

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 A Flexible PVC Compound

No synthetic polymer appears to find as many different uses as PVC. The compoundability of PVC ultimately relates to its regular structure: the effect a given additive will have is relatively uniform throughout the polymer. The difference in polarity between the methylene and C-chlorine sections of PVC is very close to that found between the polar and nonpolar sections of a host of additives and modifiers. A flexible PVC compound has been used for many years such as PVC cable compound. The major components are PVC resin, plasticizers, lead stabilizers⁽¹⁰⁾ and minor components, added for special reasons, are mainly fillers and pigments.

PVC resin: The most important variable in PVC resin is the molecular weight. The K value, which is obtainable directly from viscosity measurements at 25°C of a solution of 0.5 g. of PVC resin in 100 ml of cyclohexanone solvent, is often used as a measure of molecular weight. In any particular series of polymers the K value determines the processing temperatures and mechanical properties. The higher the value such as K70, the higher the processing temperatures required and the lower the value such as K52, the lower the processing temperatures required. In this experiment K66 is selected since it is a typical grade that used for PVC cable compound.

Plasticizer: To convert the polymer into a flexible compound. The molecules of resin are held together by strong Van der Waals forces and it is the function of the plasticizers to insert themselves between these forces in order to weaken them, thus allowing the molecules to slip more easily past each other. And the properties of

compounds containing plasticizers will vary according to the type and quantity of plasticizer. Further details are given in Section 2.2.

Stabilizer: All PVC compounds need stabilizers for the reason that it provides acceptable heat stability to the process. Lead stabilizers are relatively low cost, tend to be lubricating and relatively easy to process. In this experiment dibasic lead stearate (DBLS) is selected since it is general purpose stabilizer and has lubricating property.

Fillers: Calcium carbonate well used as the filler for PVC compound to reduce costs, increase opacity and control of manufacture. Since, it eases to disperse and not sticking to mill, which is the precipitated calcium carbonate with coated counterparts with stearic acid⁽¹¹⁾.

2.2 Plasticizer

A plasticizer is a material added to the polymer for increasing its workability and its flexibility by increasing intermolecular space or free volume, which makes room for the change in shape and giving more opportunity for movement of the polymer molecules. In Fig. 1 plasticizer molecules are represented by relatively large frog-like symbols⁽⁴⁾.

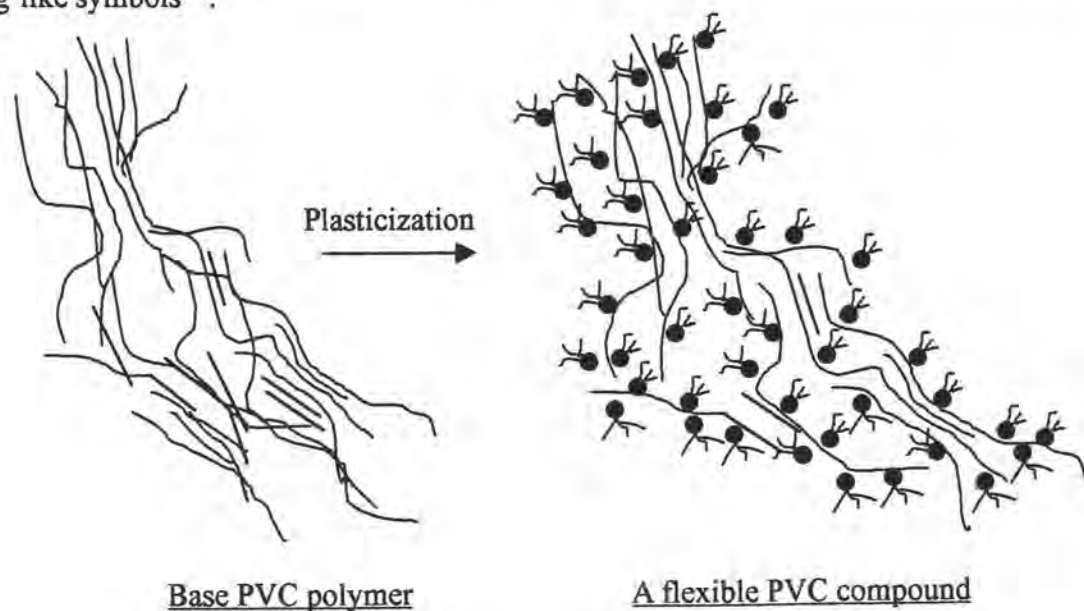


Figure 2.1: Schematic diagram of flexible PVC compound⁽⁴⁾

Plasticizers have traditionally been classified as either “primary” or “secondary”, according to the following definitions⁽¹¹⁾;

Primary plasticizer: The plasticizer which is used in major proportion of the plasticizer system or blend to impart the major performance characteristics of PVC compound, for example phthalates.

Diocetyl phthalate (DOP) is monomeric plasticizer, which is general purpose and highly compatible with PVC resin.

Secondary plasticizer: The plasticizer which is added to a primary plasticizer to impart a secondary performance requirement, e.g., low temperature, permanence properties or stain resistance, for example chlorinated paraffin.

Chlorinated paraffin is secondary plasticizer that has quite limited compatibility with PVC resin and cannot be used alone and used in relatively small proportions with primary plasticizer to reduce costs and improve flammable property.

2.3 Migration of Plasticizer

The resin-plasticizer relation is akin to the relation existing in a solid-liquid interaction. The plasticizer is not bound chemically to the resin molecule and it can be extracted from the vinyl by other materials. Much of the published work^(3,9) has been intended either to correlate migration into foods or to study migration into simpler extractants, enabling the various parameters involved in migration to be studied. Plasticizer migration from plasticized plastics to liquid media has been extensively studied mainly due to the higher intensity of the phenomenon in comparison with the solid/solid systems⁽¹⁾. Accordingly, the extent of migration of a plastics component depends on many variables, but particularly on the density of plastics, the concentration of the component in the plastics such as concentration and nature of plasticizer, surrounding medium, test condition, compatibility of the migrant with the

polymer, molecular size of the migrant, compatibility of the migrant with the phase external to the polymer, the time of contact between plastics and medium and the temperature in the system "Plastics/Medium"^(1,3,9,12,13). The migrating plasticizer can be determined either as the amount leaving the polymer or the amount entering the liquid. Two-matter transfers take place simultaneously: when the liquid enters the PVC product sometimes a swelling of the polymer occurs, and then enables the plasticizer to leave the polymer. A wide variety of experimental methods has been used, including weight loss for monitoring and measuring plasticizer migration in solid/liquid system^(1,3,13).

2.4 Compatibility of Plasticizers and PVC

Compatibility of plasticizers and PVC is difficult to predict and measure quantitatively, however it is related to the polymer-plasticizer interaction forces. A quantitative measure of the PVC and plasticizer compatibility is very important in predicting the migration and the behavior of a PVC compound during processing. A number of workers^(7,8,14) noted the relative fusion temperature depended on the ability of the plasticizer to promote fusion. Knowledge of the varied ease of fusion that plasticizers impart to PVC, resulting from the different compatibility of plasticizers, helps dictate the required processing conditions for good physical properties of the final product⁽¹⁴⁾ and migration behavior. In addition, a PVC product must reach a given fusion level to attain satisfactory properties. The fusion process is affected by a combination of external parameters such as temperature, pressure, and shear history⁽⁷⁾. During this process the PVC passes from a grain structure with very poor mechanical strength to a melted mass with very good mechanical strength. In addition, the fusion of PVC is also affected by the type and concentration of the plasticizer. Therefore, it is of great practical importance to study the compatibility of PVC with different plasticizer mixtures, and its effect over PVC fusion⁽⁷⁾.

2.5 Flammability of Flexible PVC Compound

Flexible PVC containing high concentrations of organic plasticizers are flammable. For example, rigid PVC contains 57% of chlorine content and its oxygen index is 37. When plasticized with 60 parts of an organic plasticizer such as dioctyl phthalate, the chlorine content drops to 36% and the oxygen index is 22. Hence, many additives have been used to flame retard plasticized PVC, including chlorinated Paraffin⁽¹⁵⁾. ASTM D-2863 is used to determine the relative flammability of plastics by measuring the minimum concentration of oxygen in a slowly rising mixture of oxygen and nitrogen that will just support combustion.

2.6 Literature Reviews

The phenomenon of plasticizer migration from flexible poly(vinyl chloride) (PVC) compound comprises an important aspect especially to almost every kind of surrounding medium this polymer is in contact. Much of the published work has been intended to investigate and understand these phenomena.

V. Papakonstantinou and C. D. Papaspyrides investigated plasticizer migration under two-sided diffusion conditions of the common system plasticized PVC / dioctyl phthalate / unplasticized PVC in an oven at 64°C to simulate accelerated test conditions. It was proved that the Fick's law approximation for short times can be used to describe the migration kinetics⁽¹⁾.

C. Gonzalez-Roa, et al. studied the compatibility of PVC with different plasticizers, and effect over PVC fusion. The usefulness of plasticizer mixtures lies in their ability to increase the compatibility of plasticizers having low compatibility with PVC, by mixing them with others of higher compatibility. In addition, plasticizer mixtures decrease the temperature at which PVC reaches an optimal fusion level, therefore resulting in a better combination of properties of the end product at a lower cost⁽⁷⁾.

N. Nakajima and S-Y Kwak studied effect of plasticizer type on gelation and fusion of PVC plastisol, dialkyl phthalate series : In the gelation stage the resin particles become swollen with plasticizer and in fusion stage they were fused to become a uniform mass. These process could be observed with a scanning electron microscope. As it may be expected, the shorter the alkyl chain, the higher the solvent power of plasticizer⁽¹⁶⁾.

Eniko Foldes and Andrea Szigeti-erdei studied the effects influencing the migration of different small molecular materials in polyethylene (PE) and its effect on the surface characteristics (weldability). Because polymers are practically always processed and applied in compositions with small molecular materials, like stabilizers, lubricants, etc., the effectiveness of the additives depends not only on their chemical structure, but also on physical parameters. They revealed that a decrease in weldability experienced after storage of the polymer at ambient and elevated temperatures was proved to be a result of migration of low molecular mass components of the polymer and some type of lubricants to the surface which their mobility depended on the length of the hydrocarbon chain⁽¹⁷⁾.

Paul Barnes studied on the migration of glycerol monostearate (GMS) as antistatic agent in polypropylene by using FTIR analysis. There are many factors that influence the migration process and can alter antistatic functionality, a few of which are: chemical interactions between additives, process conditions, and fatty acid source (e.g. chain length, functional groups). In this work, the use level, fatty acid source, and monoglyceride content were varied in a simple polypropylene homopolymer system to study the relationship with antistatic performance over the period of one month. He found that the FTIR comparison of the carbonyl peak to the reference polypropylene peak shows an increase in the ratio over time, confirming that glycerol esters migrate to surface and the migration of the higher monoglyceride products more than the lower mono products⁽¹⁸⁾.

T. M. Aminabhavi, et al. presented the experimental chemical compatibility of sorption, diffusion and swelling of aromatic liquids into high density polyethylene (HDPE), linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE) and polypropylene (PP) geomembranes at 25, 50 and 70°C by using gravimetric sorption technique. The diffusion coefficients of these have been calculated using Fick's equation and results of this research can be useful in selecting suitable geomembrane (which are the nonporous polymeric materials that are impermeable to aggressive organic chemical) for a specific application⁽¹⁹⁾.