EFFECT OF ADDITIVES ON THE MECHANICAL PROPERTIES OF POLYVINYL CHLORIDE

By

Elgozali A.[1] **and Hassan M.**[2]

1-Department of Plastic Engineering, College of Engineering, Sudan University of Science and Technology, Khartoum P. O. Box: 72, Sudan, E-mail: Elgozalia@hotmail.com, 2-Department of Industrial Chemistry, Faculty of Science, University of Juba, Khartoum P. O. Box: 11883, Sudan

KEYWORDS: Additives, mechanical properties, polyvinyl chloride, plastic material, compounding, cable insulation

ABSTRACT

The effects of additives mainly plasticizer and filler on the mechanic-al properties of polyvinyl chloride (PVC) compounding is examined. Two groups of samples were prepared with different plasticizer and filler content. The first group is free of filler, while the second group, contained beside filler, plasticizer at concentration of 40 parts/100 resin. The plasticizer content ranged from 21–32% by weight of sample. The filler content ranged from 6–17% by weight of sample. All samples contained stabilizer at concentration of 7 parts/100 resin.

Experimental results have shown that tensile strength decreased with increasing plasticizer content for the group of samples free of filler. The trend is completely reversed in the group where the sample contained filler. On the other hand, the elongation at break is inversely proportion to plasticizer content for the group free of filler, while it is directly proportion to plasticizer content for that containing filler. Higher values of modulus of elasticity are obtained for the group of sample contained filler, but it is decreased with increased plasticizer and filler content. Also higher values of the hardness number were obtained for the group free of filler, while it was decreased with increased plasticizer content for both groups.

الملخص:

اختبرت تأثيرات المواد المضافة-تحديداً الملدنات والمالئات - على الخواص الميكانيكية لبوليميرات متعدد كلوريد الفينيل. تم تحضير مجموعتين من العينات تحوي مقادير مختلفة من المادة الملدنة والمادة المالئة، وكانت عينات المجموعة الأولى خالية تماماً من المادة المالئة، بينما حوت عينات المجموعة الثانية

مقادير مختلفة من المادة المالئة بتراكيز بين 6–17% من وزن العينة. حوت جميع العينات في المجموعتين-لأسباب تقنية-مقادير من المادة الملدنة تراوحت في المدى 21-32% من وزن العينة. حوت جميع العينات مادة مثبتة بتركيز 7 أجزاء لكل مائة جزء من بدرة البوليمر.

بينت الاختبارات أن مقاومة الشد تنخفض تدريجياً مع زيادة تركيز الملدن بالنسبة للعينات الخالية من المادة المالئة. هذا التأثير انعكس تماماً في المجموعة المحتوية على المادة المالئة. على صعيد آخر تتناقص المطيلية مع زيادة تركيز الملدن للعينات الخالية من المادة المالئة، بينما تزداد مع زيادة تركيز المادة الملدنة في العينات المحتوية على المادة المالئة. سُجلت قيم عالية لعامل المرونة في مجموعة العينات المحتوية على المادة المالئة. من جهة أخرى يتناقص معامل المرونة مع زيادة تركيز الملدن والمادة المالئة. سُجِلت قيم عالية لرقم الصلادة بالنسبة لمجموعة العينات الخالية من المادة المالئة. تناقص رقم الصلادة مع زيادة تركيز الملدن، بينما تزايد مع زيادة تركيز المادة المالئة.

INTRODUCTION

Plastics have had a significant influence on industrial, domestic and cultural aspects of modern life throughout the nineteenth and twentieth centuries. The development of plastics also reflects economic history. After the Second World War Polyethylene was incorporated into radar systems while poly vinyl chloride replaced the limited stocks of natural rubber as cable insulation[1]. Expansion in the number of processing and fabrication techniques has allowed modern plastics to be manipulated in thin film, bulk and foam forms, and to be combined with fibers, metals and wood[2,3]. Today there are 50 different basic types of plastics, included in 60,000 different plastics formulations. Those based on polyolefins and polyvinyl chloride, have highest consumption worldwide[4]. Six new plastics materials are sent for evaluation and approval to major testing laboratories in the USA each week [5].

Baumann's polymerization of vinyl chloride in 1872 is regarded as the earliest documented preparation of PVC homopolymer[6]. The first commercial interest in PVC was shown by the Carbide and Carbon Chemical Corporation, Du Pont and IG Farben, who independently filed patents in 1928[1]. At that stage it was only possible to process the homopolymer in the melt state, at temperatures, where high decomposition rates occurred, whereas copolymers could be processed at lower temperatures. Effective, so-called external plasticization of the PVC homopolymer by incorporating plasticizers was first discovered around 1930[4]. When compounding with dibutyl phthalate and other esters a reduce in the softening point of PVC was occurred, which result in rubber-like properties at room temperature. It was also understood that alkaline-earth metal soaps acted as heat stabilizers[7]. During Second World War, plasticized PVC was recognized as an effective replacement for rubber in cable insulation and sheathing, thereby helping to relieve the acute rubber shortage. Until the 1940s, Britain and the USA had been concerned largely with plasticized PVC, while in Germany development work also concerned unplasticized PVC, a rigid material which only achieved significance in the 1960s. Two events of major significance to PVC production was seen in the 1970s. The oil crisis of 1973 and 1974 caused a shortage of raw materials and fuel accompanied with increase in prices. The world production of polymers increased from 27million tons in 1975 to about 200 million tons per year in 2000 and is still growing(8). In recent years the annual growth rates of PVC production varies between 2 and 10%[4]. Thus PVC is one of the most important synthetic materials.

Unmodified PVC polymer is a brittle, inflexible material with rather limited commercial possibilities. Attempts to process PVC in the raw form using heat and pressure, result in severe degradation of the polymer[9]. Hydrogen chloride is produced and discoloured rapidly from white to yellow to brown to black. These changes observed at processing temperatures, around 150°C. Commercially,compounding PVC contains sufficient modifying components to the raw polymer to produce a homogeneous mixture suitable for processing and requiring performance at the lowest possible price.

Depending on how PVC is compounded it may have rubber–like, flexible properties or have high rigidity. The formulation is determined by the future application of the fabricated PVC product, which can be electrical insulation, medical tubing, food wrap, garden hose, flooring and clothing. The formulation is also determined by the processing technique which is employed.

Proportions of plasticizer in commercial PVC formulations range from 15–50% by weight[4]. Many plasticized PVC formulations are designed to function for less than 20years, but Sudanese industry where cable insulation is preserved for at least 50years. The formulations of cable insulation can be prepared so as to combine their high mechanical strength to a better dimensional stability.

The present study outlines the effect of additives mainly plasticizer and filler on mechanical properties of polyvinyl chloride compounding, i.e. modulus of elasticity, stress at break, ratio of elongation at break, and shore hardness.

MATERIALS AND METHODS

PVC resin with the *K*–value 70 and bulk density of 500kg/m^3, manufa-ctured by SABIC in Kingdom of Saudi Arabia was used in this study. Di-octyl phthalate (DOP) $C_6H_4[COOCH_2CH(C_2H_5(CH_2)_3CH_3]_2$, produced by AUKYING SPECIALTY CHEMICALS in South Korea, was used as plasticizer. It has molecular weight of 390.56kg/kmol. Its boiling point is 202–204°C at 207Mbar, and has density of 985kg/m^3 at 25°C. Di-lead sulphite was chosen as stabilizer. The filler was chosen to be calcium carbonate.

Two groups of samples were prepared. The first group contained PVC resin, plasticizer, stabilizer and filler, (group with filler), for which the effect of filler was studied. The second group contained PVC resin, stabilizer and plasticizer, (group without filler), for which the effect of plasticizer was studied. Mechanical tests were made for these samples using American Society of Testing and Materials techniques (ASTM). Stabilizer was added to all samples in both groups in order to prevent decomposition or burning of the samples during preparation.

Instruments and Devices: The different compounding were prepared in a KOLSITE two-blade mixer (model KET 12405), manufactured by DEEPAK POLY-PLAST PVT, India. The specimens were prepared using two-roll type mill (model DM 12405) and a hydraulic type press (model DP 12405), manufactured by DEEPAK POLY-PLAST PVT, India. The universal testing machine (model DUT 12405), manufactured by DEEPAK POLY-PLAST PVT India, was used for mechanical properties measurements. The Shore hardness tester types A (model Durometer THT-1), manufactured by HORISHIMA Co. Japan, was used for hardness tests.

Sample Preparation: Samples prepared were based on the general formula for the cable insulation found in Brydson[1]. (Table 1) shows the two groups of samples with different plasticizer and filler content. The sample index column, in (Table 1), is a string starting with either letter P corresponding to the samples free of filler content, or F corresponding to the samples with filler and plasticizer content. Then, it is followed by a number corresponding to the concentration expressed in parts per hundred resin (PHR) of plasticizer or filler. All specimens were made according to the ASTM D638 dimensions. The laboratory was supplied with temperature, humidity and pressure indicator. Prior to the measurements the test specimens were conditioned for seven days to ensure unified conditions for all samples. All experiments were carried out at 25±1°C, 25% humidity and atmospheric pressure (101.325kPa).

Table (1): Composition of the Experimental Specimens.

Sample index	Resin		Plasticizer		Filler		Stabilizer	
	PHR	Wt.%	PHR	Wt.%	PHR	Wt.%	PHR	Wt.%
P 30	100	72.99	30.00	21.90	0.00	0.00	7.00	5.11
P 35	100	70.42	35.00	24.65	0.00	0.00	7.00	4.93
P 40	100	68.03	40.00	27.21	0.00	0.00	7.00	4.76
P 45	100	65.79	45.00	29.61	0.00	0.00	7.00	4.61
P 50	100	63.69	50.00	31.85	0.00	0.00	7.00	4.46
F 10	100	63.69	40.00	25.48	10.00	6.37	7.00	4.46
F 15	100	61.73	40.00	24.69	15.00	9.26	7.00	4.32
F 20	100	59.88	40.00	23.95	20.00	11.98	7.00	4.19
F 25	100	58.14	40.00	23.26	25.00	14.53	7.00	4.07
F 30	100	56.50	40.00	22.60	30.00	16.95	7.00	3.95

MEASUREMENTS

Tensile Measurements: The tensile measurements were carried out according to the ASTM D638 using a computerized Universal Tensile Machine equipped with suitable software. The specimen was carefully placed in the grips of the testing machine and grips were firmly tightened to avoid slippage of the specimen during the test but not to point, where the specimen would be crushed. The testing machine was connected to the computer through its software. The whole process of the measurement was controlled. Prior to the start of the measurements suitable settings were chosen such as scale, dimensions, speed, etc. After the test, specimen was placed in the grips and the measurement was started by clicking start on the computer screen. During the process of the measurements the course of the load and elongation were timely illustrated on the screen.

Stress at break was evaluated from the following equation:

$$\tau_b = \frac{F}{A} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where, A is the cross – sectional area of the sample and F is the applied tensile force. The elongation at break was calculated using the following equation:

$$\Delta L_b = \left(\frac{L' - L_0}{L_0} \right) \times 100 \qquad \text{.......................................} (2)$$

Where, L' is the length of sample at break and L_0 is the initial length. The modulus of elasticity was evaluated using the following equation:

$$\varepsilon = \frac{\tau_y}{(L - L_0)/L_0} \qquad \text{.......................................} (3)$$

where, L is the length of sample at yield, and τ_y is the stress at yield.

Hardness Measurements: The shore hardness of the samples was measured using a Durometer device according to the ASTM (D 2583–67). The specimen was placed on a flat smooth surface and the measuring device was put perpendicular to the surface of the test specimen. Sufficient pressure was applied by hand for 5 seconds. The reading of the hardness was directly obtained from the Durometer.

RESULTS AND DISCUSSION

Stress at Break: The experimental data on stress at break, τ_b, for both groups of sample obtained from all experimental measurements are plotted against plasticizer content, C_P (Fig. 1). It is obvious that higher values of stress at break have been obtained in group free of filler. The effect of rising plasticizer content on stress at break was negative in group of samples free of filler, and positive in group containing filler. The addition of filler in the form of calcium carbonate to the studied samples has significant effect on stress at break. The question for polymeric material under tension is what force would be required to break one of the C-C bonds and, for polymer containing foreign atom. The same question for breaking C-foreign atom bond. The bond forces are not known from any direct measurements, but can be obtained from the association energies of those bonds. Similar consideration can be applied for weaker intermolecular interactions such as hydrogen bonding and Van Der Walls forces[4].

Effect of plasticizer on the mechanical properties of the polymer is governed by the action of the plasticizer itself on the molecules of the polymers, which is believed to act as spacer between molecules of the polymers by forming links with polymer molecules. It was mentioned that dipole interaction occurs between polar groups in the polymer and the polar groups in the plasticizer[10]. In such case, the chlorine atom in the PVC resin plays the role of the polar group, while ester group in the DOP stands for polar group in the plasticizer. The formed links weaken the bond forces of the polymer atoms and thus addition of the plasticizer to the polymer increases the free volume, which leads to lowering the hardness, modulus of elasticity and tensile strength[11]. Incorporating filler into PVC compounding leads to decrease in tensile strength, but the interaction of system PVC-filler is not yet understood. Our results are in agreement with previous studies[1, 10, 12].

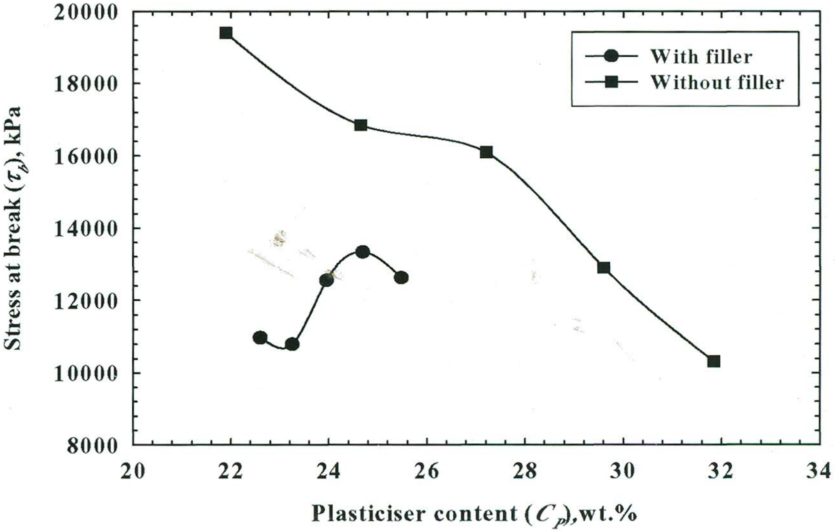

Fig. (1): Effect of plasticizer content on the breaking tensile

Elongation at Break: The experimental data on elongation at break, ΔL_b, for both groups of sample obtained from all experimental measurements are plotted in (Fig. 2), against plasticizer content, C_P. Higher values of elongation at break are obtained in group free of filler. The elongation at break decreases with increasing plasticizer content in-group free of filler. As cited above that plasticizer acts on PVC as spacer and increases the free volume, which allows

PVC to be stretched longer to certain concentration above which it becomes softer and weaker, thus breaks at low loads and elongations. The obtained result of plasticizer effect on the elongation at break is in accord with that reviewed by Jenkins and Nielsen[10,13]. The effect of plasticizer on elongation at break is reversed in group containing filler. This is because inorganic fillers like calcium carbonate are stiffer than the matrix (PVC polymer) and deform less, causing an overall reduction in the matrix strain, especially in the vicinity of the particle as a result of the particle/matrix interface[3]. The filler pinches the polymer in its vicinity, reducing strain and increasing stiffness. The obtained result of filler effect on the elongation at break is similar to that cited by Xanthos[14].

Modulus of Elasticity: Effect of plasticizer content on the modulus of elasticity is shown in (Fig. 3). The experiment is carried out in the range of plasticiser content 21–32 wt.% of sample. The corresponding modulus of elasticity ranged between 8.5–15.5MPa. It is noticed that the modulus of elasticity decreases with increasing plasticizer content up to certain level and then increases in both groups of samples. On a molecular level, plasticization is the weakening or selective breaking of bonds between molecules, while leaving others intact, to increase intermolecular space, known as free volume[4]. The increased space allows for changes in shape, flexing or molding of the final material. The PVC polymer is amorphous rigid material and may be thought of as comprising small areas of order, crystallites, among amorphous areas of molecules[3,4]. When using the infrared spectroscopy, and when plasticizer is incorporated into the PVC resin, it solvates the amorphous chain segments, but not the crystalline ones[15]. When a small amount of plasticizer is incorporated into PVC, polymer chains rearrange to become more ordered and increase the proportion of crystallites. This has been detected by X-ray diffraction by Horsley[16]. In the present work it is clear that addition of plasticizer leads to softening the PVC resin and hence the sample withstands small magnitudes of stresses to reach the yield point.

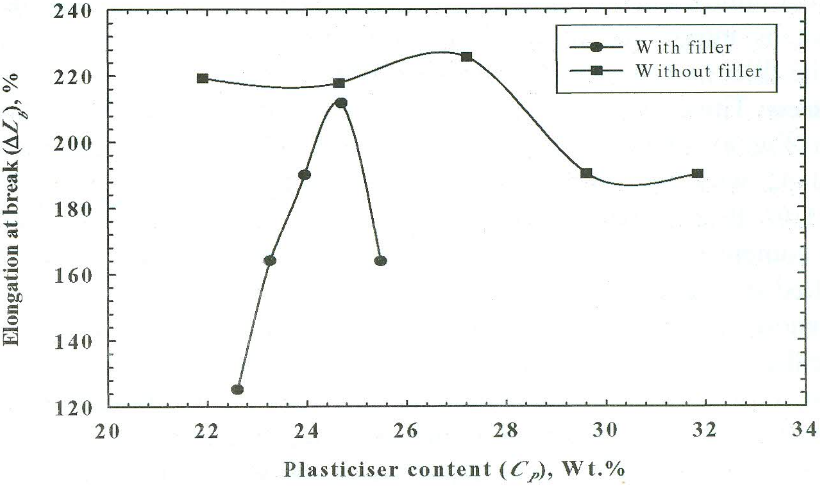

Fig. (2): Effect of plasticizer content on the elongation at break

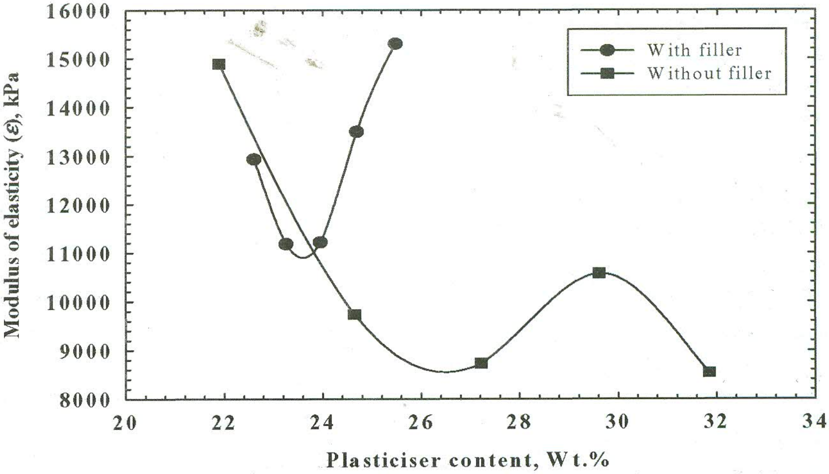

Fig. (3): Effect of plasticizer content on modulus of elasticity

The addition of filler to PVC resulted in decreasing modulus of elasticity up to certain value after which modulus of elasticity increases markedly. Also the effect of plasticizer is dominant when its content up to 23.8 wt. % (12 wt. % filler concentration). The increase in modulus of elasticity with increasing filler content can be interpreted in terms of hardening of the sample. So far, the action of the filler on PVC is not understood well.

Shore Hardness: The effect of plasticizer and filler content on the shore hardness is given in (Fig. 4). The experiments were carried out in the range of plasticiser content 21–32 wt.% of sample. The corresponding shore hardness ranged between 85–97. It is shown that the shore hardness decreasing with increasing plasticiser content for both groups of samples. It is obvious that the addition of filler resulted in decreasing the shore hardness, while increasing filler content increases shore hardness. As explained previously the plasticizer softens the PVC by weakening the intermolecular interaction, while incorporating the filler the effect is completely reversed as the filler increases the hardness of the PVC.

Brydson, Mark, Nielsen, Schmitz, Ritchie, and Fried[1,12,13,17,18,19] found that addition of filler increases the hardness of the PVC and this is probably, which makes PVC breaks at low loads.,.

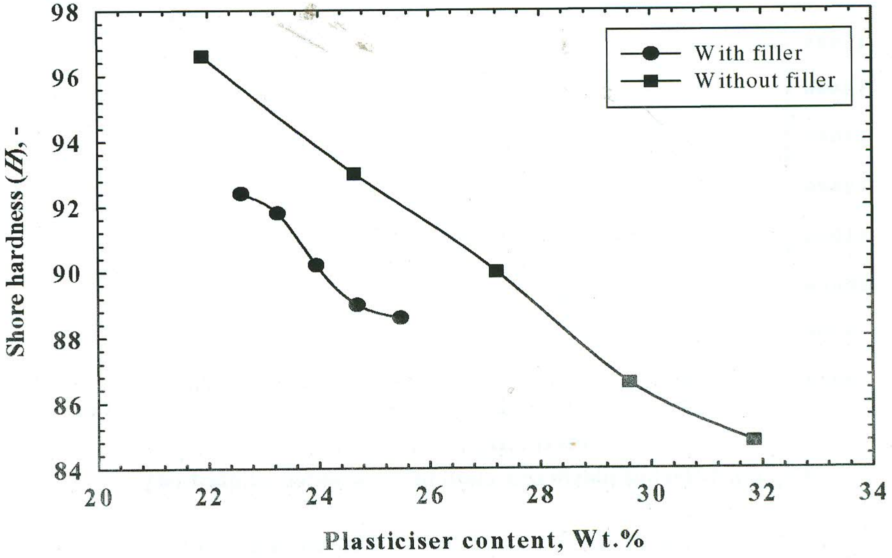

Fig. (4). Effect of plasticizer content on the hardness

CONCLUSIONS

From the experimental results the following conclusions are obtained:

1- Tensile strength decreases with increasing plasticizer content. The maximum obtained value for tensile strength is 197.78N/m^2. Tensile strength also decreases with increasing filler content and corresponding maximum value is 135.94N/m^2. Stress at break decreased by 50% with increasing plasticizer content for group of samples free of filler.

2- Elongation at break decreases with increasing plasticizer content for group of sample free of filler, while it increases with increasing plasticizer content for group of sample containing filler. The maximum obtained elongation at break for samples without filler–contains only plasticizer–is 225.64%. Samples with filler showed maximum elong-ation at break at 211.69%. The ratio of elongation at break decreased by 15% with increasing plasticizer content for group of sample free of filler. The filler decreased sharply the ratio of elongation at break upto 44% for the maximum filler content.

3- Modulus of elasticity decreases with increasing plasticizer and filler content. Maximum obtained values for plasticizer and filler are 151.87N/m^2 and 155.97N/m^2 respectively. Addition of filler resulted in decreasing modulus of elasticity up to filler content of 14.5% by weight of sample, after which it increases.

4- Shore hardness decreases with increasing plasticizer content and showed maximum value at 96.60, while shore hardness increases with increasing filler content with maximum value at 92.40. Addition of filler resulted in increasing shore hardness by 3.34% for maximum filler content.

It could be concluded, that increasing plasticizer and filler content results in decreasing mechanical properties i.e. tensile strength, modulus of elasticity and shore hardness. On the other hand increasing the filler content only increased the hardness.

RECOMMENDATIONS

Addition of plasticizer and filler must be chosen with great care and attention regarding the final application, as plasticizer leads to soften material and filler increases the hardness of the material. It is recommended that other properties of PVC, such as electrical, optical and chemical should be studied in the future.

ACKNOWLEDGEMENT

Our sincere thanks and appreciation to the head and staff of IMMAM GROUP for their help.

REFERENCES

1- **Brydson J.A. (2000).** Plastics Materials. 7th Eddition. Elsevier, Oxford, England.
2- **Guo G., Rizvi G.M., Park C.B., and Lin W.S. (2004).** Critical processing temperature in the manufacture of fine-celled plastic/wood-fiber composite foams. Journal of Applied Polymer Science, **91**, [621–629].
3- **Stark N.M. and Rowlands R.E. (2003).** Effects of wood fiber characteristics on mechanical properties of wood/polypropylene composites. Wood and Fiber Science, **35**, [167–174].
4- **Shashoua R. (2001).** Inhibiting the deterioration of plasticized polyvinyl chloride. Ph.D. Thesis, Danish Polymer Center, The Technical University of Denmark.
5- **Quye, A. and Williamson, C. (1999).** Plastics, Collecting and Conserving. NMS Publishing Ltd, Scotland, United Kingdom.
6- **Tester, D.A. (1973).** Developments of PVC Technology. Applied Science Publishers J.H.L.Henson and A.Whelan, London, England.
7- **Titow, W.V. (1984).** PVC Technology. 4th edit., Elsevier Applied Science, London, England.
8- **SCHENCK, H.U. (2001).** Special Issue: 'Polymers in Europe, Quo Vadis? Eur. Polym. Fed., AIM Magazine, [15-18].
9- **Nass, L.I. (1977).** Encyclopedia of PVC, Marcel Dekker, New York, **Vol. 2.**
10- **Jenkins A.D. (1972).** Polymer Science **Vol. 1**, Northholand, Amsterdam.
11- **Saunders K.J. (1973).** Organic Polymer Chemistry, Chapman and Hall, New York.
12- **MarK F. H. (1970).** Encyclopedia of Polymer Science and Technology. **Vol. 12**, Interscience Publishers, New York.
13- **Nielsen E. Lawrence (1962).** Mechanical Properties of Polymers, Van Norstrand Reinhold Company, New York.
14- **Xanthos M. (2005).** Functional Fillers for Plastics, Wiley-vch Verlag GmbH & Co KGaA.
15- **Tabb, D.L. and Koenig, J.L. (1975).** Fourier transform infrared study of plasticiz-ed and unplasticized poly(vinyl chloride), Macromolecules, **8,6,**[929-934].
16- **Horsley, R.A. (1957).** The properties of lightly plasticized PVC compounds. In Progress in Plastics (ed. P. Morgan), Iliffe and Sons, London, [77-88].
17- **Schmitz J.V. (1965).** Testing of Polymer, **Vol.1**, Interscience Publishers, New York.
18- **Ritchie P.D. (1972).** Plasticizers, Stabilizers and Fillers Iliffe Books Ltd, London.
19- **Fried R. Joel (2003).** Polymer Science and Technology, 2nd Edition, Princehall Publishers, New York.