استابلایزرهای حرارتیِ آلی برای PVC: جایگزینی بی‌خطر و سازگارتر با محیط زیست

چکیده

استابلایزرهای آلی فناوری جدیدی هستند که با فراهم آوردن شرایط حرارتی سازگار با محیط زیست در لوله های PVC استفاده شده و جایگزینی مناسب برای استابلایزرهای سربی همچون کلسیم زینک هستند. در این تحقیق، نمونه های PVCبا ٥ نوع استابلایزر حرارتی تثبیت شدند که عباتند از: استابلایزر سربی تجاری، ۲) استابلایزر کلسیم زینک تجاری، ۳) استابلایزر آلی تجاری (OBS)، ٤) ۱و۳-دی متیل-٦-آمینو اوراسیل (DAU) و ٥) اوژنول. پس از آنالیز مکانیکی، مشخص شد که مدول ذخیرهPVC های تثبیت شده با DAU در دمای اتاق، دارای بالاترین مقدار در میان سایر استابلایزرها است. دمای انتقال شیشه در PVC های تثبیت شده با اوژونول 890C و برای سایر استابلایزرهای حرارتی در حدود 990C بود. علاوه بر این، PVC های تثبیت شده با استابلایزرهای سربی، کلسیم زینک و OBS را می توان حداقل تا ٥ چرخه بازفراوری کرد. در حالیکه مشخص شد که PV های تثبیت شده با DAU بیشترین میزان پایداری حرارتی کوتاه مدت را نشان داده و رنگ اصلی آن می تواند حداقل بیش از ٤ چرخه بازفرآوری ثابت باقی بماند. در نهایت، پردازش های تکرار شده از PVC های تثبیت شده با هر کدام از استابلایزرها، اثر ناچیزی بر روی خواص مکانیکی برای دست کم ۳ چرخه بازفرآوری نشان دادند. با توجه به نتایج فوق واضح است که DAU پتانسیل بالقوه ای برای جایگزینی ترکیبات معمولی همچون سرب و کلسیم زینک به عنوان استابلایزرهای حرارتی آلی و ایمن در PVC هستند.

۱-مقدمه

پلی (وینیل کلراید) (PVC) یک کالای پلاستیکی شناخته شده است که پس از پلی اتیلن و پلی پرو پیلن در رده سوم ببیشترین میزان تولید در جهان قرار دارد [1]. تولید جهانی PVC به طور تقریبی در حدود ٤٠ میلیون تن در سال ۲۰۱۲ تخمین زده شده است. این ماده یک پلیمر مقرون به صرفه است که طیف گسترده‌ای از خواص (انعطاف‌پذیری و سختی) را دارد. در تایلند، یکی از کاربردهای اصلی PVC، لوله های آب است که عموما از ترکیبات سربی به عنوان استابلایزر حرارتی در آنها استفاده می شود.

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Organic Based Heat Stabilizers for PVC: A Safer and More Environmentally Friendly Alternatives

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Abstract. Organic based stabilizers have been considered as a new technology providing environmentally friendly heat stabilizer for PVC pipe production to substitute conventional lead stabilizer as well as calcium zinc stabilizer. In this research, PVC samples stabilized with 5 types of heat stabilizers i.e. 1) commercial lead stabilizer, 2) commercial calcium zinc stabilizer, 3) commercial organic based stabilizer (OBS), 4) 1,3-dimetyl-6-aminouracil (DAU) and 5) eugenol, were investigated. From dynamic mechanical analysis, storage modulus at room temperature of PVC stabilized with DAU was found to provide the highest value among those stabilizers. Glass transition temperature of the PVC stabilized with all types of heat stabilizers was determined to be approximately 99°C except the value of about 89°C in eugenol stabilized PVC. Furthermore, PVC stabilized with commercial lead, calcium zinc stabilizer and commercial OBS could be reprocessed up to at least 5 cycles. Whereas, PVC stabilized with DAU was found to be able to withstand the processing cycle up to 4 cycles. Additionally, PVC stabilized with DAU showed the most outstanding short term thermal stability and can maintain its original color for at least up to 4 processing cycles. Finally, repeated processing of PVC stabilized with each type of heat stabilizers showed negligible effect on mechanical properties for at least up to 3 processing cycles. From the above results, it is evident that DAU showed high potential use as a safe and effective organic based heat stabilizer for PVC to substitute traditional lead or calcium zinc compounds.

Introduction

Poly(vinyl chloride) (PVC) is a well-known commodity plastic of which production is the third largest in the world after polyethylene and polypropylene [1]. The world production of PVC had been approximately estimated to be 40 million tons in 2012. It is a cost-competitive polymer with broad spectrum of properties (flexible to rigid). In Thailand, water pipe is a major product of PVC application and it generally uses lead compound as a heat stabilizer.

Technically, however, PVC is known to degrade at high temperature and gives off hydrochloric acid that in turn accelerates the thermal degradation process. The number of the conjugated double bonds formed during the process determines the level of color in the sample ranging from yellow, orange, red, brown, and black [2]. The decomposition by-product, HCL, can also deteriorate mechanical, thermal as well as physical properties of the polymer [3]. Without the discovery of heat stabilizers, PVC would not be an industrially useful polymer.

Lead stabilizers are used to improve the decomposition temperature in order to obtain high-quality PVC products. Although lead stabilizers have high efficiency in heat stabilization, they are limited as stabilizers applied in PVC on account of their toxicity [4]. Initiative of limiting lead consumption has led to the development of alternative stabilizers in the last ten years. These include calcium/zinc based products for profiles and sewage or drainage pipes and organic based products for drinking water pipes. Ca/Zn stabilizers are typical nontoxic heat stabilizers [5], however, they have some disadvantages in their long-term stability [6]. In recent years, organic based stabilizers (OBS) are new technology providing environmentally friendly stabilization for rigid PVC pipe applications and of major interest both academically and industrially.

One organic compound reported as a potential OBS is uracil derivatives. There are several literatures confirming that uracil derivatives have good efficiency to suppress thermal degradation of PVC [7, 8]. Another interesting organic stabilizer is eugenol which is a main component of clove oil. Eugenol is an organic stabilizer bearing a multifunctional group which has been reported to intervene with the chain degradative products resulting from the thermal treatment of poly(vinyl chloride), together with the fact that it is a safe material to living organisms[2].

The main objective of this research is to suggest suitable organic based stabilizers to substitute conventional lead stabilizer as well as Ca/Zn stabilizer for PVC pipe. In this research, performance of uracil derivative and eugenol as PVC heat stabilizers are compared with commercial heat stabilizers i.e. lead stabilizer, Ca/Zn stabilizer and commercial organic based stabilizer in dynamic mechanical analysis, color measurement, flexural property and recycle ability which are essential for typical pipe application.

Experimental

Materials. Suspension grade PVC with K-value of 66 obtained from Vinythai Public Company Limited., Thailand, was used in this investigation. The additives used in PVC compound are calcium carbonate as filler whereas lead stabilizer, Ca/Zn stabilizer and three types of OBS are used as heat stabilizers. Calcium carbonate and lead stabilizer were provided by Vinythai Public Company Limited., Thailand whereas Ca/Zn stabilizer was supported by Chemson Co., Ltd., China and organic based stabilizer (OBScomm) was supported by Sunace Co., Ltd. Singapore. Eugenol and 1,3-dimethyl-6-amino-uracil (DAU) was purchased from Aldrich Ltd., Germany.

PVC Dry Blend. PVC resin, heat stabilizers (3 phr) and calcium carbonate (10 phr) are blended in a high speed mixer model Plasmec Turbomixer. The mixing process consists of two mixing tanks, operating with 2 steps of hot and cold mixers.

PVC Processing. PVC dryblend was processed by two-roll mills with 0.125 mm gap at temperatures of 180ºC for 3 minutes to yield a homogeneous sample. The total amount of material loading on two-roll mills should not exceed 300 g. The obtained sample was preheated at 180ºC for 200 s and then pressed into sheet by compression molding at 180ºC and pressure of 150 bars for 30 s. The compression-molded sheets were then cut into test pieces for further property evaluations.

Recycling Ability. PVC stabilized with various stabilizers samples after processed by two-roll mills and compressed by compression molder was cut by using cutting mills (Model:Fritsch pulverisette 15 cutting mill). The PVC samples were cut at a speed of 3000 rpm to reduce the size to 3-7 mm. Then, the cut sample (reduced size) was fed into the two-roll mills and further compressed by the compression molder as noted in PVC processing section above. This process was repeated up to 5 times.

Dynamic Mechanical Analysis (DMA). Viscoelastic properties of PVC stabilized with various heat stabilizers were examined by a dynamic mechanical analyzer (NETZSCH, DMA242). The dimension of the specimen was 2 mm× 10 mm× 50 mm**.**The three point bending mode of deformation was used under a test temperature range from 30°C to 150°C with a heating rate of 2 °C/min. The test amplitude and frequency were 30µm and 1Hz, respectively.

Color Measurement. PVC stabilized with various heat stabilizers were investigated by a color spectrophotometer instrument to find out their yellowness index values, according to ASTM D1925-70. The yellowness index is a measure to have an idea on the physical deterioration of PVC samples. The change in color due to high temperature will be a differentiating point in this test.

During the calculation of yellowness index, the tristimulus values according to illuminant C and 2° observer are used as a standard.

Flexural Property. Flexural modulus and flexural strength of the PVC specimens were measured by a Universal Testing Machine (Instron Instrument, model 5567) according to ASTM D790. Three-point bending test was carried out at room temperature and at the crosshead speed of 1.2 mm/min with a support span of 48 mm. The dimension of the specimen was 4 mm×12.7 mm×64 mm. Five specimens from each samples were examined and the average values were reported.

Results and Discussion

Dynamic Mechanical Analysis. Dependence of storage modulus on temperature of PVC stabilized with various types of heat stabilizers were shown in Fig 1(a). From the results, storage modulus at 30°C of the PVC stabilized with heat stabilizers i.e. lead, Ca/Zn, OBS_{comm}, DAU and eugenol were approximately 2.9, 2.8, 2.8, 3.0 and 3.0 GPa respectively. The higher storage modulus of the PVC stabilized with DAU and eugenol stablilizers compared to the other suggesting that the PVC stabilized with DAU and eugenol were more rigid than the others. Moreover, it was likely that commercial stabilizer, i.e. lead, Ca/Zn, OBS_{comm}, might contain additives that can lower modulus of the PVC such as external lubricant, internal lubricant etc. As heating continued, PVC stabilized with eugenol lost their rigidity at elevated temperature more readily than the others.

The glass transition temperature (T_g) assigned to the maximum of tan δ of the PVC stabilized with the heat stabilizers could also be determined from the plots of tan δ against temperature from dynamic mechanical analysis curves (DMA) as shown in Fig 1(b). The glass transition temperatures of all PVC samples were determined to be 99°C except the value of about 89°C in eugenol stabilized PVC. The Tg of PVC stabilized with eugenol was the lowest because of liquid nature of eugenol at room temperature. The results suggested that the excessive use of liquid type heat stabilizer might not be appropriate as demonstrated by this result in the lowering of thermal properties of the sample possibly due to the plasticizing effect of the additive.

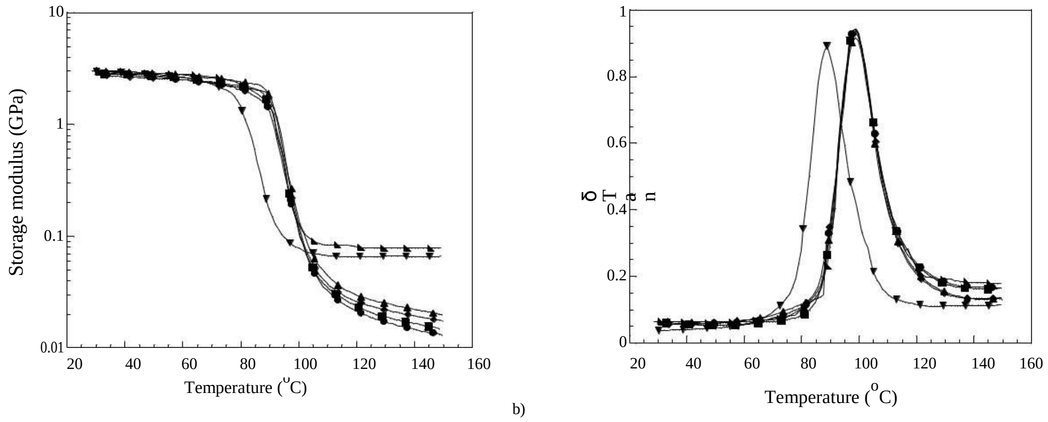

Figure. 1 Effects of types of heat stabilizers in PVC resin on a) storage modulus and b) tan δ: commercial PVC from local Thai company ( ),PVC_{Lead} ( ), $PVC_{Ca/Zn}$ ( ), $PVC_{OBScomm}$ ( ), PVC_{DAU} ( ) and $PVC_{Eugenol}$ ( ).

Color measurement. Yellow index values (YIs) of PVC stabilized with various stabilizers were depicted in Fig. 2. Yellowness index represented the change in color of PVC samples in terms of white color to yellow color. The higher the YI, the yellower the sample, indicating more degradation. From our results, it was observed that the addition of lead, Ca/Zn, OBS_{comm}, DAU and eugenol in our PVC provided different YIs. PVC stabilized with commercial lead, Ca/Zn, and OBS could withstand processing cycles up to 5 cycles. However, the PVC stabilized with DAU was found to be able to withstand the processing cycles up to 4 times. Whereas PVC stabilized with eugenol was able to undergo only one processing cycle. The YIs of the PVC stabilized with commercial lead, Ca/Zn, and OBS at the first processing cycle and at the 5th reprocessing cycles were measured to be 29.5 to 71.4, 41.7 to 115.2, and 33.5 to 72.3, respectively. In case of the PVC stabilized with DAU, the YI value was changed from 24.3 in the first processing cycle to 63.4 in the 4th processing cycle. Finally, the YI value of the PVC stabilized with eugenol even at the first processing cycle was relatively high with the value of 87.3. From the above results, it was evident that was PVC stabilized with DAU effectively retained its initial color up to 3 cycles which is also the lowest YI as a result of repeated processing cycles indicating the highest thermal stability compared to the others. In practice, the ability for the PVC sample to sustain up to 3 repeated processing cycles should be sufficient for typical applications. Also it was to be reminded that the DAU and eugenol stabilizers were single organic component stabilizers, while the others are formulated multi-component systems. Moreover, DAU provides better color stabilization and recyclability than eugenol because DAU acts primarily as HCl scavenger [7] that could reduce the rate of degradation and avoids the very fast process that eventually causes PVC blackening.

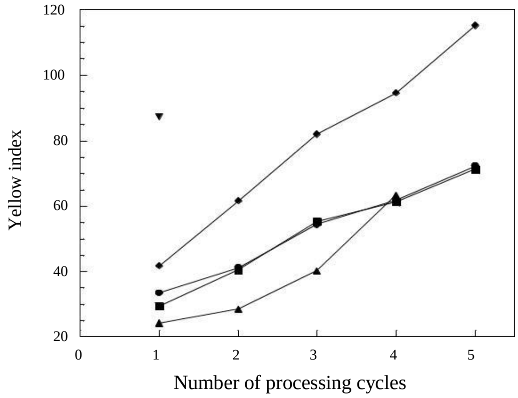

Figure 2 Effects of repeated processing cycles on YI of PVC stabilized with various heat stabilizers: PVC_{Lead} ( ), $PVC_{Ca/Zn}$ ( ), $PVC_{OBScomm}$ ( ), PVC_{DAU} ( ) and $PVC_{Eugenol}$ ( ).

Flexural Property. Flexural strength of PVC stabilized with various heat stabilizers, i.e. lead, Ca/Zn, OBS_{comm}, DAU and eugenol as a function of reprocessing cycles is plotted in Fig. 3(a). From the figure, the flexural strengths of our PVC stabilized with commercial lead, Ca/Zn and OBS were about 75.3-77.6 MPa, 77.6-79.5 MPa and 75.4-79.5 MPa, respectively. From these results, the PVC stabilized with commercial lead, Ca/Zn and OBS stabilizers could still maintain the flexural strength for the repeated processing tests up to 5 cycles. Furthermore, in case the PVC stabilized with DAU and eugenol organic stabilizers, the flexural strength values of the PVC stabilized with DAU subjected to 1 to 3 processing cycles were in the range of 78.3-80.5MPa, while that of the PVC stabilized with eugenol stabilizer that could be processed with only 1 processing cycle was about 82.5 MPa. Flexural strength of PVC stabilized with DAU and eugenol were higher than the PVC stabilized with commercial lead, Ca/Zn and OBS. This characteristic might be due to the relatively better compatibility of eugenol and DAU heat stabilizers with PVC upon mixing compared with the heterogeneous nature of the lead, Ca/Zn and OBS stabilized with PVC. Additionally, the flexural strength values of all PVC samples were in agreement with that of PVC pipes from Georg Fisher Co., Ltd. , i.e. flexural strength = 78.5-98.1 MPa [9].

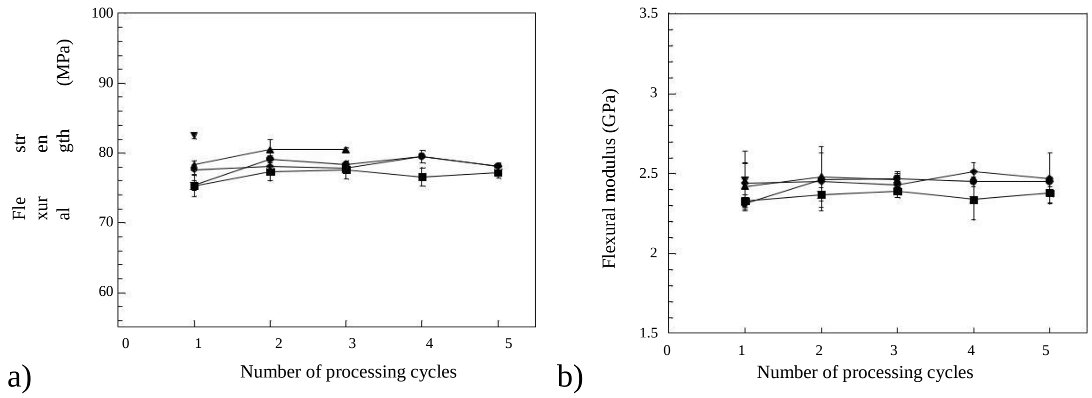

Figure 3: Effects of repeated processing cycles on a) flexural strength and b) flexural modulus of PVC stabilized with various heat stabilizers: PVC_{Lead} ( ), $PVC_{Ca/Zn}$ ( ), $PVC_{OBScomm}$ ( ), PVC_{DAU} ( ) and $PVC_{Eugenol}$ ( ).

Moreover, flexural modulus determined from the initial slope of the stress-strain curves for the PVC with different types of heat stabilizers at repeated processing cycles in flexure mode was depicted in Fig. 3(b). From the figure, flexural modulus of each stabilized PVC sample at each repeated processing cycle was similar, i.e, 2.33-2.39 GPa, 2.43-2.51 GPa, 2.31-2.47 GPa, 2.42-2.46 GPa and 2.46 GPa for the PVC stabilized with lead, Ca/Zn, OBS_{comm}, DAU and eugenol, respectively. Therefore, the repeated processing cycles showed negligible effect on the flexural modulus of the PVC samples. The flexural modulus values of PVC samples in this research are also good agreement with the value of 2.48 GPa for PVC pipe produced by Georg Fisher Co., Ltd. [9].

Summary

Potential organic based heat stabilizers which are non-toxic and safer in pipe application compared to traditional lead or Ca/Zn stabilizers for PVC are evaluated in this work. From the results, PVC stabilized with DAU and eugenol, which are, single organic component, were found to provide greater storage modulus, flexural strength, and flexural modulus than commercial lead Ca/Zn and OBS stabilizers, which are multi-component stabilizers. From recycle ability test, PVC stabilized with commercial stabilizers could be processed up to at least 5 cycles. However, PVC stabilized with DAU was found to be able to withstand the processing cycle up to 4 cycles. From color change investigation, PVC stabilized with commercial lead and commercial OBS stabilizers effectively retained their small color change up to 5 times of processing cycles, whereas PVC stabilized with DAU provided a lowest color change value up to 3 times of processing cycles, suggesting its best short-term performance among those stabilizers. Furthermore, effects of repeated processing cycle of PVC stabilized with each heat stabilizer showed negligible effect on mechanical properties at least up to 3 processing cycles except for eugenol. From the above results, it is clearly seen that DAU showed high potential use as a safe and effective organic based heat stabilizer for PVC to substitute lead or Ca/Zn systems.

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