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Effect of Various Additives on the Physical Properties of Polyvinylchloride Resin

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Abstract

The compounding of Polyvinylchloride (PVC) with some additives was studied for the enhancement of physical and mechanical properties. Two categories of formulations (un-plasticized and plasticized PVC) were prepared with PVC (K value ranging from 60 to 70) taking as base polymer. Different additives generally categorized as plasticizers, fillers, stabilizers, pigments and processing aids, were mixed in the standard concentration unit "parts per hundred resins (phr)" with base polymer. Cable compound and shoe compound were prepared in plasticized-PVC category containing mainly plasticizing additives like diisooctyl phthalate (DIOP) (40 phr) and epoxidized soybean oil (2-3 phr) with general plasticizer (50-80 phr) respectively. Whereas the rigid pipe and sheet compounds were prepared as un-plasticized PVC category containing different fillers/stabilizers like tribasic lead sulphate (6 phr), lead stearate (1 phr), glyceryl monostearate (0.4 phr) in rigid pipe and butylin mercaptides (2-2.5 phr), fatty alcohol and fatty acid ester (0.5-0.8 phr) in rigid sheet compound. Experimental investigation was carried out for analyzing the mechanical properties like tensile strength, elongation at break, hardness and physical property i.e. specific gravity for the compounded samples. An appreciable increase was observed in tensile strength from 460 Kg/cm^2 (base PVC-polymer) to a range of 550 Kg/cm^2 for un-plasticized PVC compounds (rigid PVC-pipe and sheet) with little increase in elongation at break from 56% (base polymer) to 124.33% and 150% (for Pipe and Sheet compounds respectively). On the other side the elongation at break for plasticized PVC compounds was increased from 56% to 250.67% (for cable compound) and 351.33% (for shoe compound), where as the tensile strength was decreased from 460 Kg/cm^2 to 150.33 Kg/cm^2 (for cable compound) and 120.33 Kg/cm^2 (for shoe compound). The hardness (shore A, D) was increased from 40 to 80 for all the compounds except shoe compound with hardness of 65.33. The impact of plasticizers was found in direct proportion on elongation at break but having inverse proportion on tensile strength.

Keywords: Polyvinylchloride, Additives, Resin, Physical properties.

Introduction

Polyvinyl chloride, more commonly known as PVC, is a building block of various products, such as electronic items, constructional materials, stationeries, chemical equipments, wires, cables etc. It is one of the major thermoplastics used today and produced in a huge amount worldwide [1, 2]. Presently there are 50 different basic types of plastics, included in 60,000 different plastics formulations. Those based on polyolefins and polyvinyl chloride, have highest utilization worldwide [3]. As per one estimate, each week in USA, six new plastics materials are sent for

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evaluation and approval to major testing laboratories [4].

The worldwide production tonnage of PVC is second only to that of low-density polyethylene. However, PVC has inferior processability and thermal stability to those of other commodity plastics, like polyethylene and polystyrene [5]. PVC is thermoplastic and due to its low thermal stability the use of PVC polymer is limited in industry. Several attempts have been made to enhance the thermal stability and mechanical properties of PVC in recent years [6-8]. Unmodified PVC polymer is a brittle, inflexible material with rather limited commercial possibilities. The processing of PVC in the raw form using heat and pressure resulted in severe degradation of the polymer [9]. Hydrogen chloride is produced and discolored rapidly from white to yellow to brown to black. These changes observed at processing temperatures, around 150ºC [10].

The utilization of PVC is based on the "Compounding" (addition of additives with base polymer) of PVC all over the world. The method of preparing typical recipe for the compounding is known as "Formulation". With the addition of additives like plasticizers, heat stabilizers, lubricants, fillers and copolymerization with other monomers, the poor properties of PVC can be improved [1, 2]. 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 [10]. The proper compounding and processing PVC resin using suitable additives produces a complex material whose behavior and properties are quite different from the PVC resin by itself [11, 12].

The selection of particular additive is dependent on the end use of the PVC product like PVC-resin is not plasticized for the use in making rigid products such as water pipe, plumbing fittings, and phonograph records.

For use in making piping or structural panels that require high resistance to impact, polyvinyl chloride often is blended with small proportions of rubbery synthetic polymers. The modification of rigid poly (vinyl chloride) (PVC) having relatively low toughness carried out by incorporation of a rubbery phase [13]. Resins more easily plasticized than polyvinyl chloride can be prepared by adding various properties of vinyl acetate to vinyl chloride before polymerization the mixture; stiffer resins result from treatment of polyvinyl chloride with chlorine. In commercial PVC formulations, proportions of plasticizer range from 15-50% by weight [3, 10]

Even at low processing temperatures polyvinyl chloride decomposes and loses HCl. The apparent replacement of active hydrogen is assumed in PVC. There is possibility of inhibition of the eliminated HCl through organometallic salts, and stabilize PVC or suppressed the catalytical activity of HCl in this reaction by epoxides [14, 15].

To achieve better sealing properties PVC is modified with elastomers and special plasticizers [16-23]. These modifiers cause decrease of glass transition temperature, increase deformability, elasticity, abrasion resistance, elastic recovery, resistance to oils, fuels and many cleaning chemicals [16, 17, 20, 24, 25 and 26].

The physical state and morphology of a polymer have a strong influence on its mechanical properties. A simple measure of the differences produced in mechanical behavior is the *elongation* that occurs when a plastic is loaded (stressed) in tension. Almost all plastics exhibit some elongation on being stressed that is not recovered when the stress is removed. The most commonly specified mechanical properties of polymers include stiffness and breaking stress are *flexural modulus* and *tensile strength.* Mechanical properties are considerably affected by the type and amount of plasticizer. To a lesser extent fillers will affect the physical properties. Un-plasticized PVC is a rigid material whilst the plasticized material is flexible and even rubbery at high plasticizer loadings.

Due to wide variety of PVC compounds it is important to note the physical properties of PVC resins getting an idea about the formulation of PVC compounding. Table-1 represents some properties of PVC resins.

The present study outlines the effect of additives mainly plasticizer and filler on physical and mechanical properties of polyvinyl chloride compounding, i.e. specific gravity, tensile strength, elongation at break and hardness.

Table 1. **Properties of PVC.**

Property	Value
K-Value	60 – 70
Appearance	White Powder
Degree of Polymerization (°C)	170±30
Volatile matter (%)	0.05
Foreign matter (phr)	<50
Apparent specific density	0.44 – 0.52
Density (g/cm^3)	1.3 – 1.6
Hardness (shore A,D)	40
Glass transition temp, Tg (°C)	85
Tensile strength (Kg/cm^2)	460
Elongation at break (%)	50
Flexural modulus (Gpa)	2.1 – 3.4

Materials and Methods
Chemicals

The chemicals that were used for preparing four formulations of PVC based compounds comes under two categories. The first one was the base polymer that is necessary for the preparation of the formulation of PVC. For the purpose, suspension polymer of PVC (ISO No. 85-100), suspension Polymer of PVC (ISO No. 125), PVC resin (K-value 60 – 65) and PVC resin (K-value 70) were used. The second category was the additives used for improving the qaulity & process conditioning of the PVC formulations. The additives used were Tribasic lead sulphate, Lead stearate, Glyceryl monostearate, Acrylic (for process aid), Di-isoctyl phthalate (DIOP), Trixylyl phosphate, China clay, Butylin mercaptides, Fatty alcohol, Fatty acid easter, Polyethylene wax, UV absorber, Plasticizer, Epoxidized soyabean oil, Liquid Ba/ Cd stabilizer, Stearic acid, Pigment. The concentration of the base polymer is referred as 100 parts in the mixture; whereas the concentration of rest of the additives used is referred as parts per 100 resins i.e., “phr”.

Table-2, 3, 4 and 5 shows the different formulations for four types of PVC based compounds which were prepared. The materials were mixed in different types of mixers. Three samples of each compound were taken and were analyzed for determining the tensile strength, elongation at break and hardness and the specific gravity.

Table 2. **Formulation of Un-plasticized PVC Pipe (Rigid).**

Materials	Concentration (phr)
Suspension polymer of PVC (ISO No. 85-100)	100
Tribasic lead sulphate	6
Lead stearate	1
Glyceryl monostearate	0.4
Acrylic process aid	2

Table 3. **Formulation of cable compound.**

Materials	Concentration (phr)
Suspension polymer of PVC (ISO No. 125)	100
DIOP	40
Trixylyl phosphate	20
China clay	20
Tribasic lead sulphate	7
Stearic acid	0.5
Pigment	2

Table 4. **Formulation of PVC Rigid sheet.**

Materials	Concentration (phr)
PVC (K-value 60-65)	100
Butylin mercaptides	2 – 2.5
Fatty alcohol	0.5 – 0.8
Fatty acid ester	0.5 – 0.8
Polyethylene wax	0.1 – 0.2
UV absorber	0.3 – 0.5

Table 5. **Formulation of shoe compound.**

Materials	Concentration (phr)
PVC (K-value 70)	100
Plasticizer	50 – 80
Epoxidized soyabean oil	2 – 3
Liquid Ba/ Cd stabilizer	1.5 – 2
Stearic acid	0.2 – 0.4

Equipments

High speed mixer with 100 Liter capacity was used (model No. SMNC-100, make: Kawata) to blend different additives with base polymer. Pipe extruder was used (model No. SE-40A, make: Shibawa) to make 1" dia pipe-compound. Universal Testing Machine (UTM) (Load Cell Capacity: 10kN, Model: Autograph, Make: Shimadzu) was used to measure Tensile Strength and Elongation at break. Shore hardness was measured with Durometer Insturment (Model: Hardmetic, Make:Mitutoyo). For specific gravity testing simple glass made Pyconometer was used. Injection Moulding machine was used to prepare required samples (Model: J550E III, Make: JSW, Clamping force: 550 tons Injection capacity: 18000g).

Test methods

Specific Gravity and Density is one of the important parameter that must be analyzed. The sample was taken in any shape with a volume of more than 1cc. 5 grams of the pellets or powdered material of sample was added to a measured volume in a pyconometer, and the specific gravity was calculated from the weight and volume change at 73.4°F. To maintain the accuracy complete air evacuation was necessary in this method.

The tensile measurements were carried out according to the ASTM D638 using a computerized Universal Tensile Machine equipped with suitable software. In this analysis, tensile strength and elongation at break were carried out. Specimens were processed through injection-molded and brought in standard shape (as shown in Fig.1) with 0.13 to 0.28 inch thickness. For the analysis, both ends of the specimen were firmly clamed in the jaws of a universal testing machine. The best results were obtained when an extensometer was attached to both ends of the narrow neck. The jaws could move apart at rates of 0.2, 0.5, 2 or 20 inches a minute, pulling the sample from both ends. Stress was plotted against strain (elongation) to produce a stress-strain curve that describes the material's response to tensile loading.

The shore hardness of the samples was measured using a Durometer device according to the ASTM (D 2583–67). The Durometer instrument has an indenter projecting below the bas (face) of the pressure foot. Two types of indenters were used: blunt-ended (Type A) for plasticized compounds and pointed (Type D) for rigid compounds. The indenter was pressed with sufficient hand force for 5 seconds into the plastic specimen perpendicularly so that the base took rest on the plastic surface. The amount of indentation registered directly on the dial indicator.

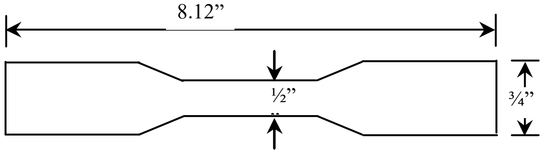

Figure 1. **Tensile test specimen.**

Results and Discussion

The four formulated compounds can be classified in two broad categories i.e., Un-plasticized PVC compounds (hard or rigid compounds) and Plasticized PVC compounds (soft compounds). The test results are tabulated for all the compounds in the Tables 6, 7, 8 and 9. The comparisons between the properties of formulated PVC compounds with that of base polymer are shown in Fig 2, 3, 4 and 5 which show great enhancements in physical properties of the PVC resins.

Table 6. **Test Results of Un-plasticized PVC Pipe (Rigid).**

Property	Samples			Mean
	1	2	3	
Specific Gravity	1.40	1.44	1.43	1.4233
Tensile Strength (Kg/cm^2)	547	551	554	550.67
Elongation at break (%)	125	145	133	134.33
Hardness (Shore D)	80	78	83	80.33

Table 7. **Test Results of PVC Rigid Sheet.**

Property	Samples			Mean
	1	2	3	
Specific Gravity	1.41	1.41	1.40	1.4067
Tensile Strength (Kg/cm^2)	551	552	549	550.66
Elongation at break (%)	151	150	149	150
Hardness (Shore D)	80	80	80	80

Table 8. **Test Results of Cable Compound.**

Property	**Samples**			**Mean**
	1	**2**	**3**	
Specific Gravity	1.37	1.36	1.39	1.373
Tensile Strength (Kg/cm^2)	149	152	150	150.33
Elongation at break (%)	250	249	253	250.67
Hardness(Shore A)	79	81	82	80.67

Table 9. **Test Results of Shoe Compound.**

Property	**Samples**			**Mean**
	1	**2**	**3**	
Specific Gravity	1.1	1.3	1.3	1.23
Tensile Strength (Kg/cm^2)	118	122	121	120.33
Elongation at break (%)	346	352	356	351.33
Hardness (Shore A)	64	65	67	65.33

There is almost equal specific gravity (Fig. 2) of all the compounds which is a strong element in pricing and thus is of great importance. It is also used in production control, both in raw material production and in molding and extrusion.

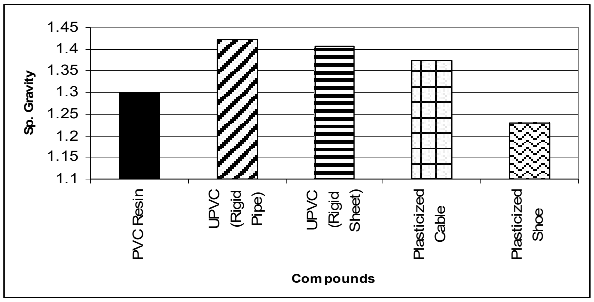

Figure 2. **Comparison of Sp. Gravity in the formulated compounds.**

The tensile strength of UPVC compound is highly increased (Fig. 3) up to the values of 550 kg/cm^2. This increase in tensile strength is due to the absence of plasticizers in formulations of these compounds. The tensile strength of flexible PVC (cable and shoe) is up to 150 kg/cm^2, which is too low as compared to UPVC compounds and that, is again because of presence of plasticizers in their formulations. The plasticizer forms links with polymer molecules and acts as spacer between molecules of the polymer. Due to this linkage plasticizer has great effects on the mechanical properties of the polymer. It was stated that dipole interaction occurs for polar groups in the polymer with the polar groups in the plasticizer [10]. In such case, the polar group played by chlorine atom in PVC resin whereas ester group in the DOP stands for polar group in the plasticizer. The bond forces of the polymer atoms weaken due to the linked established and thus free volume increases with the addition of the plasticizer to the polymer, which leads to lowering the hardness, modulus of elasticity and tensile strength [27]. Our results are in accord with previous studies [10, 28, 29 and 30].

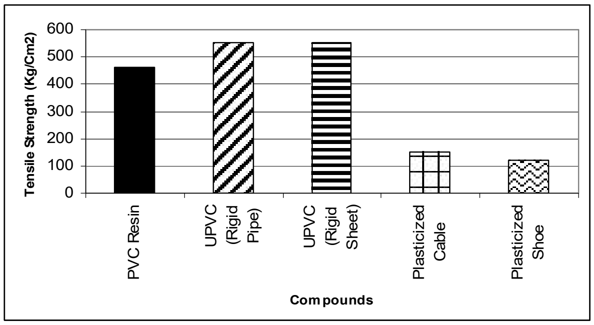

Figure 3. **Comparison of tensile Strength in the formulated compounds.**

Reverse of that, due to presence of plasticizers, the elongation at break of flexible PVC compounds is larger than UPVC compounds (Fig. 4). Higher values of elongation at break have obtained in compounds free from fillers. As mentioned above that plasticizer acts on PVC as spacer and increases the free volume, which makes PVC to become softer and weaker and allows it to be elongated longer at low loads. The obtained result of plasticizer effect on the elongation at break is in good agreement with previous studies [10, 27, 31].

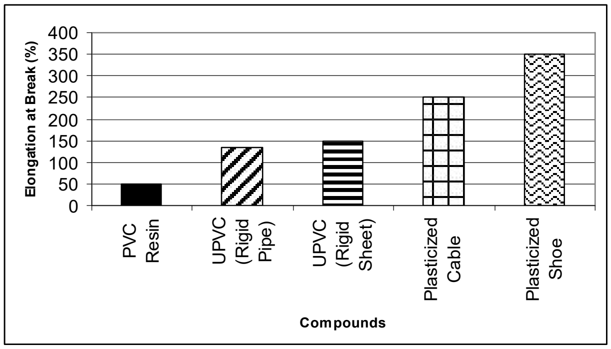

Figure 4. **Comparison of elongation at break in the formulated compounds.**

The effect of plasticizer and filler content on the shore hardness is given in (Fig. 5). The hardness of UPVC pipes and sheet is equal to that of cable compound because of the presence of moderate quantity of fillers but the hardness of shoe compound is slightly decreased, due no presence of filler. It is shown that the shore hardness decreasing with increasing plasticizer content for plasticized PVC compounds without the addition of filler. It is obvious that the lowering fillers 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. Elgozali, Brydson, Mark and Nielsen [10, 28, 30, 31] observed that addition of filler increases the hardness of the PVC which is according to our results.

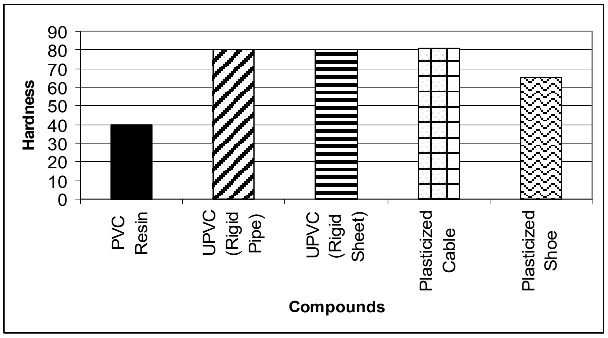

Figure 5. **Comparison of hardness in the formulated compounds.**

Generally it is seen that slight change in formulation of different additives such as plasticizers, fillers, stabilizers, lubricants, colorants, etc., make the PVC compound versatile and its properties are greatly enhanced as according to the formulation.

Conclusion

From the experimental results the following conclusions are obtained:

1. Tensile strength increases in the absence of plasticizing agents and with presence of fillers. The maximum obtained value for tensile strength is 550.67 Kg/cm^2 for rigid PVC-Pipe compound. Tensile strength decreases with increasing plasticizer content and corresponding minimum value is 120.33 Kg/cm^2 for Shoe compound.
2. Elongation at break decreases with increasing filler/stabilizer content for group of sample free of plasticizers (Rigid PVC compounds), while it increases with increasing plasticizer content for flexible compound group (Plasticized PVC compounds). The maximum obtained elongation at break for plasticized samples (containing mainly plasticizer) is 351.33 %. Samples with filler showed minimum elongation at break at 134.33%.
3. Shore hardness (shore A and D) increases for both plasticized and un-plasticized PVC compounds to the values of 80, while shore hardness decreased to a value of 65.33 for shoe compound (plasticized PVC).
4. The rigid compounds (un-plasticized PVC compounds) show a little higher values of specific gravity i.e. 1.4233 (PVC pipe) and 1.4067 (PVC sheet) than the soft compounds (plasticized PVC compounds) with values of 1.373 (cable compound) and 1.23 (shoe compound). The probable reason of this slight increase in specific gravities is that the fillers are denser than the plasticizers.

It could be concluded, that increasing plasticizer content results in decreasing tensile strength and specific gravity but increasing in elongation at break. On the other hand, increasing the filler content increased the tensile strength but reduced the elongation at break in the absence of plasticizers. It is finally concluded that the addition of various additives in the base polymer (PVC in our case) have great effect on the mechanical properties.

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