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Abstract

Polyvinylchloride (PVC) resins have been used widely as electrical insulating cables, which required standard engineering specifications and have been exposed against heat and harsh environment even under fire. Sepiolites (Sep) clays, which contain hydrous magnesium silicates, have been utilized as fillers for rubber blends to improve mechanical, morphological and thermal properties of the blends. In this works dioctylphthalate (DOP)-plastisised PVC resins have been blended with various loading of sepiolite clays in reflux reactor of tetrahydrofuran (THF) solution under stirring at optimum condition. Mechanical, morphological and thermal properties of the resulted dried resins were characterized. It was found that optimum result of the PVC resin with improved tensile strength and considerable elongation at break was obtained when loadings of Sepiolites: 10 php (per hundred resin) in constant 30 php loading of DOP. Morphological measurement of fracture surface of optimum PVC resin exhibited finely distributed of sepiolite filler, whereas that of its corresponding higher loading of sepiolite showed the presence and voids due to pullout of agglomerated bigger size sepiolite filler. Thermogravimetric analysis (TGA) of the PVC resins containing increased loadings of sepiolite fillers indicated decreased total weight loss and increased char residue at their decomposition temperature when compared to those of PVC resins without filler and, which revealed their better thermal stability.

Keywords: polyvinylchloride resins, sepiolite clay, dioctylphthalate, modifications, thermal stability

Background

Polyvinylchloride (PVC) resin, as the second largest produced thermoplastics after polyethylene (PE) followed by polypropylene (PP) and polystyrene (PS), has been used widely not only as commodity and engineering materials but also as speciality and medical materials, [1], [2]. In addition PVC is more advantageous economically as engineering materials when compared to the other thermoplastics since the PVC can be plastisised to produce wider range of hard to flexible and soft plastic goods and engineering parts, [3]. However, PVC resin is originally more susceptible to thermal degradation and combustion due to the presence of chlorine, which accelerate the release of hydrochloric acid when used in high temperature environment, [4], [5]. The presence of semi-solid plastisisers (upto 30 % weight) in flexible PVC products, such as electrical cables, also increase their thermal degradability and flammability, [6]. Therefore during manufacturing, PVC resins have been incorporated and modified with various thermal stabilizer, fire retardant additives and fillers to improve their stability against heat and fire during utilization at high temperature environments, [7], [8].

Recently, various inorganic and organic clays have been used as additives in rubber and plastic processing to improve mechanical as well as thermal characteristics of the polymer products, [9]. Sepiolite is an inorganic clay containing needle-like crystals of magnesium silicate hydrates has been utilized in rubber processing and tyre manufacturing to improve mechanical, thermal and wettability properties of the rubber products, [10], [11]. When incorporated in thermoplastic resins, such as PVC, however, compatibility of the sepiolites were lower due to their high differences of hydrophilicity with the thermoplastic matrices, [12]. Various attempts have been carried out to improve compatibility of sepiolite fillers in thermoplastics resins, such as by using organic surfactant-coated sepiolites, [13]. Other attempts were by physical and chemical modifications of the thermoplastic resins with monomeric modifiers such as maleic and acrylic derivatives prior to incorporation with the sepiolite fillers, [14]. Various adhesion promoters based on polymer-grafted maleic and acrylic as well as cellulosic crystals have also been utilized to promote adhesion of thermoplastic resins of hydrophilic filler surfaces, which hence improve mechanical and morphological characteristics of the thermoplastics resins, [15], [16].

Experimentals

Preparations of PVC resins

Fresh PVC resin, dioctylphthalate (DOP) and sepiolites (Sep) were mixed in tetrahydrofuran (THF) solvent under intensive stirring based on compositions as shown in Table 1. The mixtures were then casted on a glass plates, dried in open air and under vacuum at constant temperature 40^{o}C to constant weight. The dried PVC resins were then cut to tensile test specimens according to DIN 50125 standard, [16].

Table 1. Preparations of DOP-plastisised PVC resins containing various loadings of Sepiolites (php: per hundred polimer)

Samples	Compositions	DOP loadings (php)	Sepiolites loadings (php)
PVC Resin 1	PVC/DOP/Sep	30	5
PVC Resin 2	PVC/DOP/Sep	30	7
PVC Resin 3	PVC/DOP/Sep	30	10
PVC Resin 4	PVC/DOP/Sep	30	15

Characterisatios of PVC resins

Dumbbell-shaped specimens were cut from the casted sheets and tested for their tensile strengths and elongation at breaks, according to ASTM D412-92, using a universal testing machine (Instron 3366) at a crosshead speed of 500 mm/min with 10 kN load. Morphology of surface fractures of the PVC resins were tested using scanning electron microscopy (VPFESEM), model Zeiss Supra 35-VP, Carl Zeiss NTS GmbH, Oberkochen, Germany after coating with a thin layer of gold-palladium.

Thermal properties of the PVC resins were characterized using a Shimadzu DTG-60 thermogravimeter, (heating range 30^o – 600^{o}C, heating rate: 10^{o}C/minute), [15].

Results and discussions

Mechanical properties

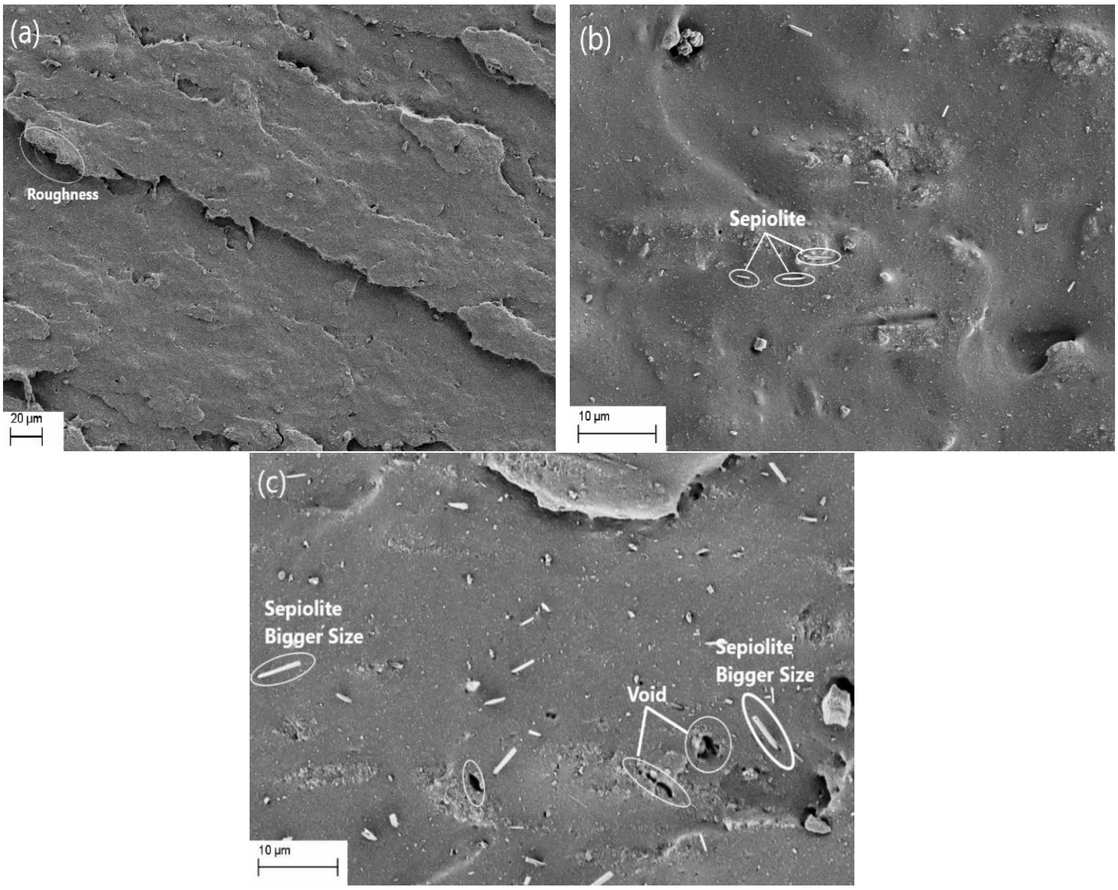
Results of mechanical tests (tensile strength and logation at break) of dioctylphthalate (DOP)-plastisised polyvinylchloride (PVC) resins were shown in Table 2, in which content of DOP were maintained constant (30 php: per hundred PVC resin), and loadings of the sepiolite clay (Sep) fillers were varied. It was indicated that at low loading (5-10 php) the sepiolite clays functioned as reinforcement, which increased tensile strengths (16.3-38.6 MPa), whereas their elongation at breaks were decreased (180.5-150.6 %). However, further increased of sepiolite loading (10-15 php) their tensile strength were decreased again (38.6-31.8 MPa), whereas their elongation at breaks were also decreased (150.6-120.8 %). These were due to that the sepiolite fillers were reaching their saturation loading, which no longer filled spaces between molecular bundle of PVC bulk and formed agglomeration, increased their particle size and decreased adhesion with the PVC matrices, [8], [15]. Therefore, optimum condition of PVC resin with improved tensile strength and considerable elongation at break was obtained when sepiolite loading was 10 php in the presence of 30 php DOP plastisiser. These phenomena will be investigated further by morphological measurement of fracture surfaces of the related PVC resins.

Table 2. Mechanical properties of DOP (30 php)-plastisised PVC resins containing various loadings (php: per hundred polimer) of Sepiolites (Sep), according to DIN 50125 standard

Sample	Compositions	DOP loadings (php)	Sepiolites loadings (php)	Tensile strength (MPa)	Elongation at break (%)
PVC Resin 1	PVC/DOP/Sep	30	5	23.4	176.3
PVC Resin 2	PVC/DOP/Sep	30	7	31.2	160.3
PVC Resin 3	PVC/DOP/Sep	30	10	38.6	150.6
PVC Resin 4	PVC/DOP/Sep	30	15	31.8	120.8
PVC Flexible	PVC/DOP	30	0	16.3	180.5
PVC Fresh	PVC	0	0	52.5	53.2

Morphological testing

Figures 1 were SEM micrographs of fracture surfaces of DOP-plastisised PVC resins containing various loadings of sepiolites (Sep). As shown in Figure 1(a) that of PVC resins without sepiolite, the fracture surface exhibited surface roughness due to tensile fracture of the PVC matrices. At optimum condition that of PVC resin containing sepiolite 10 php, Figure 1(b), the fracture surface exhibited smooth surface with well distributed sepiolite fillers which functioned as reinforcement and improved tensile strength. When the sepiolite filler were further increased to 15 php, Figure 1(c), the fracture surface exhibited bigger size of agglomerated sepiolite fillers as well as voids due to pull out of the agglomerated fillers during tensile tests, which in-turn decreased their tensile strength, [10], [16].



Figures 1. SEM micrographs of fracture surfaces of DOP-plastisised PVC resins containing various loadings of Sepiolites (Sep), (a) without sepiolite, (b) containing sepiolite 10 php, (c) containing sepiolite 15 php.

Thermogravimetric analysis

Results of thermogravimetric analysis of the PVC resins were shown in Table 3 and Figure 2. It was indicated that increased of sepiolite loadings did not affect both temperatures of 5 % loss and 50% loss of the PVC resins (252.1^{o}-260.6^{o}C and 317.7^{o}-323.8^{o}C, respectively). However it was clearly indicated that increased of sepiolite loadings (upto 15 php) have decreased maximum weight loss (68.7-62.6 %), and increased char residue at 500^{o}C (24.6-30.8 %). These revealed that the presence of sepiolite fillers functioned as thermal stabilizer, by formation of char during thermal decomposition of the PVC resins, which covered surfaces of the PVC resins, inhibited access of air oxygen and further thermal decomposition of the PVC resins, [5], [16].

Table 3. Thermogravimetric (TGA) characteristics of sepiolite-filled DOP-plastised PVC resins, heating range from 30° - 500°C, heating rate 10°C/minute

No	Sepiolite Content (php)	Temp. at 5% wt, Loss (°C)	Temp. at 50% wt, Loss (°C)	Max wt. Loss (%)	Char residue at 500°C (%)
1	0	252.1	317.7	68.7	24.6
2	5	254.4	320.6	67.4	27.8
3	10	260.6	323.7	63.1	29.7
4	15	260.6	323.8	62.6	30.8

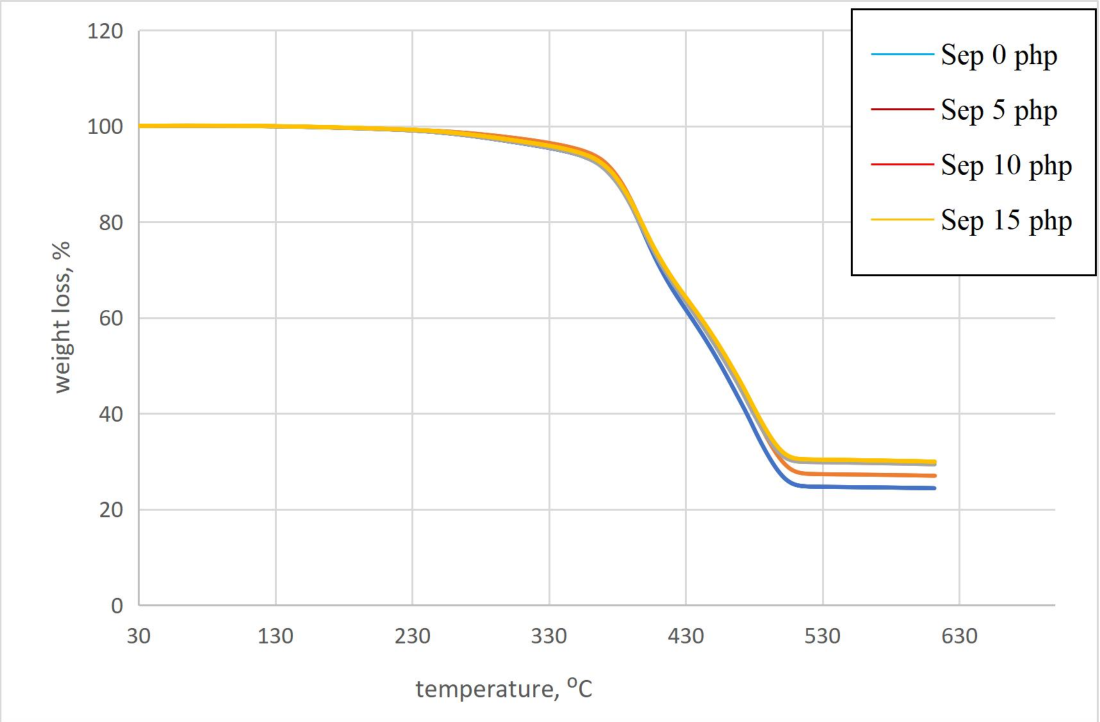


Figure 2. Thermogravimetric (TGA) thermograms of sepiolite-filled DOP-plastised PVC resins, heating range from 30° - 500°C, heating rate 10°C/minute

Conclusion

Low loading of sepiolite clays functioned as reinforcement, which increased tensile strengths and decreased elongation at breaks. However, further increased of sepiolite loading their tensile strength and elongation at breaks were decreased again, due to that the sepiolite fillers were reaching their saturation and formed agglomeration, increased their particle size and decreased adhesion with the PVC matrices.

Fracture surface sepiolit-filled PVC resin at optimum condition exhibited smooth surface with well distributed sepiolite fillers which functioned as reinforcement and improved tensile strength. When the sepiolite filler were further increased, the fracture surface exhibited bigger size of agglomerated sepiolite fillers as well as voids due to pull out of the agglomerated fillers during tensile tests,

The presence of sepiolite fillers functioned as thermal stabilizer, by formation of char during thermal decomposition of the PVC resins, which covered surfaces of the PVC resins, inhibited access of air oxygen and further thermal decomposition of the PVC resins.

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