



Peroxide Modification of Nylon 12 Elastomer

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Peroxide 개질에 따른 Nylon 12 elastomer의 특성 연구

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ABSTRACT : Nylon 12 elastomer was slightly crosslinked in molten state by the addition of small amount of dicumyl peroxide (DCP) as a crosslink agent and triallylcyanate (TAC) as a co-agent during melt compounding at 160 °C in an internal mixer. The effect of the peroxide crosslinking on mechanical, dynamic mechanical and rheological properties of the nylon 12 elastomer was investigated by means of tensile testing, dynamic mechanical analysis (DMA) and small amplitude oscillating rheometer, respectively. With modification, there is an improvement in tensile modulus and Young's modulus with decrease in elongation at break. DMA results for peroxide modified nylon 12 elastomers demonstrated that the glass transition temperature of PTMG segment shifted to higher temperature and the storage modulus remained constant above the melting temperature of nylon 12 segments. Melt rheological studies revealed that the peroxide modified nylon 12 elastomer exhibited a more solid like behavior and stronger shear thinning behavior compared to neat nylon 12 elastomer, which was more prominent at higher TAC content in the polymer matrix. The peroxide modified nylon 12 elastomer exhibited good elastic recoverability and improved mechanical properties without sacrificing melt processibility, and especially the service temperature range increased as compared to neat nylon 12 elastomer.

요약 : 용융상태에서 nylon 12 elastomer에 소량의 dicumyl peroxide (DCP) 와 triallyl cyanate (TAC)를 첨가하여 nylon 12 elastomer를 부분적으로 가교시켰으며, 이에 따른 nylon 12 elastomer의 기계적, 동적기계적 그리고 유변학적 특성을 tensile test, DMA, small amplitude oscillating rheometer를 이용하여 각각 알아보았다. TAC의 함량이 증가함에 따라 인장탄성률과 영률은 증가하고, 파단신율은 감소하였다. DMA 측정결과, DCP로 부분적으로 가교시킨 nylon 12 elastomer의 PTMG상의 유리전이온도는 순수한 nylon 12 elastomer에 비해 증가하였고, storage modulus는 nylon 12상의 용융온도 이상에서도 거의 일정한 값을 나타내었다. 부분적으로 가교시킴에 따른 유변학적 특성의 변화는 TAC의 함량이 증가함에 따라 solid like behavior와 shear thinning behavior가 점점 뚜렷하게 나타남을 알 수 있었다. 이로부터 nylon 12 elastomer를 용융상태에서 부분적으로 가교시킴으로써 용융가공성을 저하시키지 않으면서, 기계적 물성은 효과적으로 향상시킬 수 있었으며, 특히, nylon 12 elastomer의 사용가능 온도범위를 증가시킬 수 있었다.

Keywords : nylon 12 elastomer, peroxide modification, mechanical properties, rheological properties

I. Introduction

Modification of thermoplastics with organic peroxides has been regarded as an effective and economic way to improve the properties of the polymer. Many researchers have shown that the thermal, mechanical and rheological properties of various

thermoplastics and thermoplastic elastomers can be improved by the addition of a small amount of organic peroxide in a molten state¹⁻⁵. For example, Ramos *et al.*¹ investigated peroxide-induced slightly crosslinked linear low density polyethylene (LLDPE) by using dicumyl peroxide (DCP) in molten state. They found that crystallization temperature and crystallinity decreased and elasticity increased with increase of DCP concentration. Kim *et al.*^{2,3} prepared slightly crosslinked poly(butylene

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adipate-co-succinate) (PBAS) and poly(butylenes succinate) (PBS) by a simple addition of DCP in a molten state. They reported that the tensile strength, elongation at break and the melt crystallization temperature increased by crosslinking. García-quesada et al.⁴ reported that mechanical properties at evaluated temperature and thermal stability of unplasticized poly(vinyl chloride) (PVC) were enhanced by slightly crosslinking with 1,1-di-*t*-butylperoxy-3,3,5-trimethyl cyclohexane peroxide and trimethylolpropane trimethacrylate in a molten state. Sung et al.⁵ examined slightly crosslinked ethylene vinyl acetate copolymer induced by a small amount of DCP in molten state and found that storage modulus is increased and crystallinity is decrease by crosslinking. Kim et al.⁶ reported that the adhesion properties of poly(styrene-*b*-butadiene-*b*-stryene) (SBS) can be improved after the polybutaidene (PB) block was crosslinked with trimethylolpropane tris(3-mercaptopropionate) (TRIS) and benzophenone (BP) with the aid of UV irradiation. Wang et al.⁷ found that tear strength at high temperature can be improved by crosslinking PB block of SBS molecule with small amount of DCP. Sakurai et al.⁸ studied the microphase separation of crosslinked SBS by the use of 1,1-bis (tert-butylperoxy)-3,3,5-trimethylcyclohexane as a crosslinking agent and found that the degree of the microphase separation was suppressed due to the crosslinking.

Nylon 12 elastomer is one of the engineering thermoplastic elastomers and is a multiblock copolymer consisting of polyamide (PA) as hard segment, which provide physical crosslinks, and flexible polyether (PE) as soft segment, having a glass transition temperature well below room temperature, which acts as an entropic spring. Because of its good balance of physical and mechanical properties along with favorable processibility and recyclability, nylon 12 elastomer is widely used in diverse applications, such as seals, automotive clip gaskets, air bag covers, pneumatic hoses, and many others in the automotive, transportation, or medical industries^{9,10}. Owing to the blocked structure of the nylon 12 elastomer, the mechanical and physical properties are dependent upon

the composition (hard segment/soft segment ratio) of the copolymer. That is, by increasing the hard polyamide segment in the copolymer, the modulus, barrier properties, chemical resistance, and thermal stability are increased, while elastic properties and optical transparency are decreased. It is necessary to enhance the properties of nylon 12 elastomers having a certain chemical composition in order to satisfy the desirable properties in many engineering applications.

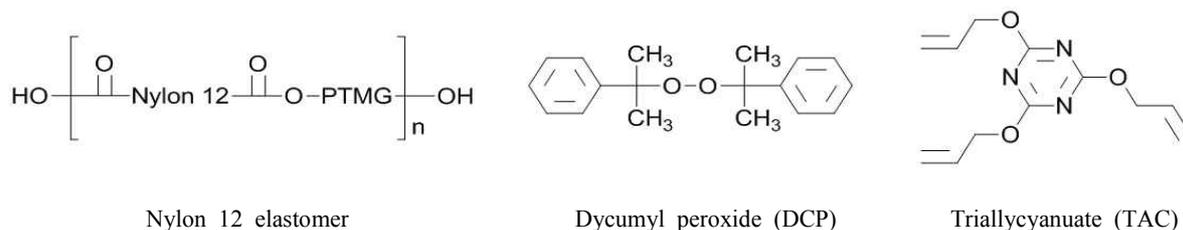
In this study, we modified the nylon 12 elastomer by incorporation of a small amount of dicumyl peroxide (DCP) as a crosslinking agent and triallylcyanate (TAC) as a co-agent in a molten state, which may induce slight crosslinking of the elastomer. Effect of the peroxide modification on mechanical, dynamic mechanical and rheological properties of nylon 12 elastomer was investigated.

II. Experimental

Nylon 12 elastomer (PEBAX 2533, HS/SS = 15/85) was purchased from Arkema. Dicumyl peroxide (DCP) used as a crosslinking agent for nylon 12 elastomer was purchased from Aldrich. Triallylcyanate (TAC) used as a co-agent for crosslinking was purchased from Tokyo Chemical Industry. All chemicals were used without further purification. Scheme 1 shows the chemical structure of nylon 12 elastomer, DCP and TAC.

Peroxide modified nylon 12 elastomers with 1.0 phr DCP and TAC from 0 to 1.0 phr were prepared by melt mixing in a Haake internal mixer at 160 °C for 10 min at a rotor speed of 60 rpm. The compounds obtained were compression molded using laboratory scale hot press into 1.0 mm thick sheets at 160 °C and were annealed at 80 °C for 24 h under vacuum before their physical properties were determined. The samples for tensile, DMA, and rheological measurements were punched out from the compression molded sheet using a specimen cutting machine.

Tensile properties were measured using a universal testing machine (UTM) (STM-10E, United calibration Corporation) at 25 °C at a crosshead speed of 10 mm/min. Five dog-bone shaped



Scheme 1. The chemical structure of nylon 12 elastomer, DCP and TAC.

samples were used for each composition of samples. Tension set was measured by stretching the specimen to 100% elongation and keeping it in that position for 10 min. The applied stress was then released and the change in length was measured after 24h. Tension set was evaluated by the following formula.

$$\text{Tension set (\%)} = (\text{Change in length} / \text{Original length}) \times 100$$

Dynamic mechanical properties were determined using a dynamic mechanical analyzer (DMA 2980, TA instruments). The sample was subjected to three points bending with amplitude of 0.2 % at a frequency of 4 Hz. The temperature was increased at a heating rate of 2 °C/min in the range of -130 to 200 °C.

Melt rheological measurement (small amplitude oscillatory shear rheometry) was carried out by advanced rheometric expansion system (ARES) (RMS 800, Rheometrics, Inc., New Jersey, USA). Dynamic oscillatory shear measurements were performed at 180 °C using a set of 25 mm diameter parallel plates and 1–2 mm thick samples. The frequency sweep was carried out within the frequency range of 0.1–100 rad/sec at a strain of 0.5 %, which is well within the linear viscoelastic range.

III. Results and Discussion

The representative tensile stress-strain curve of the neat nylon 12 elastomer and peroxide modified nylon 12 elastomers are shown in Figure 1 and the results are summarized in Table 1. The neat nylon 12 elastomer with relatively low hard segment content shows more pronounced elastomeric behavior. Hence, it exhibits low Young's modulus and a remarkably high elongation at break without a distinct yielding point. Peroxide modified nylon 12 elastomers show higher strength and modulus at lower strain region (<400% elongation) but lower strength and modulus at higher strain region (>400% elongation) as compared to the pristine counterpart. At the low strain region (<400% elongation), modulus at 300 % elongation and Young's modulus of peroxide modified nylon 12 elastomers were significantly increased with the increase in TAC concentration. For example, Young's modulus and the modulus at 300 % elongation of the peroxide modified nylon 12 elastomer containing 1.0 phr TAC are 1.80 times and 2.15 times higher than that of the neat nylon 12 elastomer, respectively.

The tension set was measured to evaluate the effect of peroxide crosslinking on the elastic recoverability of the nylon 12 elastomer, and the results are shown in Figure 2. The tension set value of the neat nylon 12 elastomer was about 4 %, which re-

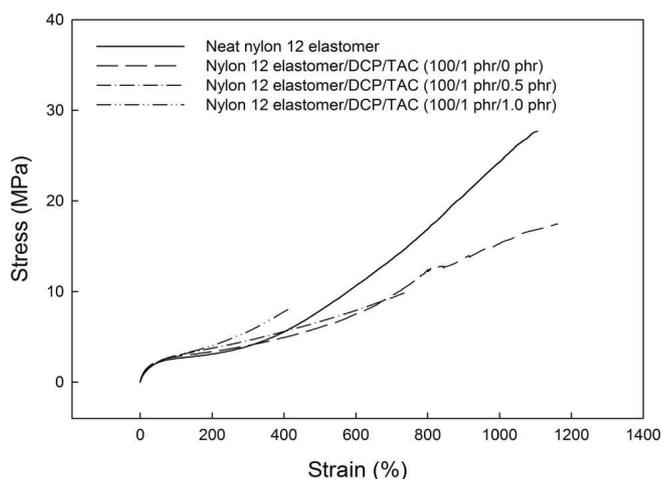


Figure 1. Tensile stress-strain plot of neat nylon 12 elastomer and peroxide modified nylon 12 elastomers.

vealed that the neat nylon 12 elastomer has good elastic recoverability. The peroxide modified nylon 12 elastomers have higher tension set value as compared to the neat nylon 12 elastomer, but the tension set value of those was about 10 %. Therefore, peroxide modified nylon 12 elastomers also have the good elastic recoverability. The results of tensile testing and tension set indicated that peroxide modified nylon 12 elastomers have not only a fairly good elastic recovery but also the enhanced mechanical properties.

DMA results for the neat nylon 12 elastomer and peroxide modified nylon 12 elastomers are shown in Figure 3a and 3b, which provide the data for storage modulus (E') and $\tan \delta$, respectively, and the results are summarized in Table 2. As shown in Figure 3(a), it can be seen that the materials are glassy at low temperatures in the range of -130 to -60 °C, but undergo a softening beginning at about -60 °C, which arises from the glass transition behavior of the polyether soft segment. Following this tran-

Table 1. Tensile properties of neat nylon 12 elastomer and peroxide modified nylon 12 elastomers.

Sample	Young's modulus (MPa)	300% modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Neat nylon 12 elastomer	12.6±0.3	3.1±0.2	27.6±0.4	1105±80
Nylon 12 elastomer/DCP/TAC (100/1 phr/0 phr)	13.2±0.3	3.3±0.3	17.4±0.4	1160±50
Nylon 12 elastomer/DCP/TAC (100/1 phr/0.5 phr)	16.6±0.4	3.7±0.3	9.8±0.5	735±60
Nylon 12 elastomer/DCP/TAC (100/1 phr/1.0 phr)	21.6±0.3	4.0±0.3	8.1±0.3	420±60

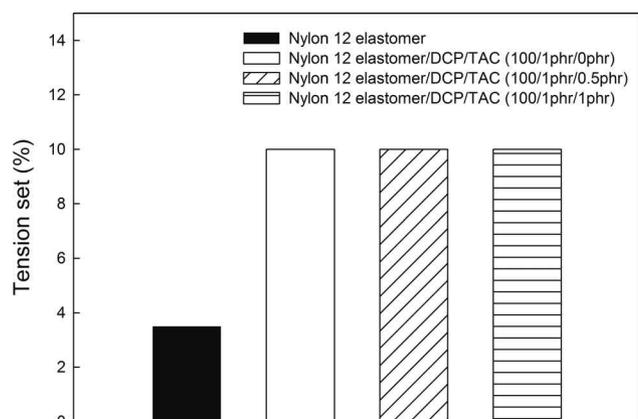


Figure 2. Tension set of neat nylon 12 elastomer and peroxide modified nylon 12 elastomers.

sition, there is a rubbery plateau behavior in the modulus that extends to about 100 °C, where polyamide hard domains in the nylon 12 elastomer start to be disrupted. It is obvious that peroxide modified nylon 12 elastomers exhibited higher storage modulus than neat nylon 12 elastomer over the entire temperature range. For example, $E\phi$ at 30 °C and 125 °C of the peroxide modified nylon 12 elastomer with 1.0 phr TAC loading was 2.0 and 4.8 times higher than those of the neat nylon 12 elastomer, respectively. It is to be noted that, when the concentration of TAC in peroxide modified nylon 12 elastomer is 1.0 phr, the storage modulus showed nearly plateau above the melting temperature (T_m) of nylon 12 segments of nylon 12 elastomer, whereas that of neat nylon 12 elastomer showed the abruption above the T_m of nylon 12 segments. It indicated that slightly crosslinking of nylon 12 elastomer in molten state enables the matrix polymer to withstand higher service temperature.

Figure 3(b) shows the variation of $\tan \delta$ with temperature of neat nylon 12 elastomer and peroxide modified nylon 12 elastomers. In all cases, the peak appearing at about -60 °C corresponds to the glass transition of the polyether phase, and a small shallow shoulder appearing at about 0 °C corresponds to the melting transition of PTMG segment and the glass transition of nylon 12 segment. It indicated that both neat nylon 12 elastomer and peroxide modified nylon 12 elastomers have a microphase separated structure. As the concentration of TAC increase in peroxide modified nylon 12 elastomers, the glass transition temperature (T_g) of the PTMG segment shifted to a higher temperature by about 10 °C with 1.0 phr TAC loading and the peak height at the T_g was decreased, but the variation of T_g of nylon 12 segment with slightly crosslinking was not observed clearly. The increase in T_g of the PTMG segment of nylon 12 elastomer and lowering

of the $\tan \delta$ peak indicated that the PTMG segment of nylon 12 elastomer is crosslinked by DCP and TAC, which restricted the movement of PTMG chains and lower the damping properties.

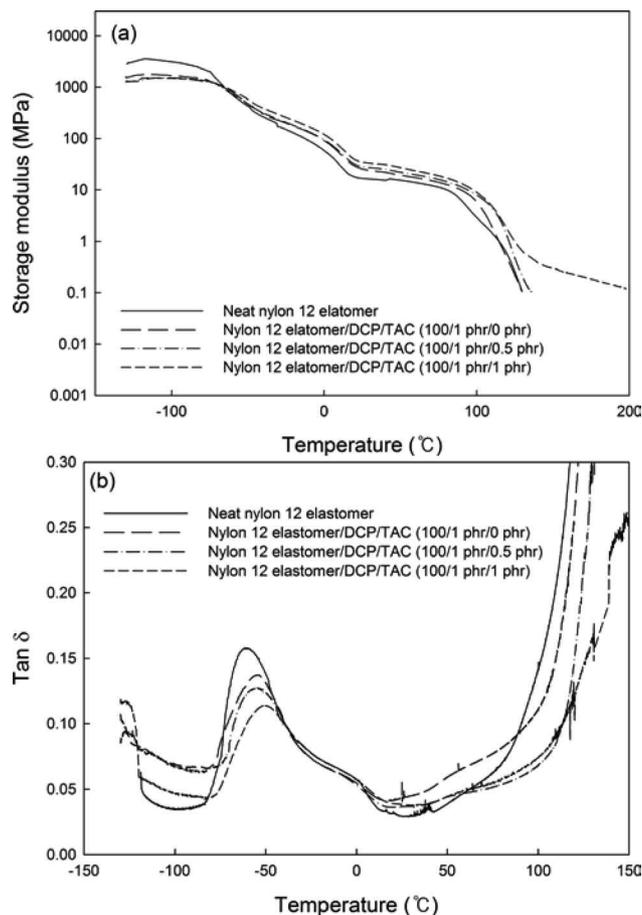


Figure 3. Temperature dependence of the (a) storage modulus and (b) $\tan \delta$ of neat nylon 12 elastomer and peroxide modified nylon 12 elastomers.

Table 2. Dynamic mechanical properties of neat nylon 12 elastomer and peroxide modified nylon 12 elastomers.

Sample	Tg of PTMG segment (°C)	Height of $\tan \delta$ max of PTMG	E' at 30°C (MPa)	E' at 125°C (MPa)
Neat nylon 12 elastomer	-61.4	0.158	16.2	0.21
Nylon 12 elastomer/DCP/TAC (100/1 phr/0 phr)	-56.0	0.137	23.7	0.24
Nylon 12 elastomer/DCP/TAC (100/1 phr/0.5 phr)	-54.0	0.127	26.9	0.46
Nylon 12 elastomer/DCP/TAC (100/1 phr/1 phr)	-49.2	0.114	33.1	1.00

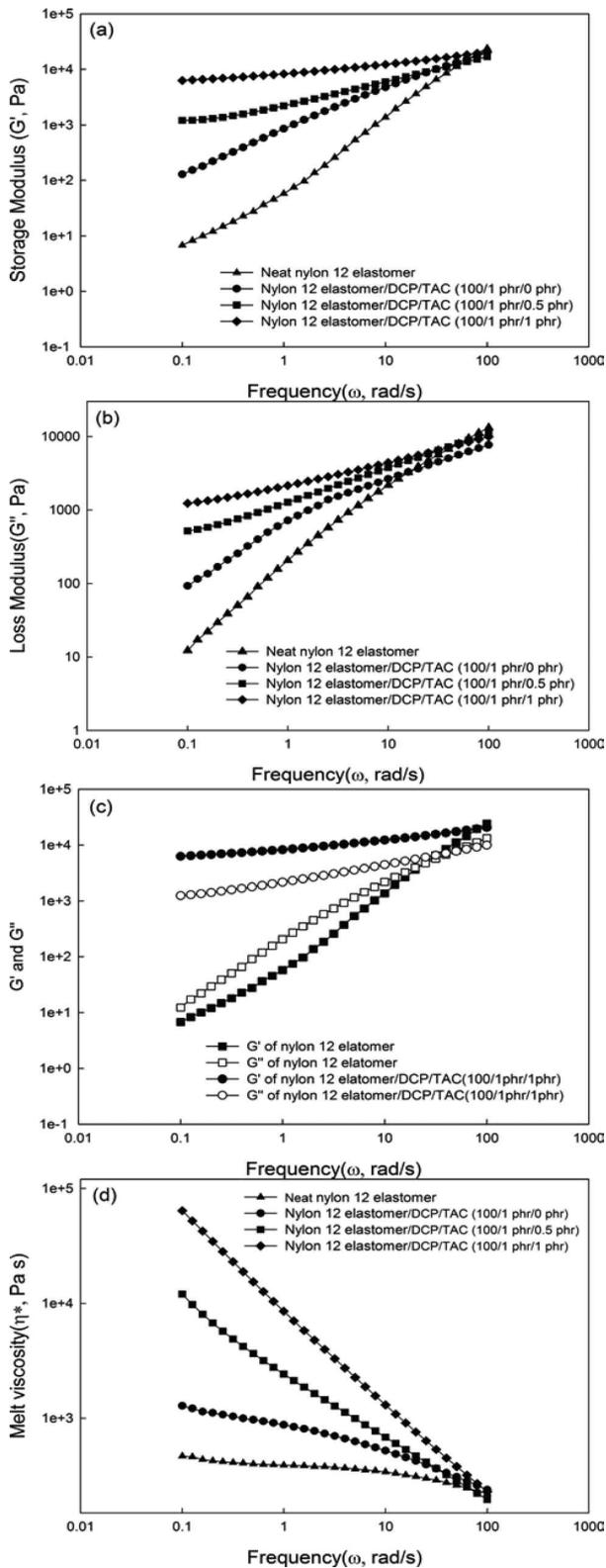


Figure 4. Frequency dependence of (a) storage modulus (G'), (b) loss modulus (G''), (c) comparison of both G' and G'' , (d) complex viscosity (η^*) of neat nylon 12 elastomer and peroxide modified nylon 12 elastomers.

Rheological properties in the molten state are important because they decide the applicability of various processing conditions. The melt rheological properties of the neat nylon 12 elastomer and peroxide modified nylon 12 elastomers were investigated by the use of oscillatory rheometer. The variation of storage modulus (G') and the loss modulus (G'') as a function of frequency (ω) of neat nylon 12 elastomer and peroxide modified nylon 12 elastomers are shown in Figure 4(a) and 4(b), respectively. The Figure 4(a) and 4(b) showed that the G' and G'' of the peroxide modified nylon 12 elastomers are higher compared to the neat nylon 12 elastomer. The increase in the modulus is prominent in the lower frequency range. At higher frequencies, the difference decreases. The slope in the terminal region was calculated in the low ω region (below 5 rad/s) and is displayed in Table 3. The slopes of G' and G'' of the DCP modified nylon 12 elastomers are smaller than those of the neat nylon 12 elastomer. The higher G' and smaller terminal slope of the DCP modified nylon 12 elastomers over neat nylon 12 elastomer indicated the increase of amount of large macromolecules in the matrix as a consequence of the crosslinking reaction by DCP and TAC.

Table 3. Terminal region slopes and complex viscosity of neat nylon 12 elastomer and peroxide modified nylon 12 elastomers.

Sample	Slope of G'	Slope of G''	η^* at 1 rad/s (Pa · s)
Neat nylon 12 elastomer	1.25	0.89	3.89×10^2
Nylon 12 elastomer/DCP/TAC (100/1 phr/0 phr)	0.79	0.55	8.75×10^2
Nylon 12 elastomer/DCP/TAC (100/1 phr/0.5 phr)	0.31	0.32	2.42×10^3
Nylon 12 elastomer/DCP/TAC (100/1 phr/1 phr)	0.15	0.19	8.54×10^3

The combined plot of G' and G'' of neat nylon 12 elastomer and peroxide modified nylon 12 elastomers are displayed in Figure 4(c). The figure showed that, for neat nylon 12 elastomer, G'' is higher than G' and beyond a certain frequency it is reversed. This indicated that, up to the certain frequency, neat nylon 12 elastomer display a liquid-like behavior and exhibit solid-like behavior only when the angular frequency exceeds a critical value. On the contrary, for peroxide modified nylon 12 elastomer containing 1.0 phr TAC, storage modulus is higher than the loss modulus over the entire frequency range, clearly indicating that the crosslinked nylon 12 elastomer displays a solid-like behavior. The solid-like behavior of the peroxide modified nylon 12 elastomer in a molten state reflects the network structure induced by

crosslinking.

The variation of complex viscosity (η^*) as a function of frequency for neat nylon 12 elastomer and DCP modified nylon 12 elastomers are shown in Figure 4d. It can be seen that, the complex viscosity of the modified nylon 12 elastomers was higher than that of neat nylon 12 elastomer and the increase in the viscosity is more pronounced at low frequency range. The enhancement of viscosity of the modified nylon 12 elastomers is due to the increased difficulty of chains disentanglement caused by the introduction of crosslinked structure in the peroxide modified nylon 12 elastomers. The neat nylon 12 elastomer as well as DCP modified nylon 12 elastomers showed typical shear thinning behavior, in which viscosity decreases with the increasing frequency, which is much more pronounced for the peroxide modified nylon 12 elastomers as compared to neat nylon 12 elastomer. In general, the shear thinning is more pronounced in the solid-like materials such as crosslinked polymer and polymer inorganic nanocomposites.¹¹⁻¹³ The strong shear thinning behavior of the peroxide modified nylon 12 elastomers indicates a good processibility.

IV. Conclusions

We attempted to modify the nylon 12 elastomer by the incorporation of small amount of peroxide during the melt compounding, which may induce slight crosslinking of the elastomer. The slightly crosslinking of nylon 12 elastomer in molten state effectively led to an effective enhancement in mechanical properties, and that enabled the nylon 12 elastomer to withstand higher service temperature. Melt rheological studies revealed that DCP modified nylon 12 elastomer exhibited a more solid-like rheological behavior and stronger shear thinning behavior as compared to neat nylon 12 elastomer. The peroxide modified nylon 12 elastomer exhibited good elastic recoverability and improved mechanical properties without sacrificing melt processibility.

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