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Üretim Yönteminin, Dioctyl Phthalate (DOP) ve Dolgu Maddesi Miktarlarının, Geri Dönüşüm Polivinil Klorid (PVC) Bazlı Kompozitlerin Mekanik Özellikleri Üzerine Etkileri

Effects of Processing Methods, Dioctyl Phthalate (DOP) Amount and Filler Content on the Mechanical Properties of Recycled Polyvinyl Chloride (PVC) Composites

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ÖZET

Polivinil Klorid (PVC) endüstriyel ve ev eşyaları uygulamalarında en çok kullanılan ve en çok ticarileştirilmiş (satılan) termoplastik malzemelerden biridir. Plastikler, atık maddelerin büyük bir kısmını oluşturmaktadır ve bunların geri dönüşümü hayati öneme sahiptir. PVC üretiminde ve geri dönüşümünde plastikleştirici kullanımı da gerekmektedir. Bu çalışmanın amacı, üretim yönteminin, dioctyl phthalate (DOP) ve odun unu miktarlarının geri dönüştürülmüş PVC kompozitlerin mekanik özellikleri üzerindeki etkilerini belirlemektir. Bu çalışmada iki farklı DOP miktarı ve üç farklı odun unu miktarı çalışılmıştır. Her yüz gram PVC için 15 ve 30 gram DOP, 0, 15 ve 30 gram odun unu kullanılmıştır. Kompozitler enjeksiyon ve pres kalıplama yöntemi kullanılarak üretilmiştir. Çekme, eğilme, darbe, sertlik (shore D) özelliklerinin yanı sıra kompozitlerin yoğunlukları da belirlenmiştir. Sonuç olarak, DOP ve dolgu maddesi miktarlarının ve üretim yönteminin mekanik özellikler üzerinde önemli bir etkiye sahip olduğu belirlenmiştir. PVC matrisinin içerisinde DOP'un kullanılması nihai ürünü daha yumuşak ve esnek yapmıştır. Üretilen nihai malzemeler daha yüksek kopmada uzama ve darbe direnci değerine ve daha düşük sertlik (shore D) değerine sahiptir. Bu iyi sonuçların aksine, çekme ve eğilme mukavemeti ve modül değerleri düşmüştür. Odun unu dolgu maddesinin matrise eklenmesi ile modül değerleri yükselirken, direnç değerlerini düşürmüştür. Üretim yöntemleri ele alındığında, enjeksiyon kalıplama yöntemi ile üretilen örnekler pres kalıplama yöntemi ile üretilen örneklere nazaran daha iyi özellikler sağlamıştır. Enjeksiyon kalıplama yönteminde makinadaki vida nedeniyle numunelerin daha iyi karıştırılması sağlanmıştır. PVC'nin geri dönüştürülmesi hayati bir konudur ve daha fazla çalışma gerekmektedir.

Anahtar Kelimeler: Geri Dönüşüm PVC, Odun Unu, Enjeksiyon Kalıplama, Pres Kalıplama, Mekanik Özellikler.

ABSTRACT

PVC is one of the most commercialized thermoplastic materials with industrial and household applications. Plastic possesses an important percentage in waste stream and its recycling is vital. Plasticizer usage is also essential for the PVC manufacturing and recycling. It is the purpose of this study to determine the effects of processing methods, dioctyl phthalate (DOP) concentration and wood flour amount on the mechanical properties of recycled PVC composites. 15 and 30 phr (per-hundred-resin) DOP and 0-15-30 phr wood flour was studied. Composite materials were produced using injection and compression molding methods. Tensile, flexural, impact, hardness (shore D) and density of the composites were determined. Based on these results, DOP and filler content and process had a significant effect on mechanical properties. Utilization of DOP in the PVC matrix made material softer and flexible. Resulting materials had higher elongation at break and impact strength and smaller shore D values. In an expense to these good results, it reduced the tensile and flexural strength and modulus values. Addition of wood filler in the system, increased modulus values while reducing strength values. In the case of processing methods, injection molded samples provided overall better properties than compression molded ones. It should be noted that, in the case of injection molding, samples were better mixed due to the screw in the machine. Recycling of PVC is a vital subject and more study is needed.

Keywords: Recycled PVC, Wood Flour, Injection Molding, Compression Molding, Mechanical Properties.

1. INTRODUCTION

Plastics are produced by the use of hydrocarbons obtained from natural sources such as petroleum and natural gas. There are two basic types of plastics as thermoset and thermoplastic. Structure and size of the polymer molecule determine properties of plastics. Thermoplastics melt with heat and again harden when they cooled. On the other hand, thermosets never softness after they harden (Alp, 2003).

PVC is one of the first used thermoplastics and among the most used thermoplastics in the world (Belmares, 2004). The most important advantage of PVC is being compatible with very various additives. Furthermore, it is used in many sectors such as automobile and construction due to high performance and cheap cost of PVC (Kıralp et al., 2007). PVC has global consumption of approximately 16 million tonnes per annum. The only Adana branch of Kastamonu integrated Industry and trade limited company in Turkey obtains waste PVC of 126 thousand tons annually. Thus, the amount of waste PVC is increasing rapidly day by day and this problem leads to environmental pollution.

Several studies were conducted to investigate the possible re-usage of waste thermoplastics. Colom et al. (2014) studied acoustic and mechanical properties of recycled polyvinyl chloride/ground tyre rubber composites. Mengeloglu and Karakus (2008) studied polymer-composites from recycled high density polyethylene and waste lignocellulosic materials. In another study, Fukushima et al. (2010) investigated study on dechlorination technology for municipal waste plastics containing polyvinyl chloride and polyethylene terephthalate. Pivnenko et al. (2016) studied recycling of plastic waste: presence of phthalates in plastics from households and industry. There is a need for further studies on waste thermoplastics recycling. There is large amount of waste thermoplastic material in Turkey. This materials recycling can be useful to environment.

In this study, effect of processing methods, dioctyl phthalate (DOP) amount and filler content on the mechanical properties of recycled polyvinyl chloride composites was investigated.

2. MATERIAL AND METHODS

In this study, recycled polyvinyl chloride (r-PVC) as a polymeric matrix and wastes of forest trimming as filler were used. Recycled PCV supplied by Kastamonu Integrated industry and trade limited company. Recycled PCV (k values=58) and wood flours were 30-mesh (0.59 mm) and 200-mesh size (0.074 mm), respectively. Dioctyl phthalate (DOP) were obtained from ENPAK Chemical Industry and Trade Ltd. Co., Turkey and its chemical and physical properties were presented in Table 1.

Table 1. The chemical and physical properties of Dioctyl phthalate (DOP)

Properties	
Appearance	Clear, Colorless Liquid
Odor	Slight odor, Typical
Molecular Weight	390
Water Concentration	Max. %0,05 (ASTM D 1364)
Viscosity	76-84 cp (20 ºC) (ASTM D 1045)
Density	0,980 - 0,984 g/cm3 (20 ºC) (ASTM D 1045)
Refractive Index	1,4825 - 1,4865 (20 ºC) (ASTM D 1045)
Acid Index	Max. 0.08 mg KOH /g (ASTM D 1045)
Flash Point	Min. 205 (20 ºC) (AÇIK KAP)
Chemical Formula	C6H4 (COOC8H17)2

The composition of recycled polyvinyl chloride composites is presented in Table 2. Twelve different polymer composites were produced. Composite materials were produced using compression and injection molding methods.

Recycled PVC, recycled PET flour and DOP were mixed with high-speed mixer, speed range 5–1000rpm, for 5 min and production started after 24 hours. The compounding was accomplished using a laboratory scale single screw extruder (Teknomatik, Turkey) to produce homogenous composite pellets. The extruder screw speed was set to 40 rpm and the temperature was set to 170 °C, 175 °C, 180 °C, 185 °C, and 190 °C for five heating zones. Pellets were cooled in water and granulated. Granulated pellets were dried at 105 °C for 24 h. These pellets were used for either compression or injection molding. One half of the pellets were compressed into a 4mm-thick 175 x 160mm panels at 200 °C temperature, 100 bar pressure and 10 pressing time. Other half of the pellets were injection molded with 102 kg/cm² injection pressure and 80 mm/s injection speed to produce the test samples. The temperature used for injection molded samples using an HDX-88 injection molding machine was 180-200 °C from feed zone to die zone. After manufacturing, all tests samples were conditioned in a climatic room with the temperature of 20 °C and the relative humidity of 65%. Tensile, flexural, impact strengths, were determined according to ASTM D 638 (5.0 mm/min), ASTM D 790 (2.0 mm/min) and ASTM D 256, respectively.

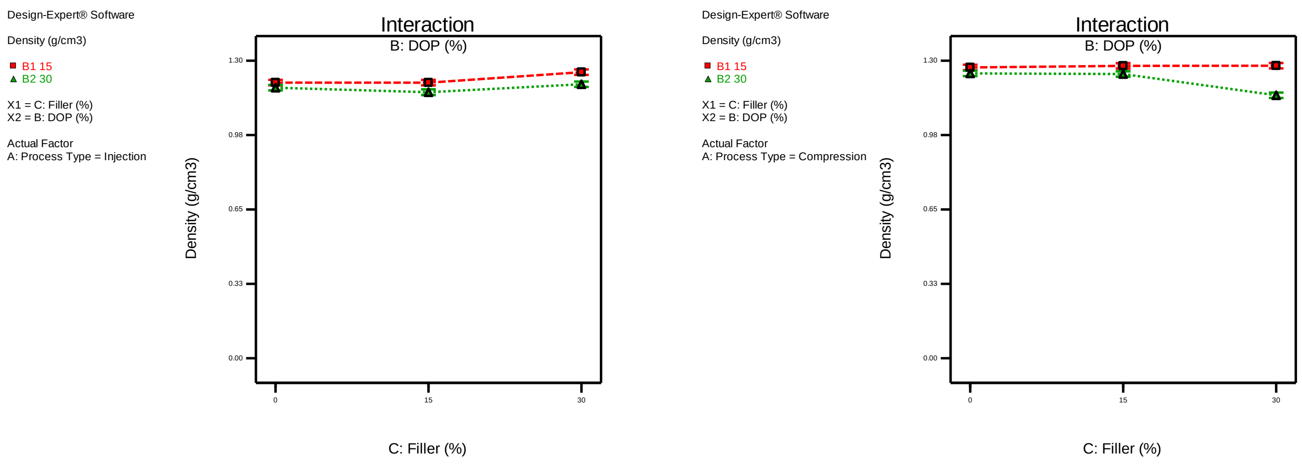
Table 2. The Composition of Recycled Polyvinyl Chloride Composites

Specimen ID	PVC (%)	Wood flour (phr*)	DOP (phr)
PP15D	100	0	15
PP30D	100	0	30
PP15D15O	100	15	15
PP15D30O	100	30	15
PP30D15O	100	15	30
PP30D30O	100	30	30
EP15D	100	0	15
EP30D	100	0	30
EP15D15O	100	15	15
EP15D30O	100	30	15
EP30D15O	100	15	30
EP30D30O	100	30	30

*P: Pressing method, E: Injection method
*phr: per hundred resins

3. RESULTS AND DISCUSSION

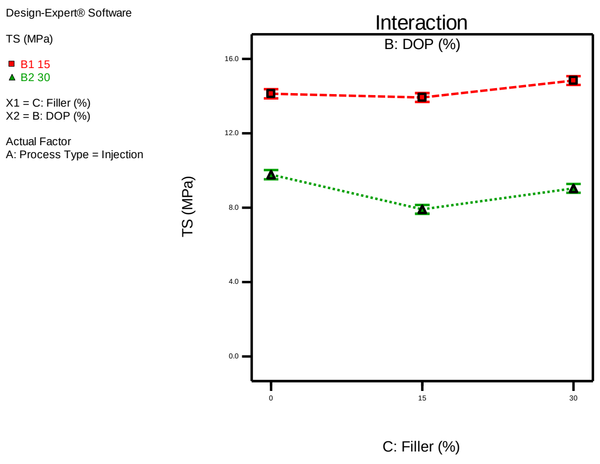
The effect of processing methods, DOP amount and filler content in recycled PVC matrix was investigated. Interaction graph of density of the manufactured recycled polyvinyl chloride composites was presented in Figure 1. X axis denoting the filler concentrations while Y axis shows measured properties. Rectangular and triangle shapes present 15% DOP and 30% DOP, respectively. Densities of the samples were in the range of 1.125 – 1.295g/cm^3. Statistical analysis showed that processing methods have significant effect on density value ($P<0.0001$). Compression molded samples had higher density compared to injection molded samples. In the case of DOP amount, it has also a significant effect ($P<0.0001$). Densities of the samples were increased with the rising of DOP amount in the matrix. Statistical analysis showed that filler content did not have significant effect on density value ($P=0.5054$). There is a significant interaction between the factors ($P=0.0017$).



(a) (a)[I]

Figure 1. Interaction graph of processing methods, DOP amount and filler content on density; a) injection density a)[I] compression density

Tensile strength values of the samples were in the range of 4.96 – 15.19MPa. Figure 2a shows the interaction graph of tensile strength. Statistical analysis showed that processing methods, DOP amount and filler content had a significant effect on tensile strength ($P<0.0001$). Injection molded samples provided higher tensile strength values compared to compression molded ones. In addition, regardless of processing types, tensile strength values were reduced with rising of DOP amount in the matrix. Tensile strength values of 30% DOP filled composites were reduced with rising of wood flour content while tensile strength values of 15% DOP filled composites were increased with rising of wood flour content. In the case of tensile modulus, values were in the range of 62.53 – 475.68MPa (Figure 2b). Similar to tensile strength, processing methods, DOP amount and filler content had a significant effect on tensile modulus ($P<0.0001$). Injection molded samples were outperformed the compression molded ones. It should be noted that rising of DOP amount in recycled PVC matrix significantly reduced the tensile modulus regardless of processing methods. 30% wood flour filled samples provided higher tensile modulus values compared to 0% and 15% filled ones. Elongation at break values of the samples was in the range of 9.98 – 105.85%. Their interaction graph was presented in Figure 2c. Based on the statistical analysis, processing methods, DOP amount and filler content had a significant effect on elongation at break values ($P<0.0001$). Injection molded samples provided higher values compared to compression molded ones. In addition, regardless of processing method, elongation at break values were reduced with rising of filler content in the matrix. 30% DOP filled samples provided higher elongation at break values compared to 15% DOP filled ones.



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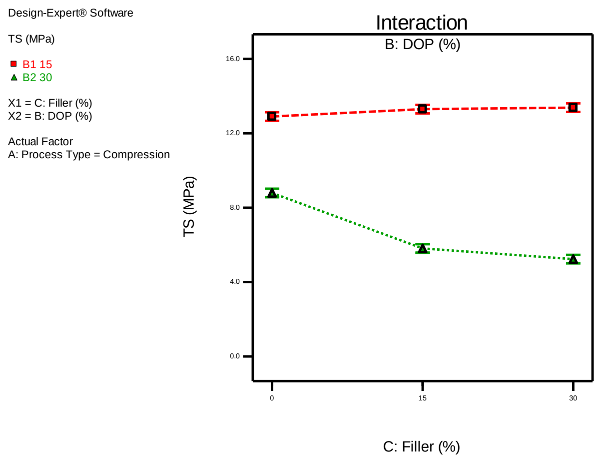

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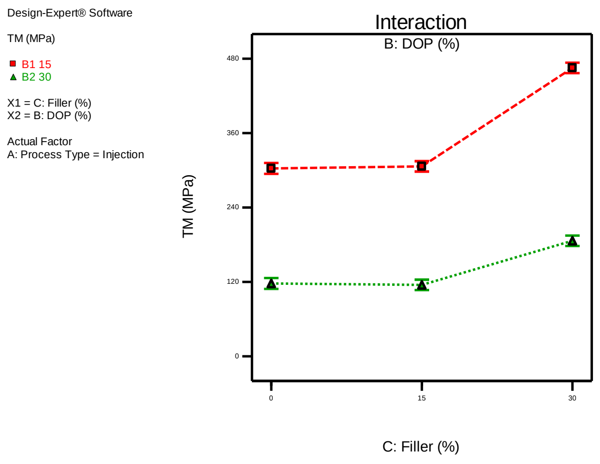

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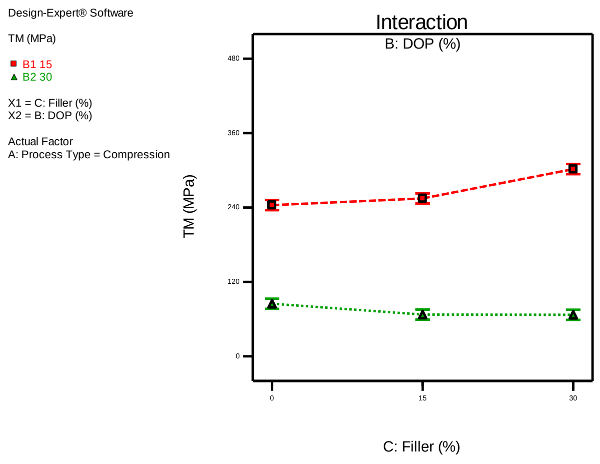

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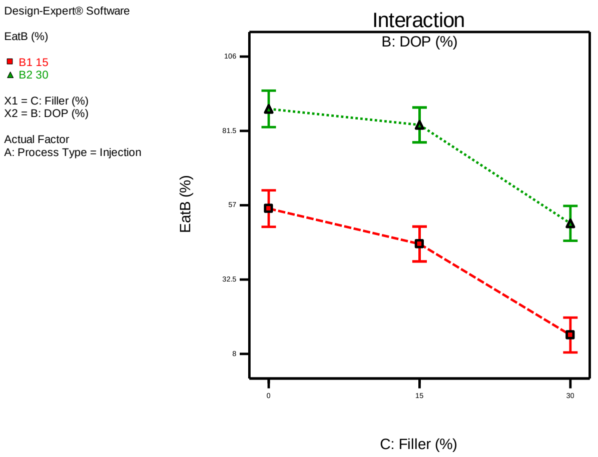

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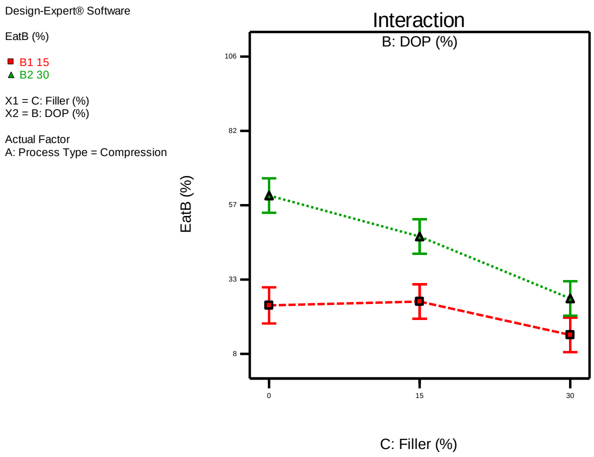

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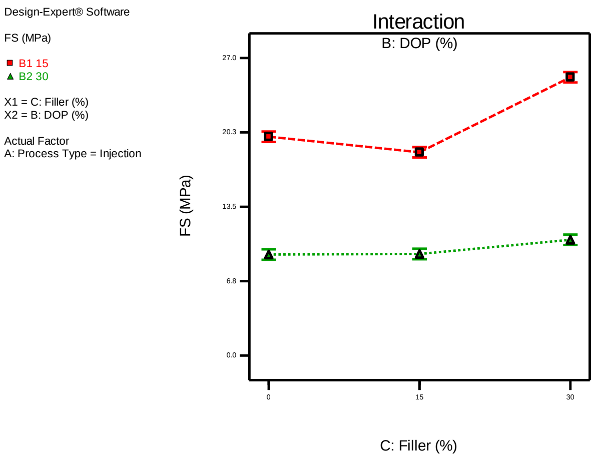
Figure 2. Interaction graph of processing methods, DOP amount and filler content on tensile properties; a) injection tensile strength, a)ǀ compression tensile strength b) injection tensile modulus, b)ǀ compression tensile modulus and c)injection elongation at break, c)ǀ compression elongation at break

Flexural strength values of the samples were in the range of 6 – 26.34 MPa. Figure 3a shows the interaction graph of flexural strength. Statistical analysis showed that processing methods, DOP amount and filler content had a significant effect on flexural strength (P<0.0001). Injection molded samples provided higher flexural strength values compared to compression molded ones. There is an interaction between processing method and DOP amount (P<0.0001). Rising of DOP amount significantly reduced flexural strength values regardless of processing types. Flexural strength values of the samples were reduced with rising to 15% from 0% wood flour content in 15% DOP filled the matrix while increased with rising to 30% from 15% wood flour content. In the case of flexural modulus, values were in the range of 131.27 – 1154.15 MPa (Figure 3b). Processing methods, DOP amount and filler content had a significant effect on flexural modulus (P<0.0001). Injection molded samples provided higher flexural strength values compared to compression molded ones. Rising of DOP amount reduced flexural modulus values of the samples. Flexural modulus values of the samples were reduced with rising to 15% from 0% wood flour content in 15% DOP filled the matrix while increased with rising to 30% from 15% wood flour content.



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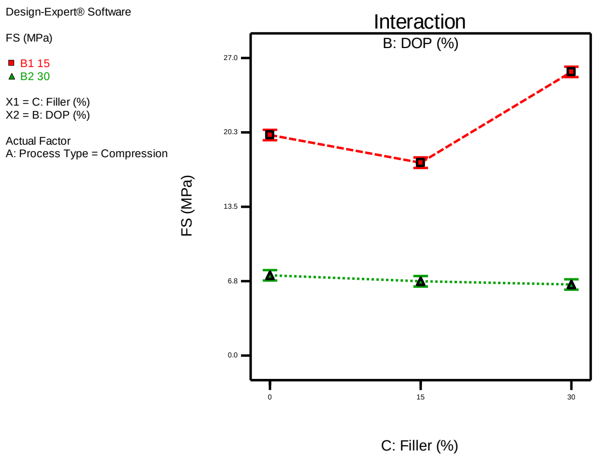

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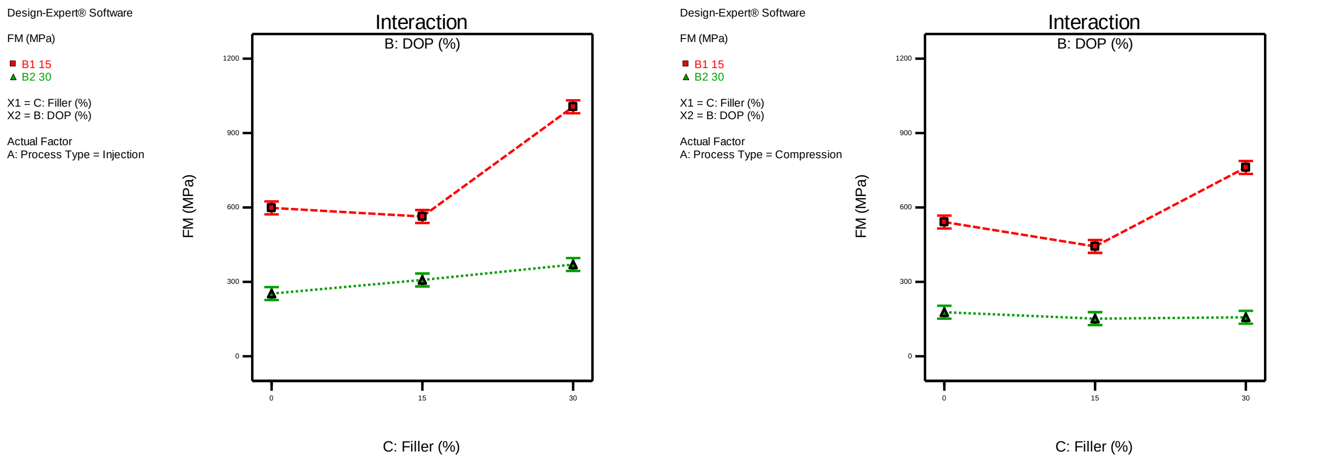

(b) (b)ˡ

Figure 3. Interaction graph of processing methods, DOP amount and filler content on flexural properties; a) injection flexural strength, a)ˡ compression flexural strength and b) injection flexural modulus, b)ˡ compression flexural modulus

In the case of impact strength, produced samples were in the range of 2.19 – 35.91 kJ/m2. Figure 4 shows the interaction graph of impact strength. Processing method, DOP amount and filler content has a significant effect on impact strength (P<0.0001). Injection molded samples had higher impact strength values than compression molded ones. In the case of DOP amount, regardless of procession method, rising of DOP amount increased the impact strength significantly (P<0.0001). Rising of wood flour content reduced impact strength values of samples.

Hardness of the produced samples was also evaluated and they were in the range of 47 – 71.6 Shore D. In the case of hardness, interaction graph was given in Figure 5. Processing methods, DOP amount and filler content had significant effect on hardness values (P<0.0001). In the case of DOP amount, regardless of procession method, rising of DOP amount reduced the hardness values significantly. Hardness of the samples were reduced with rising to 15% from 0% wood flour content in 30% DOP filled the matrix while increased with rising to 30% from 15% wood flour content.

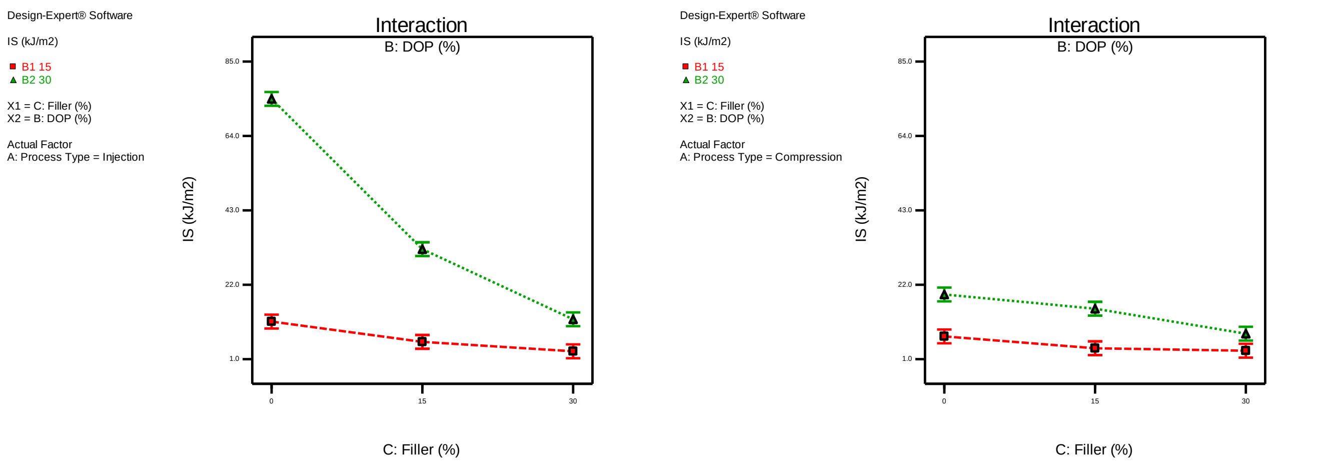

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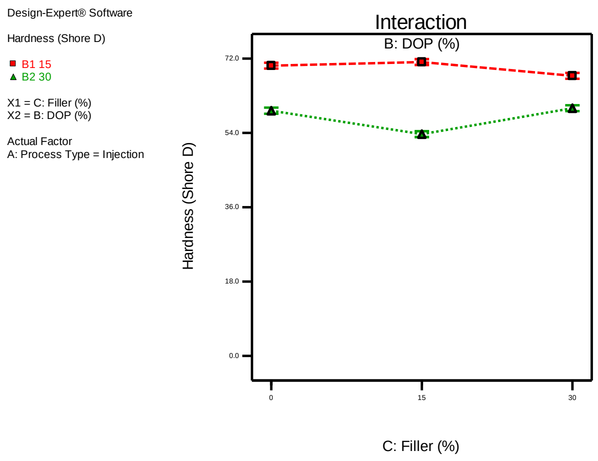
Figure 4. Interaction graph of processing methods, DOP amount and filler content on impact strength; a) injection impact strength, a)ˡ compression impact strength



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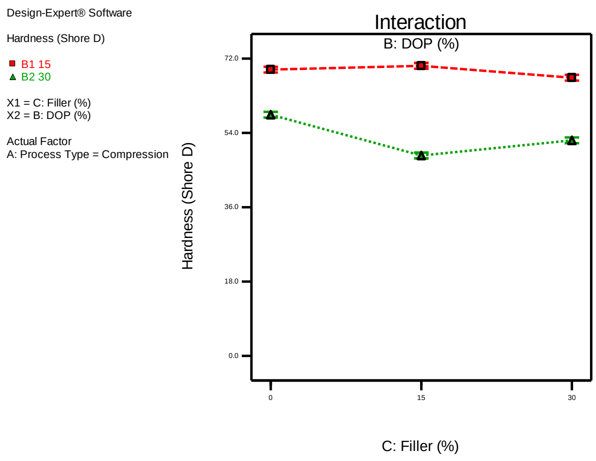

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Figure 5. Interaction graph of processing methods, DOP amount and filler content on hardness; a) injection hardness, a)ˡ compression hardness

4. CONCLUSION

Recycled PVC composites were successfully manufactured with addition of DOP and wood flour. Processing methods, DOP amount and filler content had a significant effect on mechanical properties. Best tensile strength and tensile modulus values were achieved with 30% wood flour and 15% DOP filled injection molded samples. The highest elongation at break values were provided with 0% wood flour and 30% DOP filled injection molded samples. In the case of flexural properties, best flexural strength and flexural modulus values were achieved with 30% wood flour and 15% DOP filled samples. Best impact strength results were achieved with 0% wood flour and 30% DOP filled injection molded samples. Highest shore D values were measured with 15% wood flour and 15% DOP filled samples. There is need more study with using of waste PVC. In the future studies, composites would be manufactured using different plasticizers and fillers.

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