the range of 0–90 degrees. Thus 100% SI will mean 90 degrees angle between the lines indicate the strongest presence of interaction and 0% SI will indicate parallel lines and non existence of the same. But, when columns are not reserved for the interactions, more and exact information about their presence should be utilized for future repeat experiments.

The significant interaction of lubricant–lubricant ratio can be due to the different roles of the used lubricants. Stearic acid is somewhat polar to be soluble in polymer and to reduce the attractive van der Waals forces among the chains whereas paraffin has low compatibility with the polymer and form a film at the interface between the polymer melt and the metal as they exude.²¹

Also, there is a considerable interaction between the stabilizer and lubricant ratio. It can be related to the overlapping effect of stearic acid as a lubricant and stabilizers. As mentioned in the literature,²¹ lubricants with costabilizing groups act as secondary

stabilizers by altering the stability of a PVC compound by various mechanisms. According to the mechanism of stabilization, the stabilizers should ionize to be able to displace labile chlorine.¹⁷ However, when stearic acid ionizes, two mechanisms emerge as follows: the first is the existence of stearate group which plays the same role as the stabilizers and the second one is the role of H^+ , which reduces stabilization as a Lewis acid.²¹ These two mechanisms have opposite effects on the stabilization and thus shrinkage. To investigate, which of the mentioned mechanisms is dominant, more detailed studies should be carried out.

Shrinkage behavior of PVC sheets at optimum conditions

Two parameters, shrinking temperature and ultimate shrinkage, characterize the shrinkage behavior of PVC sheets prepared at optimum conditions. Figure 3 illustrates the percent shrinkage versus shrinking temperature for two different stretching temperatures (100 and 120°C). The results show that the sample stretched at 120°C shows a higher shrinking temperature, compared with that stretched at 100°C. This behavior can be due to the effect of different stretching temperatures on the characteristics of crystalline domain, i.e., the higher stretching temperature results in an increase in the thickness of the crystal lamella and subsequently an increase in the melting point of the crystalline domain which is the determining factor in the shrinkage behavior of PVC sheets.

Thermal analysis for DOP evaporation

To examine the evaporation of DOP during processing, thermogravimetric analysis has been carried out. In Figure 4(a), thermal analysis of the optimum PVC sheet, based on the experimental design results, has

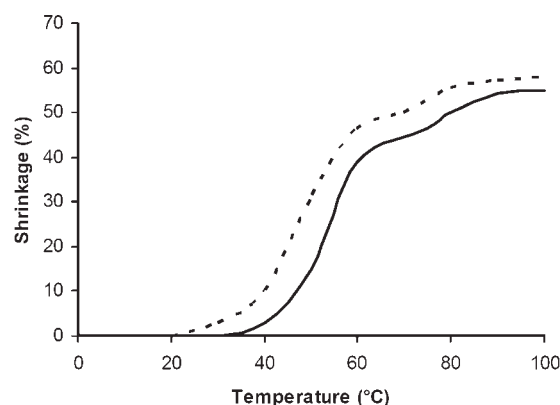


Figure 3 Effect of stretching temperature on the shrinkage behavior of optimum PVC sheet (---, 100°C; —, 120°C).

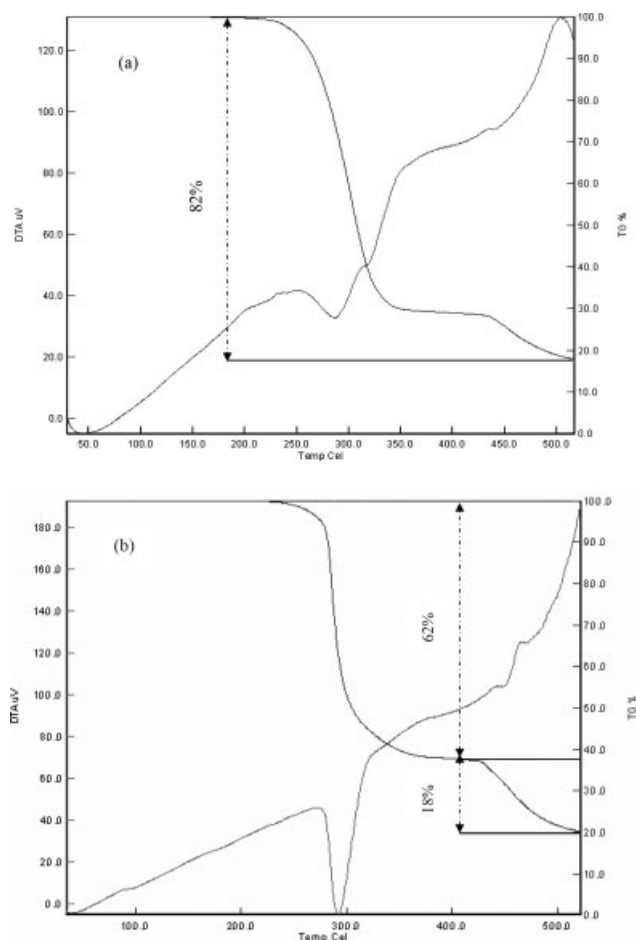


Figure 4 TG-DTA curve for (a) optimum PVC sheet, (b) pure PVC.

been presented. As shown in this Figure, total degradation is about 82 wt % up to 550°C. Also, thermal analysis of pure PVC sheet has been shown in Figure 4(b). The obtained results show that total degradation of pure PVC is about 80 wt % at the same range of temperature. Hence, considering that the resin (PVC) percentage in the optimum PVC sheet was 59 wt %, about 47% of the total degradation of the optimum sheet is related to PVC and the rest (35%) can be due to the contribution of DOP evaporation. Therefore, owing to the initial weight percent of DOP in the manufactured optimum PVC sheet, it is obvious that no significant evaporation of plasticizer has occurred during processing.

CONCLUSIONS

The effect of different additives such as plasticizer, stabilizer, lubricant, and filler on the shrinkage behavior of heat shrinkable PVC sheets prepared by uniaxial compression method was investigated using

Taguchi experimental design method. The results showed that plasticizer and filler have significant effects on the shrinkability of PVC sheets, which can be not only due to the structural effects, but also due to the important reduction of the resin amount in the bulk. Also, optimum conditions were determined for the preparation of PVC sheets with maximum shrinkage and then, stretching temperature and shrinking temperature effects on the shrinkability of the prepared sheets were investigated. The obtained results revealed that an increase in the stretching temperature produces a considerable increase in the shrinking temperature.

The authors thank coworkers and technical staff in the research center for polymeric materials of SUT, Mr. Khademian and Mr. Haghghian for their help during various stages of this work.

APPENDIX

Analysis of Variance

The variance of the percentage of shrinkage was calculated to identify the most important factors. Equations for conducting the variance are presented in this section:

The conversion of a set of observations into a single number, the S/N ratio, is performed in two steps. First, the mean squared deviation (MSD) of the set is calculated. Second, the S/N ratio is computed from the MSD by the equation:

$$\text{SNR} = \frac{S}{N} = -10 \log_{10}(\text{MSD}) \quad (\text{A1})$$

The bigger is better quality characteristic:

$$\begin{aligned} \text{MSD} &= \frac{(1/Y_1^2 + 1/Y_2^2 + \dots + 1/Y_n^2)}{n} \\ &= \left[\text{Average} \left(\frac{1}{Y^2} \right) \right] = \frac{1}{Y_{\text{exp}}^2} \end{aligned} \quad (\text{A2})$$

where Y_1, Y_2, \dots, Y_n are the set of observations, n , is the number of observations and Y_{exp} is the expected result (or overall evaluation criteria). Sum of squares (S_i) of factor i is calculated according to the equation:

$$S_i = \sum_k^L 1 / N_k \left(\sum_j^N \text{SNR}_j \right)^2 - \frac{\left(\sum_j^N \text{SNR}_j \right)^2}{N} \quad (\text{A3})$$

where N , is the total number of experiments (18 in our case), L , is the number of levels of factor i and

N_{k_i} is the number of experiments at level k . The total sum of squares (S_T) is calculated using equation:

$$S_T = \sum_j^N \text{SNR}_j^2 - \frac{\left(\sum_j^N \text{SNR}_j\right)^2}{N} \quad (\text{A4})$$

Experimental error (S_e) is calculated as follows:

$$S_e = S_T - \sum S_i \quad (\text{A5})$$

Mean square of factor i (V_i) is computed using the following equation:

$$V_i = \frac{S_i}{f_i} \quad (\text{A6})$$

where f_i is degree of freedom (DOF), which is one less than the number of levels. The total degree of freedom of the results (f_T) is one less than the total number of experiments. The degree of freedom for error variance (f_e) is the total degree of freedom minus sum of degree of freedom of factors.

The next step was the calculation of the variance ratio (F_i or F -Ratio), which is the quotient of mean square of factor and error.

The fraction of importance of each factor (in percents), X_i , is calculated according to the equation:

$$X_i = \frac{S'_i}{S_T} \times 100 \quad (\text{A7})$$

where S'_i is the net sum of square and is presented as follows:

$$S'_i = S_i - (V_e \times f_i) \quad (\text{A8})$$

References

- Kim, H. C.; Gilbert, M. *Polymer* 2004, 45, 7293.
- Khonakdar, H. A.; Morshedian, J.; Mehrabzadeh, M.; Wagenknecht, U.; Jafari, S. H. *Eur Polym J* 2003, 39, 1729.
- Rahman, M.; Brazel, C. S. *Prog Polym Sci* 2004, 29, 1223.
- Oosterhout, J. T.; Gilbert, M. *Polymer* 2003, 44, 8081.
- Pita, V. J. R. R.; Sampaio, E. E. M.; Monteiro, E. E. C. *Polym Test* 2002, 21, 545.
- Wang, Q.; Storm, B. K. *Polym Test* 2005, 24, 290.
- Latini, G. *Clin Chimica Acta* 2005, 361, 20.
- Latini, G.; Felice, C.; Verrotti, A. *Reprod Toxicol* 2004, 19, 27.
- Marcilla, A.; Garcia, S.; Garcia-Quesada, J. C. *J Anal Appl Pyrolysis* 2004, 71, 457.
- Vinhas, G. M.; Souto-Maior, R. M.; Almeida, Y. M. B.; Neto, B. B. *Polym Degrad Stabil* 2004, 86, 431.
- Okieimen, F. E.; Eromonsele, O. C. *Eur Polym J* 2000, 36, 525.
- Sabaa, M. W.; Mohamed, R. R.; Yassin, A. A. *Polym Degrad Stabil* 2003, 81, 37.
- Arkis, E.; Balkose, D. *Poly Degrad Stabil* 2005, 88, 46.
- Steenwijk, J.; Langerock, R.; Es, D. S.; Haveren, J.; Geus, J. W.; Jenneskens, L. W. *Polym Degrad Stabil* 2006, 91, 52.
- Benaniba, M. T.; Belhaneche-Bensemra, N.; Gelbard, G. *Polym Degrad Stabil* 2003, 82, 245.
- Atek, D.; Belhaneche-Bensemra, N. *Eur Polym J* 2005, 41, 707.
- Kann, Y.; Billingham, N. C. *Polym Degrad Stabil* 2004, 85, 957.
- Facio, A. C.; Cantu, R. B.; Pardo, M. E. M.; Abrego, H. C. *Radiat Phys Chem* 2004, 71, 245.
- Richter, E. *Plast Additives Compound* 2000, 2, 14.
- Fras, I.; Cassagnau, P.; Michel, A. *Polymer* 1999, 40, 1261.
- Heiberger, C. A.; Nass, L. I. In *PVC Handbook*, 2nd ed.; Marcel Dekker: New Jersey, 1984; Vol. 4, pp 123–124.
- Markarian, J. *Plast Additives Compound* 2004, 6, 26.
- Mishra, J. K.; Raychowdhury, S.; Das, C. K. *J Reinforced Plast Compos* 2002, 21, 195.
- Morshedian, J.; Khonakdar, H. A.; Mehrabzadeh, M.; Eslami, H. *Adv Polym Technol* 2003, 22, 112.
- Phadke, M. S. In *Quality Engineering Using Robust Design*; Prentice-Hall International, AT & Bell Laboratories: USA, 1989; pp 98–128.
- Roy, R. K. In *A Primer on the Taguchi Method*; Van Nostrand Reinhold: New York, 1990; pp 145–155.
- Kokabi, M.; Babaluo, A. A.; Barati, A. *J Eur Ceram Soc* 2006, 26, 3083.
- Gedde, U. W. In *Polymer Physics*; Chapman & Hall: London, 2000; pp 157–164.