

Study on the Mechanical Performance of Aged Foamed PVC/PMMA Blends

Emma Johansson^{*1}, Henrik Lindberg² and Lars Nilsson³

¹Department of Chemical Engineering, Lund University, Lund, Sweden

²Department of Mechanical Engineering, Chalmers University of Technology, Gothenburg, Sweden

³Department of Industrial Engineering, Uppsala University, Uppsala, Sweden

KEYWORDS: PVC/PMMA foam, mechanical tests, polymer blends.

ABSTRACT

This paper presents a study of aged mechanical properties of PVC/PMMA blends. For that purpose, composite of variable agent specimens from 1 to 4 year were prepared. The effect of strength values to increasing therefore PMMA polymer was used. As the PVC and PMMA are thermodynamically compatible polymers, therefore these polymers can be easily mixed with each other. The PMMA is causes significant modification in the blends structure and cells morphology. Several of mechanical tests, such as; tensile test, impact test, bending test and hardness test was investigated for the all blends. Based on the result the mixture has a stable foam structure, which is also resistant the aging. The mechanical properties were greatly influenced by the cellular structure of the foam. During the aging test the blends external changes can be determined. Due to this test, we can deduce the life of product.

INTRODUCTION

In the past decades the world market of the polymer foam was quickly increasing. Most of polymer foam are used in construction industry, due to their stability structure; good thermal and mechanical properties; price/values/weight ratio. For instance, rigid PVC foam was used at pipes insulation; coatings and etc. The PVC foams are characterized to have excellent thermal insulation properties, non- flammable and good mechanical properties [1]. To achieve at better properties of composite, different polymers can be blended to use the own physical characteristics of both polymers. It is well known that the PVC is miscibility wit PMMA polymer [2].

The PVC was partially miscible with atactic and syndiotactic PMMA, but immiscible with isotactic PMMA [3]. Basically, the PVC/PMMA mixtures were higher compatibility due to hydrogen bonding of PVC and specific interaction between carbonyl groups of PMMA (H-C-Cl;O=C) [4]. The blends have specific interactions, between the groups or polymer segments, finally lead to decrease of the Gibbs energy of the mixing [5].

The mixing method of the blend is very important in determining the final homogeneity. The mixing method of the composite is very important in determining the final homogeneity [2]. PMMA [poly(methyl-methacrylate)] is an significant polymer for mechanical and optical properties due to its excellent tensile strength, surface resistivity, good insulation properties, high rigidly and of course cost friendly materials [6]. The PMMA is evidently increasing the effect of strength properties of blends. Furthermore, it's increasing the melt strength; melt elasticity and reduce the sticking to the metal parts. The polymers have a property enhancing effect with the PVC [7]. The time constraint of composites is important, mostly at construction industry, because it must withstand several years of external factors. The formulations of rigid and flexible materials with minimum content of chemical additives are increased the service lifetime of blends, and the product will be become safe and environmentally friendly [8]. Polymers, during fabrication and storage or transport, sometimes for long periods to effect of moderate or high temperature; ultraviolet radiation; air or other potential oxidants may be exposed [9]. The UV degradation also affected the molecular chain entanglements changes. The PVC/PMMA blends have excellent ultraviolet toughness [8].

The performed tests were of six types:

- a. UV tests at 32.4Wcm⁻² UV intensity
- b. Spectrophotometer
- c. Hardness (Shore D)test
- d. Tensile test at 100 mm/min
- e. Impact test (Charpy, notched)
- f. Three-point bending at 10mm/min speed

MATERIALS AND METHODS

Materials

Poly(vinyl-chloride)(PVC) K-value=58 was used as based materials of the samples from BorsodChem Zrt. The additive polymer poly (methyl-methacrylate) (PMMA) was added at 100/10 weight percent ratios at 3 mm thick granulate. The density of PVC/PMMA blend is 0.8279 g/cm³.

Mixture and sample preparation

Powder mixing was carried out in a high-speed dry mixer. The final temperature of material was up to 110 °C. PVC powder; PMMA granulate with additives (processing aids, stabilizers, foaming agent, fillers) were used at every specimens.

Finally, the mixture was mixed in melt using a laboratory size extruder (screw D=30mm; L/D=20 compression rate 1:3) at 180°C. The die was a flat one; 100mm width and 4mm thickness. The extruded sheets were directly used for specimen preparation.

Specimens were die cut with a pneumatic punching machine [10]. Most tests were carried out in machine and cross directions on the samples

UV test

The thermal stability of PVC is poor without stabilizers. During the processing and application it suffers from degradation. The major degradation processes of polymers are: photo- and photooxidative-, thermal-, chemical-, biological- and mechanical degradation [11]. These degradation processes usually run simultaneously. A typical example of this is the influence of sunlight. It can affect to molecular stability, by this way the mechanical properties of the products. The temperature of the product may rise up to 80 °C. The UV irradiation of the sunlight in presence of O₂ initiates the degradation of the polymer molecules. The molecular weight is rapidly decreasing, the material lose its mechanical strength [12]. The wavelength range of solar radiation that reaches the earth's surface is between 295 and 3000 nanometers. The ultraviolet (UV) range is between 295 and 400 nm.

It is considered according to ASTM G 113-94 that the radiation wavelengths of UV components are shorter than of the visible light. The visible range is 400 to 800 nm. The spectral range for the UV:

- UV-A: 315- 400 nm
- UV-B: 280-325 nm
- UV-C: <280 nm

The UV device measured according to ISO 4892-3 [13]. The testing was carried out by homemade equipment. The power of UV chamber is 32. 4 W/cm² [14]. The average solar energy in Hungary is 1368.6 kWh/m² year; furthermore the actual sunny hours are 2057 h/year [15]. The selected UV irradiation time (1hour) was equivalent to 486.97 natural hours.

Color measurements

The color of surfaces of the original and aged samples was measured by spectrophotometer type (CM-2600d) hand held instrument. Spectrophotometric data were converted to L*, a*, b* color coordinates calculated to D65 illumination. For color change (ΔE) calculations the original, not aged sample was used as reference. The colors changes give information about the degradation level [10]. ΔL represents the lightness change, in case of $+\Delta L$ the color tends to red, $-\Delta a$ means changing to green. Similarly, $+\Delta b$ means yellowing and $-\Delta b$ bluing [16]. The measurements were made on plane surfaces.

Tensile test

Tensile test was performed by INSTON 5566 testing machine according to ASTM D638-10 [17]. During the test the tensile stress-strain behavior can be determined. The test speeds was 100 mm/min at room temperature (23±1°C).

Impact test

From the measurements the materials impact resistance can be determined. The impact tests were carried out by Charpy method (EN ISO 179) with CEAST 6545 testing machine. Radius of notches was 0.25mm. Exact thickness of specimen was individually determined because the thickness of extruded sheets was 3.7 to 4 mm. During the test used Hammer of 2J energy was used.

Bending test

The flexural properties were carried out at INSTRON 5566 testing machine using three point bending head. The tests method was according to ISO 178:2010 [18]. This is a standard test method for the properties determination.

Hardness test

The hardness test was measured at Zwich/Roell Shore D equipment. During the test the punching tool was steel cone and it pressing for a few seconds into the specimen surface. The all specimens (different aged) measured according to the ISO 868 standard [19]. Usually Shore D is used for harder materials, such as composite or rigid PVC [20].The values were calculated as average of 20 points.

RESULTS AND DISCUSSION

Tensile test

Fig.1 and 2.show the tensile stress and elongation values in both direction. Generally, the original (not aged) foam has a higher stress and strain values. The maximum strength – strain values of the ageing samples were less than the result of original foam. The reason for this the molecular structure can suffer from oxidative degradation.

The PVC is a hard-persistent material, so it could be used this foam -with similar stability and strength similar to the original foam- at several decades later. As it can be seen in the Table I. the specimen’s maximum tensile stress was determined.

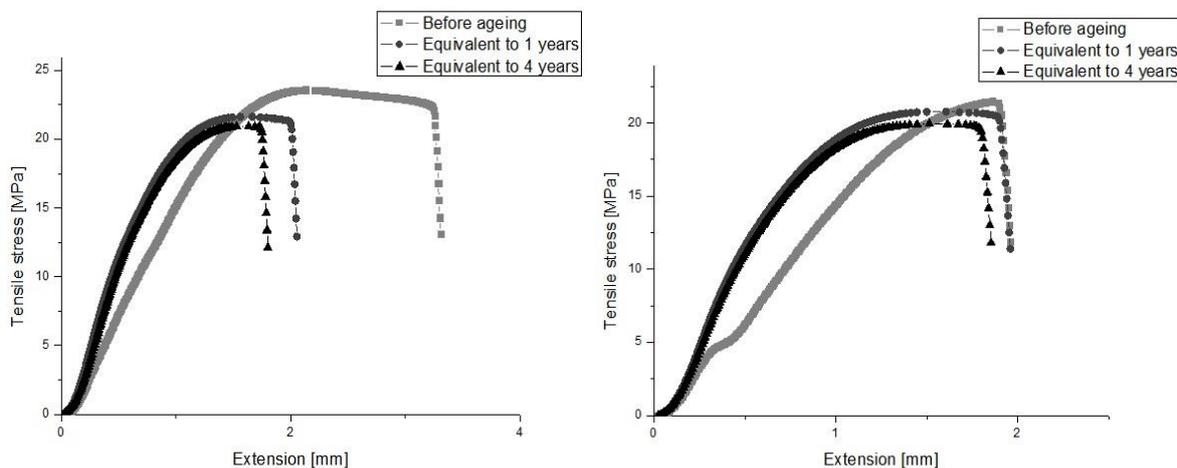


Fig. 1. Tensile test in machine(left) and cross (right) direction

Table 1: Results of tensile tests

Samples	Maximum Tensile strength [MPa]		
	Before ageing	Equivalent to 1 years	Equivalent to 4 years
PVC/PMMA - M	23.6	21.6	20.9
PVC/PMMA - C	21.6	20.8	19.9

Impact test

It is well known that the pure PMMA material has poor impact properties. Accordingly, it was combined with PVC. During the test the dynamic maximum strength of plastic can be determined. The maximum impact bending strength values are shown in the Table II.

Table 2: Results of impact tests

Samples	Maximum Impact strength [MPa]		
	Before ageing	Equivalent to 1 years	Equivalent to 4 years
PVC/PMMA - M	0.53	0.8	0.56
PVC/PMMA - C	0.39	0.6	0.29

Bending test

The flexure test gives information about the stress- deformation relation under bending. The tests were performed in both directions on the specimen. *Table III.* shows that the increased UV radiations cause the decrease flexural strength. The UV photons degrade the backbone of polymer; mechanical properties are deteriorated by these structural changes.

Table 3: Results of flexural tests

Samples	Flexural strength [MPa]		
	Before ageing	Equivalent to 1 years	Equivalent to 4 years
PVC/PMMA - M	35.1	17.1	16.0
PVC/PMMA - C	27.6	18.5	18.9

Table 4: Results of flexural modulus

Samples	Flexural modulus [MPa]		
	Before ageing	Equivalent to 1 years	Equivalent to 4 years
PVC/PMMA - M	1136	323	337
PVC/PMMA - C	923	362	435

Hardness test

Slight changes in the hardness values can be observed. After 1 year energy the hardness decreased but finally increased over the unaged sample's hardness. According to the industrial experience a hardening can occur after certain ageing. Because the hardness test is a low deformation one the tensile- and impact properties might apparently contradictory.

Table 5: Results of Hardness tests

Samples	Flexural strength [MPa]		
	Before ageing	Equivalent to 1 years	Equivalent to 4 years
PVC/PMMA	55.1	53.7	56.3

Spectrometer test

The obtained ΔE values are extremely high in particular the ΔL lightness change. According to Δa the color tends to red and Δb to yellow. Interestingly, the Δb decreased after longer UV exposition which is probably the result of oxidation of conjugated system.

Table 6: Result of Spectrometer test

Samples	Spectrometer		
	Before ageing	Equivalent to 1 years	Equivalent to 4 years
L	89.93	76.42	31.67
a	-0.47	3.93	7.30
b	5.42	25.70	7.77
ΔL		-13.5	-58.3
Δa		4.40	7.77
Δb		20.3	2.34
ΔE		24.8	58.8

CONCLUSION

PVC/PMMA foamed sheets were prepared by slot die extrusion. The sheets were aged in UV chamber. The irradiation energy was determined and compared to the domestic sunlight intensity. The selected UV irradiation time was equivalent to 1 and 4 years natural ageing.

Mechanical and color measurements were carried out on virgin and aged samples. High deformation mechanical test (tensile, Charpy impact) proved the loss in strength as consequence of degradation. However, the hardness slightly changed only, namely increased after 4 year equivalent ageing. It is supposed that some additives were oxidized causing the surface hardening.

The color change of samples was very high. The color became darker ($-\Delta L$) and red ($+\Delta a$). The Δb value was also positive i.e. the color changed to yellow direction, but interestingly decreased after 4 year equivalent irradiation. That means that the conjugated double bond system formed in the first stage of degradation suffered from oxidation causing disappearing of conjugated chromophore structure.

REFERENCES

1. B.Notrio,J.Pinto, M.A. Rodríguez-Pérez, "Towards new generation of polymeric foams: PMMA nanocellular foams with enhanced physical properties" Polymer, 2015
2. Hyun Sik Moon, Won Mook Choi, Mun Ho Kim, O-Ok Park, "Miscibility and Rheological Properties of Poly(vinyl chloride)/Styrene-Acrylonitrile Blends Prepared by Melt Extrusion" InterScience 2006
3. Kamira Aouachria, Naima Belhaneche-Bensemra, "Miscibility of PVC/PMMA blends by vicat softening temperature, viscometry, DSC and FTIR analysis" Polimer Testing, 2006, vol. 25,1101-1108,
4. Eeisheng Li, Lianghe Shi, Deyan Shen, "On the Interactions and Miscibility of PVC/PMMA Blends" Polymer International 1992, 57-62
5. S.Ramesh, A.H.Yahaya, .K.Arof, "Miscibility studies of PVC blends (PVC/PMMA and PVC/PEO based polymer electrolytes" Solid State Ionics, 148, 2002, 483-186
6. Yan Li, Chngchun Zeng, "Poly(Methyl Methacrylate) (PMMA) Nanocomposite Foams" ResearchGate 2013
7. R. Hernández, J.J. Pena, L. Irusta, A. Santamaría, "The effect of a miscible and an immiscible polymeric modifier on the mechanical and rheological properties of PVC European Polymer Journal", 1999, Volume 36, 1011-1025.
8. George Wypych, "PVC Degradation & Stabilization 3rd Edition" ChemTec Publishing, 2015 p.22-23; p.132-159
9. Rober Q.Ebewele, Polymer Science and Technology, CRC Press, 2000, p.246-248
10. Richard Gendron, Thermoplastic foam processing 76-79, 2005
11. Marta Lenartowicz, Beata Swinarew, Andrzej Swinarew, Grazyna Rymarz, "The Evaluation of Long-Term Aged PVC" International Journal of Polymer Analysis and Characterization, 2015
12. J.Owen, "Degradation and Stabilisation of PVC" Elsevier Applied Science Publishers, 1984 p.112-122
13. Atlas Material testing solutions, Weathering testing guidebook; (10.04.2018), Available: www.stenomometer.dk/Files/Downloads/Guidebook.pdf
14. Juhász Noémi, "Thera-Band szalag mechanikai tulajdonságainak változása gyorsított UV öregítés hatására", BSc-thesis, 2014, Miskolci Egyetem
15. 5 milliárd nap mind nap, Available: <http://5milliard.hu/eves-napsugarzasi-terkep-magyarorszagon/> (10.04.2018)
16. Konica Minolta, Available: <https://sensing.konicaminolta.us/products/cm-2600d-spectrophotometer/> (10.04.2018)
17. ASTM International; Standard test method for tensile properties of plastic Available: <https://www.astm.org/DATABASE.CART/HISTORICAL/D638-10.htm> (10.04.2018)
18. International Organization for standard, Available: <https://www.iso.org/standard/45091.html> (10.04.2018)
19. Miner Elastomer Products Corporation, Available: <https://minerelastomer.com/technical-data/tecspak-features/shore-shore-d-comparison/> (10.04.2018)
20. Matweb; Material property data, <http://www.matweb.com/reference/shore-hardness.aspx> (10.04.2018)